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Article

Synthesis and Structural Characterization of Novel Neutral Hexacoordinate Silicon(IV) Complexes with *Si*O_2N_4 Skeletons Containing Cyanato-*N* or Thiocyanato-*N* Ligands[†]

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A series of novel hexacoordinate silicon(IV) complexes with an *Si*O_2N_4 skeleton (compounds (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, (*OC*-6-12)-**6**, and (*OC*-6-2′2)-**7**) were synthesized, starting from $Si(NCO)_4$ or $Si(NCS)_4$. These compounds contain (i) two bidentate *O*,*N*-chelate ligands (or one tetradentate *O*,*N*,*N*,*O*-chelate ligand) derived from 4-aminopent-3-en-2-ones of the formula type Me–C(NRH)═CH–C(O)–Me (R = organyl) and (ii) two monodentate cyanato-*N* or thiocyanato-*N* ligands. Formally, the bidentate singly negatively charged *O*,*N*-chelate ligands (tetradentate 2-fold negatively charged *O*,*N*,*N*,*O*-chelate ligand) behave as ligands of the imino–enolato type. In addition, the adduct *trans*-**8** was synthesized by reaction of $Si(NCS)_4$ with 2 molar equiv of Me–C(N*i*-PrH)═CH–C(O)–Me. This hexacoordinate silicon(IV) complex contains (i) four monodentate thiocyanato-*N* ligands and (ii) two neutral monodentate ligands of the iminio–enolato type. All compounds synthesized were structurally characterized by single-crystal X-ray diffraction and solid-state and solution NMR spectroscopy. To get more information about the stereochemistry of these compounds, the experimental investigations were complemented by computational studies.

Introduction

In transition metal coordination chemistry, bidentate *O*,*N*-chelate ligands derived from β-ketoenamines play an important role, and the structural chemistry of complexes containing such ligands in their monodeprotonated form and the bonding situation in these compounds have been studied extensively.[1] In contrast, the chemistry of higher-coordinate silicon(IV) complexes with ligands of this type is significantly less explored. The existence of such compounds has been claimed in the literature,[2] but almost nothing is known about their structure; to the best of our knowledge, no crystal structures have been reported. However, there is some structural information about related higher-coordinate silicon(IV) complexes with tetradentate *O*,*N*,*N*,*O*-chelate ligands derived from bis(salicyliden)ethylenediamine (H_2salene) and its derivatives.[3]

In context with our studies on higher-coordinate silicon compounds (for recent publications, see ref 4; for selected reviews dealing with higher-coordinate silicon compounds, see ref 5), we aimed at the synthesis and structural characterization of novel neutral hexacoordinate silicon(IV) complexes with (i) two bidentate *O*,*N*-chelate ligands (or one tetradentate *O*,*N*,*N*,*O*-chelate ligand) derived from β-ketoenamines of the formula type Me−C(NRH)═CH−C(O)−

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[†] Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday.

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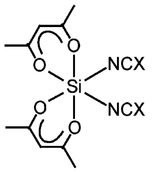
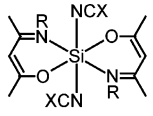
Me (R = organyl) and (ii) two monodentate cyanato-*N* or thiocyanato-*N* ligands. In two recent publications, we have reported on the synthesis and structural characterization of the neutral hexacoordinate silicon(IV) complexes **1**[4b] and **2**.[4a] These compounds contain an *Si*O$_4$N$_2$ skeleton, with two bidentate acetylacetonato ligands and two monodentate cyanato-*N* or thiocyanato-*N* ligands bound to the silicon(IV) coordination center, the monodentate ligands occupying *cis*-positions. We have now succeeded in synthesizing a series of neutral hexacoordinate silicon(IV) complexes with *Si*O$_2$N$_4$ skeletons, compounds **3**−**8**. From a formal point of view, the chelate complexes **3**−**6** can be regarded as derivatives of **1** and **2** (O/NR exchange; R = Bn, Ph, *i*-Pr); however, in contrast to **1** and **2** (*cis*-configuration each), the cyanato-*N* and thiocyanato-*N* ligands in **3**−**6** occupy *trans*-positions. Compound **7** is a derivative of **5** and **6**, with one tetradentate *O*,*N*,*N*,*O*-chelate ligand instead of two bidentate *O*,*N*-chelate ligands. The silicon(IV) complex **8**, which contains six monodentate ligands, can be regarded as an intermediate in the formation of **6**.

We report here on the synthesis of compounds **3**−**6** (isolated as the (*OC*-6-12)-isomers), (*OC*-6-2′2)-**7**, and *trans*-**8** and their structural characterization in the solid state (single-crystal X-ray diffraction; VACP/MAS NMR spectroscopy (^{13}C, ^{15}N, ^{29}Si)) and in solution (^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy). These experimental investigations were complemented by computational studies (RI-MP2 geometry optimizations of (i) the three possible stereoisomers of **7**, (ii) the five possible stereoisomers of the model compound **9**, and (iii) the two possible stereoisomers of the model compound **10**; calculations of the ^{29}Si NMR chemical shifts of **7**, **9**, and **10** using the optimized structures). The studies presented in this paper were performed with a special emphasis on the stereochemistry of these novel hexacoordinate silicon(IV) complexes and the bonding characteristics of the *O*,*N*- and *O*,*N*,*N*,*O*-chelate ligands. Preliminary results of the investigations reported here have already been presented elsewhere.[6]

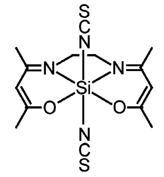


1: X = O
2: X = S



3–6

	R	X
3	Bn	O
4	Ph	O
5	Ph	S
6	*i*-Pr	S



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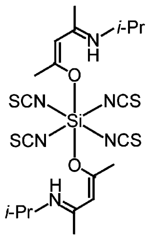

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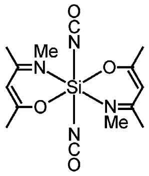

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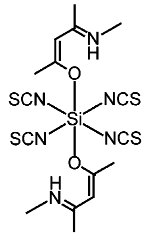

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Experimental Section

General Procedures. The 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 CDCl$_3$ and CD$_2$Cl$_2$ as the solvents. Chemical shifts (ppm) were determined relative to internal CHCl$_3$ (^{1}H, δ 7.24; CDCl$_3$), internal CHDCl$_2$ (^{1}H, δ 5.32; CD$_2$Cl$_2$), internal CDCl$_3$ (^{13}C, δ 77.0; CDCl$_3$), or internal CD$_2$Cl$_2$ (^{13}C, δ 53.8; CD$_2$Cl$_2$).[7] Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments and ^{13}C,^{1}H correlation 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

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(7) The solution NMR spectra of (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, and (*OC*-6-12)-**6** are characterized by multiple sets of resonance signals, indicating the presence of more than one species. The data given in the Experimental Section correspond to the respective major species. In the case of (*OC*-6-12)-**3** and (*OC*-6-12)-**6**, no solution NMR data are given because the NMR spectra could not be interpreted unequivocally.

mm) containing ca. 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; δ 0) or glycine (^{15}N, δ −342.0); 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 ^{14}N,^{29}Si spin system in *trans*-**8** was analyzed using the program WIN-DAISY 4.05.[8] The precursors $Si(NCO)_4$ and $Si(NCS)_4$ were synthesized according to ref 9 (for the synthesis of $Si(NCS)_4$, toluene instead of benzene was used as the solvent[4a]).

(*OC*-6-12)-Bis[4-(benzylimino)pent-2-en-2-olato(1−)-*N,O*]di(cyanato-*N*)silicon(IV) ((*OC*-6-12)-3). Tetra(cyanato-*N*)silane (500 mg, 2.55 mmol) was added at 20 °C to a solution of 4-(benzylamino)pent-3-en-2-one (965 mg, 5.10 mmol) in acetonitrile (10 mL), and the mixture was then stored undisturbed at 20 °C for 24 h and at −20 °C for a further 48 h. The resulting crystalline solid was isolated by filtration, washed with diethyl ether (20 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h). Yield: 808 mg (1.65 mmol, 65%); mp 145 °C (dec). ^{13}C VACP/MAS NMR: δ 21.7 (1 C, *C*H$_3$), 23.2 (3 C, *C*H$_3$), 54.6 (N*C*H$_2$), 103.2 (C═*C*H−C), 119.3 (N*C*O), 126.3, 127.8, 129.3, and 138.8 (Ph), 174.1 (*C*O or *C*N), 175.0 (*C*O or *C*N). ^{15}N VACP/MAS NMR: δ −241.0 (*N*CO), −169.2 (*N*Bn). ^{29}Si VACP/MAS NMR: δ −206.2. Anal. Calcd for $C_{26}H_{28}N_4O_4Si$ (488.62): C, 63.91; H, 5.78; N, 11.47. Found: C, 63.6; H, 5.6; N, 11.7.

(*OC*-6-12)-Di(cyanato-*N*)bis[4-(phenylimino)pent-2-en-2-olato(1−)-*N,O*]silicon(IV) ((*OC*-6-12)-4). The synthesis was carried out analogously to that of (*OC*-6-12)-**3** using tetra(cyanato-*N*)silane (500 mg, 2.55 mmol), 4-(phenylamino)pent-3-en-2-one (894 mg, 5.10 mmol), and tetrahydrofuran (10 mL). Yield: 904 mg (1.96 mmol, 77%); mp 153 °C (dec). ^{1}H NMR (CDCl$_3$): δ 1.26 (s, 6 H, C*H*$_3$), 1.71 (s, 6 H, C*H*$_3$), 5.28 (s, 2 H, C═C*H*−C), 7.13−7.50 (m, 10 H, Ph). ^{13}C NMR (CDCl$_3$): δ 22.3 (*C*H$_3$), 24.4 (*C*H$_3$), 100.8 (C═*C*H−C), 121.8 (N*C*O), 126.2, 126.4, 128.2, and 146.4 (Ph), 173.1 (*C*O or *C*N), 175.6 (*C*O or *C*N). ^{29}Si NMR (CDCl$_3$): δ −207 (br, poor signal-to-noise ratio, 7716 signal accumulations). ^{13}C VACP/MAS NMR: δ 21.7 (*C*H$_3$), 23.9 (*C*H$_3$), 100.9 (C═*C*H−C), 122.8 (N*C*O), 126.2, 126.7, 127.6, and 145.5 (Ph), 172.4 (*C*O, *C*N). ^{15}N VACP/MAS NMR: δ −241.1 (*N*CO), −153.8 (*N*Ph). ^{29}Si VACP/MAS NMR: δ −207.6. Anal. Calcd for $C_{24}H_{24}N_4O_4Si$ (460.56): C, 62.59; H, 5.25; N, 12.16. Found: C, 62.6; H, 5.4; N, 12.0.

(*OC*-6-12)-Bis[4-(phenylimino)pent-2-en-2-olato(1−)-*N,O*]di(thiocyanato-*N*)silicon(IV) ((*OC*-6-12)-5). The synthesis was carried out analogously to that of (*OC*-6-12)-**3** using tetra(thiocyanato-*N*)silane (664 mg, 2.55 mmol), 4-(phenylamino)pent-3-en-2-one (894 mg, 5.10 mmol), and tetrahydrofuran (10 mL). Yield: 890 mg (1.81 mmol, 71%); mp 88 °C (dec). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.28 (s, 6 H, C*H*$_3$), 1.76 (s, 6 H, C*H*$_3$), 5.41 (s, 2 H, C═C*H*−C), 7.12−7.46 (m, 10 H, Ph). ^{13}C NMR (CD$_2$Cl$_2$): δ 22.3 (*C*H$_3$), 24.9 (*C*H$_3$), 101.7 (C═*C*H−C), 126.8, 127.0, 129.0, and 146.3 (Ph), 134.3 (t, $^{1}J(^{13}\mathrm{C},^{14}\mathrm{N})$ = 24.1 Hz, N*C*S), 175.6 (*C*O or *C*N), 176.3 (*C*O or *C*N). ^{29}Si NMR (CD$_2$Cl$_2$): δ −210 (br, poor signal-to-noise ratio, 7093 signal accumulations). ^{13}C VACP/MAS NMR: δ 23.3 (*C*H$_3$), 25.9 (*C*H$_3$), 102.9 (C═*C*H−C), 124.9, 127.8, 129.5, 130.0, 131.1, and 146.3 (Ph), 137.0 (N*C*S), 177.4 (*C*O, *C*N). ^{15}N VACP/MAS NMR: δ −229.9 (*N*CS), −160.2 (*N*Ph). ^{29}Si VACP/MAS NMR: δ −207.4. Anal. Calcd for $C_{24}H_{24}N_4O_2S_2Si$ (492.70): C, 58.51; H, 4.91; N, 11.37; S, 13.02. Found: C, 58.1; H, 5.1; N, 11.1; S, 13.0.

(*OC*-6-12)-Bis[4-(isopropylimino)pent-2-en-2-olato(1−)-*N,O*]di(thiocyanato-*N*)silicon(IV) ((*OC*-6-12)-6). Method A. A solution of tetra(thiocyanato-*N*)silane (664 mg, 2.55 mmol), 4-(isopropylamino)pent-3-en-2-one (720 mg, 5.10 mmol), and triethylamine (516 mg, 5.10 mmol) in acetonitrile (10 mL) was stirred at 20 °C for 24 h. The resulting precipitate was filtered off and discarded, the filtrate was layered with *n*-pentane (10 mL), and the resulting mixture was kept undisturbed at −20 °C for 48 h. The resulting crystalline solid was isolated by filtration, washed with diethyl ether (20 mL), and dried in vacuo (20 °C, 2 h, 0.01 mbar). Yield: 755 mg (1.78 mmol, 70%); mp 116 °C (dec). ^{13}C VACP/MAS NMR: δ 21.0 (*C*H$_3$), 22.3 (CH(*C*H$_3$)$_2$), 25.5 (*C*H$_3$), 52.0 (*C*H(CH$_3$)$_2$), 106.3 (C═*C*H−C), 129.8 (N*C*S), 172.3 (*C*O or *C*N), 175.5 (*C*O or *C*N). ^{15}N VACP/MAS NMR: δ −230.6 (*N*CS), −157.4 (*N*(*i*-Pr)). ^{29}Si VACP/MAS NMR: δ −204.3. Anal. Calcd for $C_{18}H_{28}N_4O_2S_2Si$ (424.66): C, 50.91; H, 6.65; N, 13.19; S, 15.10. Found: C, 50.6; H, 6.6; N, 12.8; S, 15.0.

Method B. Triethylamine (279 mg, 2.76 mmol) was added at 20 °C to a stirred suspension of *trans*-**8** (750 mg, 1.38 mmol) in acetonitrile (10 mL), and the reaction mixture was stirred at 20 °C for 24 h. The resulting precipitate was filtered off and discarded, the filtrate was layered with *n*-pentane (10 mL), and the resulting mixture was kept undisturbed at −20 °C for 3 days. The resulting crystalline solid was isolated by filtration, washed with diethyl ether (20 mL), and dried in vacuo (20 °C, 2 h, 0.01 mbar). Yield: 307 mg (723 μmol, 52%). The spectroscopic data of the product were identical with those obtained for the product synthesized according to method A. Anal. Calcd for $C_{18}H_{28}N_4O_2S_2Si$ (424.66): C, 50.91; H, 6.65; N, 13.19; S, 15.10. Found: C, 50.5; H, 6.6; N, 12.9; S, 14.9.

(*OC*-6-2′2)-{4,4′-(Ethane-1,2-diyldinitrilo)bis[pent-2-en-2-olato(1−)]-*N,N′,O,O′*}di(thiocyanato-*N*)silicon(IV) ((*OC*-6-2′2)-7). Tetra(thiocyanato-*N*)silane (664 mg, 2.55 mmol) was added at 20 °C to a stirred solution of 4,4′-(ethane-1,2-diyldiimino)bis[pent-3-en-2-one] (572 mg, 2.55 mmol) in acetonitrile (10 mL), and the mixture was stirred at 20 °C for 24 h. The resulting precipitate was filtered off and discarded, and the filtrate was kept undisturbed at −20 °C for 48 h. The resulting crystalline solid was isolated by filtration, washed with diethyl ether (20 mL), and dried in vacuo (20 °C, 2 h, 0.01 mbar). Yield: 651 mg (1.78 mmol, 70%); mp 113 °C (dec). ^{1}H NMR (CDCl$_3$): δ 2.03 (s, 6 H, C*H*$_3$), 2.10 (s, 6 H, C*H*$_3$), 3.71 (s, 4 H, C*H*$_2$), 5.28 (s, 2 H, C═C*H*−C). ^{13}C NMR (CDCl$_3$): δ 22.6 (*C*H$_3$), 24.4 (*C*H$_3$), 43.8 (*C*H$_2$), 100.3 (C═*C*H−C), 134.5 (N*C*S), 171.2 (*C*O or *C*N), 177.6 (*C*O or *C*N). ^{29}Si NMR (CDCl$_3$): δ −207 (br, poor signal-to-noise ratio, 512 signal accumulations). ^{13}C VACP/MAS NMR: δ 22.9 (*C*H$_3$), 24.8 (*C*H$_3$), 44.5 (N*C*H$_2$), 102.2 (C═*C*H−C), 130.3 (N*C*S), 171.4 (*C*O or *C*N), 178.4 (*C*O or *C*N). ^{15}N VACP/MAS NMR: δ −230.4 (*N*CS), −157.5 (*N*CH$_2$). ^{29}Si VACP/MAS NMR: δ −209.3. Anal. Calcd for $C_{14}H_{18}N_4O_2S_2Si$ (366.54): C, 45.88; H, 4.95; N, 15.29; S, 17.50. Found: C, 45.6; H, 5.1; N, 15.5; S, 17.4.

***trans*-Bis[4-(isopropyliminio)pent-2-en-2-olato(1−)]tetra(thiocyanato-*N*)silicon(IV) (*trans*-8).** A solution of tetra(thiocyanato-*N*)silane (664 mg, 2.55 mmol) and 4-(isopropylamino)pent-3-en-2-one (720 mg, 5.10 mmol) in tetrahydrofuran (20 mL) was carefully layered with *n*-pentane (40 mL), and the resulting mixture was kept undisturbed at 20 °C for 48 h. The resulting crystalline solid was isolated by filtration, washed with diethyl ether (20 mL), and dried in vacuo (20 °C, 2 h, 0.01 mbar). Yield: 1.20 g (2.21 mmol, 87%); mp 126 °C (dec). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.51 (d, $^{3}J_{\mathrm{HH}}$ = 6.5 Hz, 12 H, CH(C*H*$_3$)$_2$), 2.23 (s, 6 H, C*H*$_3$), 2.45 (s, 6 H, C*H*$_3$), 3.92−4.08 (m, 2 H, C*H*(CH$_3$)$_2$), 5.21 (s, 2 H, C═C*H*−C), 10.4 (br s, 2 H, N*H*). ^{13}C NMR (CD$_2$Cl$_2$): δ 20.5 (*C*H$_3$), 22.6 (CH(*C*H$_3$)$_2$),

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[8] (a) *WIN-DAISY 4.05*; Bruker-Franzen GmbH: Bremen, Germany, 1998. (b) Weber, U.; Germanus, A.; Thiele, H. *Fresenius' J. Anal. Chem.* **1997**, *359*, 46−49.

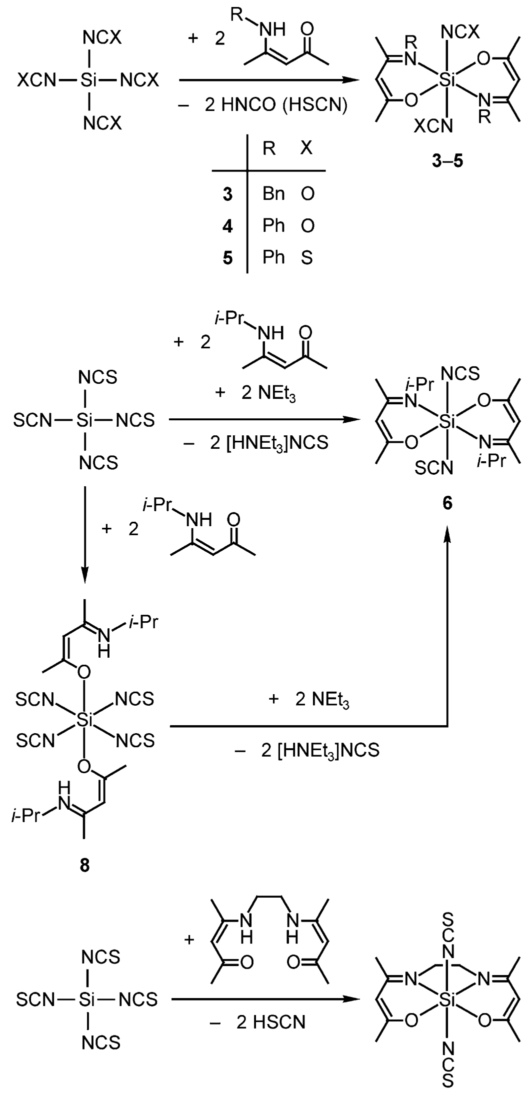
[9] Neville, R. G.; McGee, J. J. In *Inorganic Syntheses*; Holtzclaw, H. F., Jr., Ed.; McGraw-Hill: New York, 1966; Vol. VIII, pp 23−31.

23.6 (*C*H$_3$), 48.8 (*C*H(CH$_3$)$_2$), 100.7 (C═*C*H−C), 131.4 (t, ^1J(^{13}C,^{14}N) = 26.3 Hz, N*C*S), 132.1 (t, ^1J(^{13}C,^{14}N) = 26.7 Hz, N*C*S), 171.8 (*C*O or *C*N), 181.6 (*C*O or *C*N). ^{29}Si NMR (CD$_2$Cl$_2$): δ −231 (br, poor signal-to-noise ratio, 4768 signal accumulations). ^{13}C VACP/MAS NMR: δ 20.6 (*C*H$_3$), 23.0 (*C*H$_3$), 23.1 (*C*H$_3$), 24.1 (*C*H$_3$), 48.8 (*C*H(CH$_3$)$_2$), 100.6 (C═*C*H−C), 130.3 (N*C*S), 173.7 (*C*O or *C*N), 178.3 (*C*O or *C*N). ^{15}N VACP/MAS NMR: δ −229.4 (*N*CS), −228.8 (*N*CS), −202.5 (*N*(*i*-Pr)). ^{29}Si VACP/MAS NMR: δ −233.0 (nonet, ^1J(^{14}N,^{29}Si) = 28.0 Hz). Anal. Calcd for $C_{20}H_{30}N_6O_2S_4Si$ (542.85): C, 44.25; H, 5.57; N, 15.48; S, 23.63. Found: C, 43.9; H, 5.7; N, 14.9; S, 23.2.

Crystal Structure Analyses. Suitable single crystals of (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, (*OC*-6-12)-**6**, (*OC*-6-2′2)-**7**, and *trans*-**8** 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 Kα radiation, λ = 0.710 73 Å; temperature, 173(2) K). All structures were solved by direct methods.[10] The non-hydrogen atoms were refined anisotropically.[11] A riding model was employed in the refinement of the C*H* hydrogen atoms. The Flack parameter of compound (*OC*-6-2′2)-**7** was refined with the program SHELXL-97.[11] The value of +0.31(17) with its high standard uncertainty does not allow a conclusion about the absolute structure of the molecule in the investigated crystal and might indicate twinning. However, refinement in a centrosymmetric space group failed. In addition to the Supporting Information described at the end of this paper, crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-253785 ((*OC*-6-12)-**3**), CCDC-253786 ((*OC*-6-12)-**4**), CCDC-253787 ((*OC*-6-12)-**5**), CCDC-253788 ((*OC*-6-12)-**6**), CCDC-253789 ((*OC*-6-2′2)-**7**), and CCDC-253790 (*trans*-**8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)-1223/336033; e-mail, deposit@ccdc.cam.ac.uk).

Computational Studies. RI-MP2[12] geometry optimizations of (*OC*-6-2′2)-**7**, (*OC*-6-1′3)-**7**, (*OC*-6-32)-**7**, **9**α−ε, *cis*-**10**, and *trans*-**10** were carried out at the TZP level (with a TZVP auxiliary basis for the fit of the charge density)[13,14] using the TURBOMOLE program system.[15] 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 all 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 zero-point vibrational energies obtained by HF calculations.

Scheme 1



	R	X
3	Bn	O
4	Ph	O
5	Ph	S

Results and Discussion

Compounds (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, and *trans*-**8** were synthesized according to Scheme 1 by treatment of tetra(cyanato-*N*)silane or tetra(thiocyanato-*N*)silane with 2 molar equiv of the respective 4-aminopent-3-en-2-ones Me−C(NRH)═CH−C(O)−Me (R = Bn, Ph, *i*-Pr). The products were isolated in good yields as crystalline solids (**3**, 65%; **4**, 77%; **5**, 71%; **8**, 87%). Treatment of tetra(thiocyanato-*N*)silane with 4,4′-(ethane-1,2-diyldiimino)bis[pent-3-en-2-one] (molar ratio 1:1) gave (*OC*-6-2′2)-**7** in 70% yield as a crystalline solid (Scheme 1). Surprisingly, the reaction of tetra(thiocyanato-*N*)silane with 4-(isopropylamino)pent-3-en-2-one did not lead to the expected chelate complex (*OC*-6-12)-**6** under the reaction conditions used for the synthesis of (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, and (*OC*-6-12)-**5**; instead, we isolated the adduct *trans*-**8**.[16] However, the formation of (*OC*-6-12)-**6** could be achieved by addition of

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(10) (a) Sheldrick, G. M. *SHELXS-97*; University of Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

(11) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

(12) (a) Weigend, F.; Häser, M. *Theor. Chem. Acc.* **1997**, *97*, 331−340. (b) Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R. *Chem. Phys. Lett.* **1998**, *294*, 143−152.

(13) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571−2577.

(14) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829−5835.

(15) Program system TURBOMOLE: Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165−169.

(16) Structurally related *trans*-adducts were also obtained by treatment of TiCl$_4$ and ZrCl$_4$ with Me−C(N*i*-PrH)═CH−C(O)−Me: Jones, D.; Roberts, A.; Cavell, K.; Keim, W.; Englert, U.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1998**, 255−262.

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, (*OC*-6-12)-**6**, (*OC*-6-2′2)-**7**, and *trans*-**8**

	(*OC*-6-12)-**3**	(*OC*-6-12)-**4**	(*OC*-6-12)-**5**	(*OC*-6-12)-**6**	(*OC*-6-2’2)-**7**	*trans*-**8**
empirical formula	$C_{26}H_{28}N_4O_4Si$	$C_{24}H_{24}N_4O_4Si$	$C_{24}H_{24}N_4O_2S_2Si$	$C_{18}H_{28}N_4O_2S_2Si$	$C_{14}H_{18}N_4O_2S_2Si$	$C_{20}H_{30}N_6O_2S_4Si$
formula mass, g mol^{-1}	488.61	460.56	492.68	424.65	366.53	542.83
cryst syst	monoclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic
space group (No.)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$C2$ (No. 5)	$P2_1/n$ (No. 14)
a, Å	17.273(3)	7.8647(11)	17.299(2)	7.0217(9)	13.554(3)	9.5949(13)
b, Å	9.9050(11)	8.9206(13)	11.8942(16)	8.6194(11)	8.7110(17)	10.7216(14)
c, Å	15.552(2)	9.0668(13)	12.1345(16)	9.3688(13)	8.7748(18)	13.339(2)
α, deg	90	80.584(17)	90	76.053(15)	90	90
β, deg	116.242(17)	89.652(17)	104.082(14)	84.672(15)	121.99(3)	100.570(17)
γ, deg	90	64.888(16)	90	82.245(14)	90	90
V, Å^3	2386.5(6)	566.79(14)	2421.7(5)	544.20(12)	878.7(3)	1349.0(3)
Z	4	1	4	1	2	2
μ, mm^{-1}	0.140	0.143	0.299	0.320	0.385	0.425
2*θ* range, deg	4.88−52.92	7.08−54.14	4.20−53.86	7.38−55.86	5.48−52.74	4.84−49.48
no. collected reflns	32224	6024	10007	6999	6115	9480
no. independent reflns	4867	2277	2603	2373	1721	2301
R_{int}	0.0450	0.0236	0.0502	0.0263	0.0512	0.0605
no. params	320	153	153	128	108	158
R1^a [$I > 2\sigma(I)$]	0.0344	0.0343	0.0355	0.0312	0.0426	0.0304
wR2^a (all data)	0.0947	0.0943	0.0996	0.0877	0.0981	0.0701
S^a	1.050	1.057	1.048	1.064	1.075	0.917
max/min Δ*ρ*, e Å^{-3}	+0.211/−0.271	+0.240/−0.220	+0.315/−0.339	+0.315/−0.250	+0.337/−0.285	+0.245/−0.208

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$; $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$, with n = no. of reflections, p = no. of parameters; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2]/3$, and a and b are constants suggested by the refinement program (see Supporting Information).

2 molar equiv of triethylamine to the reaction mixture (Scheme 1; yield, 70%). Alternatively, the chelate complex (*OC*-6-12)-**6** was also obtained by reaction of the adduct *trans*-**8** with 2 molar equiv of triethylamine (Scheme 1; yield, 52%). This gives some insight into the possible mechanism for the formation of compounds (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, and (*OC*-6-12)-**6**: the neutral 4-aminopent-3-en-2-ones add twice to the tetracoordinate silicon center to give a hexacoordinate (formally zwitterionic) intermediate, with two monodentate neutral ligands of the iminio−enolato type. Upon deprotonation of the two iminium groups and elimination of HNCO or HSCN, the chelate complex is formed, with two bidentate negatively charged ligands of the imino−enolato type.

The identities of compounds (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, (*OC*-6-12)-**6**, (*OC*-6-2′2)-**7**, and *trans*-**8** were established by elemental analyses (C, H, N, S), single-crystal X-ray diffraction studies, solid-state VACP/MAS NMR experiments (^{13}C, ^{15}N, ^{29}Si), and solution NMR studies (^1H, ^{13}C, ^{29}Si).

The crystal data and the experimental parameters used for the crystal structure analyses are given in Table 1. The molecular structures in the crystal are shown in Figures 1−6; selected bond distances and angles are given in the respective figure legends.

Compounds **3**−**6** each crystallize as the (*OC*-6-12)-isomer, with a slightly distorted octahedral Si-coordination polyhedron. Except for (*OC*-6-12)-**3** (*C*$_1$ symmetry), their molecular structures are characterized by crystallographic C_i symmetry, with the silicon atom as the center of inversion. The Si−O (Si−N) bond distances in the chelate rings of (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, and (*OC*-6-12)-**6** are in the range 1.7318(10)−1.7406(10) Å (1.9131(13)−1.9328(11) Å). The Si−NCO bond distances of (*OC*-6-12)-**3** and (*OC*-6-12)-**4** (1.8199(11)−1.8356(13) Å) are slightly longer than those of *cis*-**1** (1.8024(12) Å),[4b] and the Si−NCS distances of (*OC*-6-12)-**5** and (*OC*-6-12)-**6** (1.8401(12)−1.8619(11) Å) are also slightly longer than those of *cis*-**2** (1.8093(17)−1.8145(16) Å).[4a]

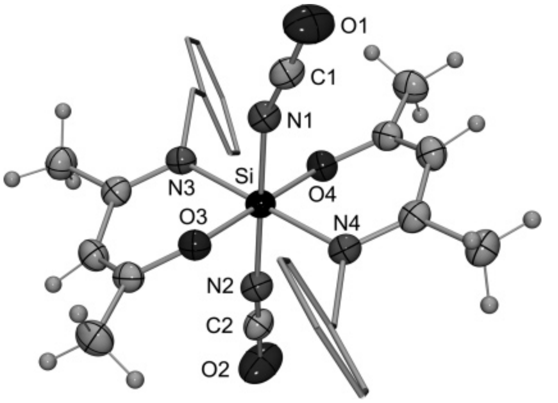

Figure 1. Molecular structure of (*OC*-6-12)-**3** in the crystal (probability level of displacement ellipsoids 50%). The benzyl groups are represented as stick models for clarity. Selected bond lengths (Å) and angles (deg) are as follows: Si−O3 1.7385(10), Si−O4 1.7406(10), Si−N1 1.8299(13), Si−N2 1.8356(13), Si−N3 1.9131(13), Si−N4 1.9171(13), N1−C1 1.1664(19), N2−C2 1.1593(19), C1−O1 1.1866(19), C2−O2 1.1895(19); O3−Si−O4 179.21(5), O3−Si−N1 89.11(5), O3−Si−N2 90.68(5), O3−Si−N3 90.95(5), O3−Si−N4 88.90(5), O4−Si−N1 91.59(5), O4−Si−N2 88.62(5), O4−Si−N3 88.70(5), O4−Si−N4 91.45(5), N1−Si−N2 179.78(6), N1−Si−N3 89.12(5), N1−Si−N4 90.39(5), N2−Si−N3 90.94(5), N2−Si−N4 89.55(5), N3−Si−N4 179.49(5), Si−N1−C1 157.33(12), Si−N2−C2 164.13(12), N1−C1−O1 177.47(16), N2−C2−O2 178.10(18).

Comparison of (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, and (*OC*-6-12)-**6** with (*OC*-6-2′2)-**7** (which cannot exist as the (*OC*-6-12)-isomer for geometric reasons) shows a significant shortening of the Si−N bond lengths (1.871(3) Å) and a lengthening of the Si−O distances (1.759(2) Å) in the chelate rings of (*OC*-6-2′2)-**7**, whereas almost no effect was observed for the Si−NCS bond distances (1.857(2) Å).

The adduct **8** crystallizes as the *trans*-isomer, with a slightly distorted octahedral Si-coordination polyhedron. The molecular structure of *trans*-**8** is characterized by crystal-

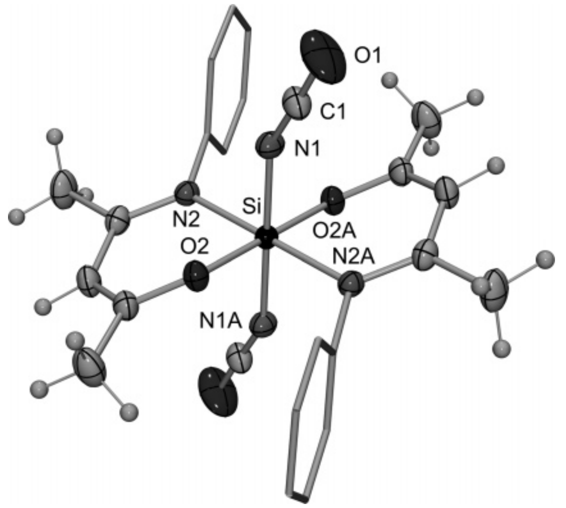

Figure 2. Molecular structure of (*OC*-6-12)-**4** in the crystal (probability level of displacement ellipsoids 50%). The phenyl groups are represented as stick models for clarity. Selected bond lengths (Å) and angles (deg) are as follows: Si−O2 1.7388(10), Si−N1 1.8199(11), Si−N2 1.9328(11), N1−C1 1.1614(17), C1−O1 1.1809(18); O2−Si−O2A 180.0, O2−Si−N1 91.21(5), O2−Si−N1A 88.79(5), O2−Si−N2 91.46(5), O2−Si−N2A 88.54(5), N1−Si−N1A 180.0, N1−Si−N2 90.11(5), N1−Si−N2A 89.89(5), N2−Si−N2A 180.0, Si−N1−C1 151.62(12), N1−C1−O1 177.96(18).

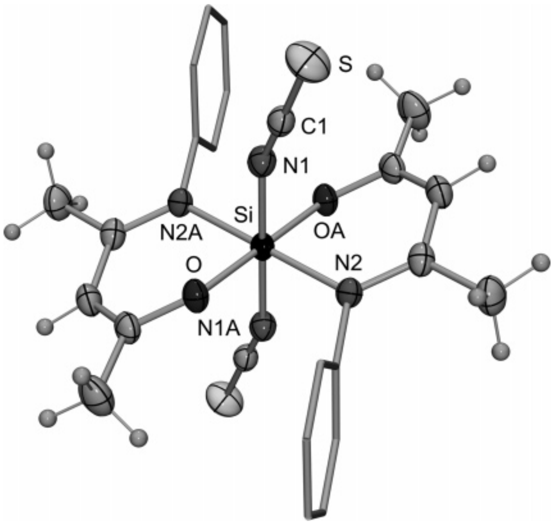

Figure 3. Molecular structure of (*OC*-6-12)-**5** in the crystal (probability level of displacement ellipsoids 50%). The phenyl groups are represented as stick models for clarity. Selected bond lengths (Å) and angles (deg) are as follows: Si−O 1.7318(10), Si−N1 1.8401(12), Si−N2 1.9138(12), N1−C1 1.1684(19), C1−S 1.5925(14); O−Si−OA 180.0, O−Si−N1 88.76(5), O−Si−N1A 91.24(5), O−Si−N2 88.74(5), O−Si−N2A 91.26(5), N1−Si−N1A 180.0, N1−Si−N2 89.21(5), N1−Si−N2A 90.79(5), N2−Si−N2A 180.0, Si−N1−C1 156.68(12), N1−C1−S 179.22(14).

lographic C_i symmetry, with the silicon atom as the center of inversion. The Si−O distances (1.7732(12) Å) are only slightly longer than those of (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, and (*OC*-6-12)-**6** but significantly shorter than those observed for (*OC*-6-2′2)-**7**. The Si−NCS bond lengths of *trans*-**8** (1.8135(16)−1.8153(16) Å) are somewhat shorter than those of (*OC*-6-12)-**5**, (*OC*-6-12)-**6**, and (*OC*-6-2′2)-**7** but very similar to those reported for *cis*-**2**.[4i] It is interesting to note that *trans*-**8** forms two intramolecular N−H···O hydrogen bonds in the crystal.[17]

The structural features observed for the Si−NCX (X = O, S) moieties of the compounds studied are similar to those

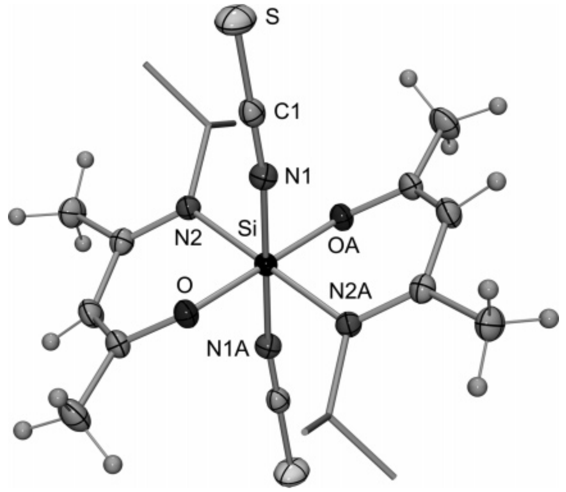

Figure 4. Molecular structure of (*OC*-6-12)-**6** in the crystal (probability level of displacement ellipsoids 50%). The isopropyl groups are represented as stick models for clarity. Selected bond lengths (Å) and angles (deg) are as follows: Si−O 1.7378(8), Si−N1 1.8619(11), Si−N2 1.9241(10), N1−C1 1.1649(17), C1−S 1.6140(13); O−Si−OA 180.000(1), O−Si−N1 88.27(4), O−Si−N1A 91.73(4), O−Si−N2 91.48(4), O−Si−N2A 88.52(4), N1−Si−N1A 180.00(6), N1−Si−N2 89.44(5), N1−Si−N2A 90.56(5), N2−Si−N2A 180.000(1), Si−N1−C1 168.99(10), N1−C1−S 179.88(14).

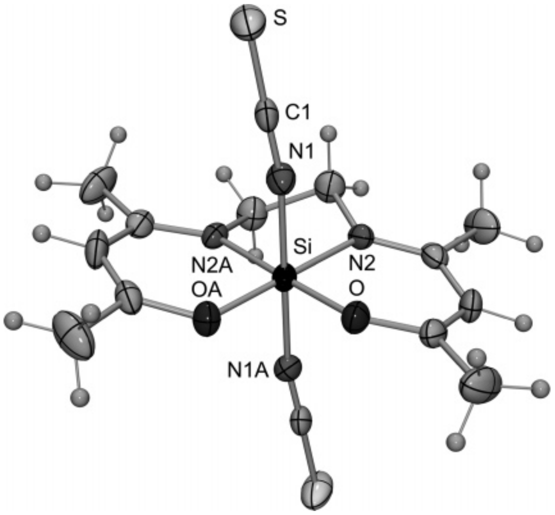

Figure 5. Molecular structure of (OC-6-2′2)-**7** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths (Å) and angles (deg) are as follows: Si−O 1.759(2), Si−N1 1.857(2), Si−N2 1.871(3), N1−C1 1.163(3), C1−S 1.604(2); O−Si−OA 86.85(17), O−Si−N1 90.67(13), O−Si−N1A 91.17(12), O−Si−N2 94.00(8), O−Si−N2A 178.78(15), N1−Si−N1A 177.5(2), N1−Si−N2 89.70(12), N1−Si−N2A 88.44(13), N2−Si−N2A 85.16(18), Si−N1−C1 170.41(19), N1−C1−S 179.0(3).

of *cis*-**1** and *cis*-**2**.[4a,b] The N−C bond lengths of the Si−NCX groups of (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, (*OC*-6-12)-**6**, (*OC*-6-2′2)-**7**, and *trans*-**8** are very similar and range from 1.1593(16) to 1.1684(19) Å. The C−X distances are in the range 1.1809(18)−1.1895(19) Å (X = O) and 1.589(2)−1.6140(13) Å (X = S), respectively. The Si−NCX moieties of all compounds are angled, with Si−N−C angles ranging from 151.62(12)° to 176.99(16)° (in this context, see also ref 4a), whereas the N−C−X angles are closer to linearity (177.47(16)−179.88(14)°).

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(17) The hydrogen-bonding system was analyzed by using the program PLATON: Spek, A. L. *PLATON*; University of Utrecht: Utrecht, The Netherlands, 1998.

Table 2. Selected Bond Lengths (Å) for the Organic Ligands of *cis*-**1**, *cis*-**2**, (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, (*OC*-6-12)-**6**, (*OC*-6-2′2)-**7**, and *trans*-**8**[a]

	cis-**1**	*cis*-**2**	(*OC*-6-12)-**3**	(*OC*-6-12)-**4**	(*OC*-6-12)-**5**	(*OC*-6-12)-**6**	(*OC*-6-2'2)-**7**	*trans*-**8**
O−C	1.2837(17) 1.2926(16)	1.292(2)−1.296(2)	1.3190(18) 1.3164(18)	1.3142(16)	1.3178(17)	1.3304(14)	1.311(5)	1.318(2)
N−C			1.3103(19) 1.3134(19)	1.3114(17)	1.3167(18)	1.3164(14)	1.313(5)	1.310(2)
C−C(O)	1.383(2)	1.383(3)−1.386(3)	1.351(2) 1.353(2)	1.3539(19)	1.352(2)	1.3476(19)	1.359(5)	1.361(3)
C−C(N)			1.424(2) 1.421(2)	1.4238(18)	1.421(2)	1.4390(17)	1.413(5)	1.418(3)

[a] The data given refer to the bond distances within the *O*CCC*O* or *O*CCC*N* skeletons of the ligands.

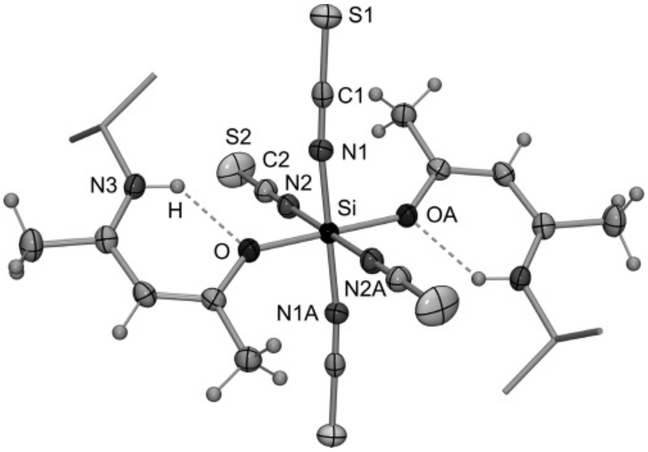

Figure 6. Molecular structure of *trans*-**8** in the crystal (probability level of displacement ellipsoids 50%). The isopropyl groups are represented as stick models for clarity. Selected bond lengths (Å) and angles (deg) are as follows: Si−O 1.7732(12), Si−N1 1.8153(16), Si−N2 1.8135(16), N1−C1 1.166(2), N2−C2 1.165(2), C1−S1 1.6013(19), C2−S2 1.589(2); O−Si−OA 180.0, O−Si−N1 87.38(6), O−Si−N1A 92.62(6), O−Si−N2 87.45(7), O−Si−N2A 92.55(6), N1−Si−N1A 180.0, N1−Si−N2 90.27(7), N1−Si−N2A 89.73(7), N2−Si−N2A 180.0, Si−N1−C1 172.66(15), Si−N2−C2 176.99(16), N1−C1−S1 178.78(16), N2−C2−S2 179.06(17). The dashed lines indicate intramolecular N−H···O hydrogen bonds (N3−H 0.86(2), H···O 1.98(2), N3···O 2.667(2), N3−H···O 135.9(19)).[17]

Table 2 summarizes the O−C, N−C, and C−C bond lengths within the *O*CCC*O* and *O*CCC*N* backbones of the organic ligands of *cis*-**1**, *cis*-**2**, (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, (*OC*-6-12)-**6**, (*OC*-6-2′2)-**7**, and *trans*-**8**. These data give some insight into the bonding situation of the compounds studied. In the case of *cis*-**1** and *cis*-**2** (bidentate symmetric *O*,*O*-chelate ligands), the O−C distances are in the range 1.2837(17)−1.296(2) Å, and the C−C(O) distances range from 1.383(2) to 1.386(3) Å,[4a,b] indicating a significant degree of delocalization of electron density in the two *O*,*O*-chelate ligands. In contrast, the degree of delocalization in the bidentate unsymmetric *O*,*N*-chelate ligands of (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, and (*OC*-6-12)-**6** is significantly less pronounced, as can be seen from the longer O−C distances and the shorter C−C(O) distances. Thus, the *O*,*N*-chelate ligands are best described as ligands of the imino−enolato type.[18] This idealized description is also supported by the similar O−C, N−C, and C−C(O) bond lengths observed for the two iminio−enolato ligands of *trans*-**8** and by the calculated bond distances for the imino−enol structure of 4-aminopent-3-en-2-one.[19]

The isotropic ^{29}Si chemical shifts obtained in solid-state VACP/MAS NMR studies of all the compounds synthesized clearly indicate the presence of hexacoordinate silicon atoms ((*OC*-6-12)-**3**, δ −206.2; (*OC*-6-12)-**4**, δ −207.6; (*OC*-6-12)-**5**, δ −207.4; (*OC*-6-12)-**6**, δ −204.3; (*OC*-6-2′2)-**7**, δ −209.3; *trans*-**8**, δ −233.0). The ^{29}Si chemical shifts of the chelate complexes (*Si*O$_2$N$_4$ skeleton) are very similar to the isotropic ^{29}Si chemical shifts observed for *cis*-**1** (δ −206.6) and *cis*-**2** (δ −210.2),[4a,b] although the latter two compounds contain an *Si*O$_4$N$_2$ framework. The isotropic ^{29}Si chemical shift of *trans*-**8** differs significantly from those observed for the chelate complexes, although all compounds contain an *Si*O$_2$N$_4$ skeleton. This high-field shift of *trans*-**8** can be explained by the presence of four thiocyanato-*N* ligands and correlates well with the even more pronounced high-field shift observed for the [Si(NCS)$_6$]$^{2-}$ dianion in [K(18-crown-6)]$_2$[Si(NCS)$_6$] (δ −253.0),[4a] which contains six thiocyanato-*N* ligands.

The ^{29}Si VACP/MAS NMR spectrum of *trans*-**8** shows accurately resolved $^1J(^{14}\text{N},^{29}\text{Si})$ couplings (Figure 7), whereas these couplings are not resolved in the ^{29}Si NMR spectra of all the other compounds where broad resonance signals were observed.

The solid-state NMR spectra (^{13}C, ^{15}N, ^{29}Si) of all the compounds studied are compatible with the structures determined by single-crystal X-ray diffraction and demonstrated that the isolated crystalline products were isomerically pure.

The ^{1}H and ^{13}C NMR spectra of (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, and (*OC*-6-12)-**6** in solution (CDCl$_3$, CD$_2$Cl$_2$) point to the existence of more than one species. In the case of (*OC*-6-12)-**4** and (*OC*-6-12)-**5**, the ^{1}H and ^{13}C NMR data of the respective major species were compatible with the structures of these compounds in the solid state, whereas the ^{1}H and ^{13}C NMR spectra of (*OC*-6-12)-**3** and (*OC*-6-12)-**6** could not be interpreted satisfactorily. For this reason, no solution NMR data for the latter two compounds are reported in the Experimental Section. In the ^{1}H and ^{13}C NMR spectra of (*OC*-6-2′2)-**7** (CDCl$_3$), only one set of resonance signals was observed, the NMR data being compatible with the solid-state structure. The ^{1}H NMR spectrum of *trans*-**8** (CD$_2$Cl$_2$) gives some hints to the existence of another species; however, the additional resonance signals are poorly resolved and show only a low intensity.

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(18) The nomenclature of the chelate complexes studied is also based on this idealized formal description.

(19) Tayyari, S. F.; Fazli, M.; Milani-nejad, F. *J. Mol. Struct.: THEOCHEM* **2001**, *541*, 11−15.

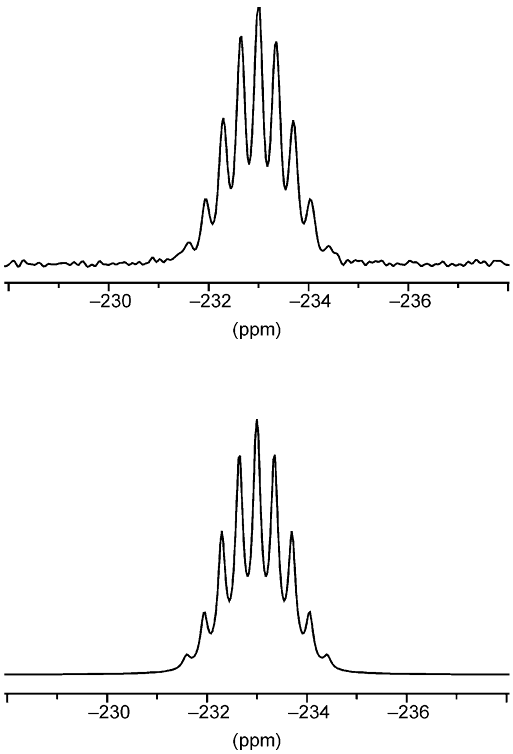

Figure 7. Comparison of the experimental solid-state ^{29}Si VACP/MAS NMR spectrum of *trans*-**8** at a spinning rate of 5000 Hz (top) and the simulated spectrum obtained with the program WIN-DAISY 4.05[8] (bottom), showing the $^{1}J(^{14}N,^{29}Si)$ couplings. The splitting of the ^{29}Si NMR signal can be explained by couplings of the ^{29}Si nucleus with four equivalent ^{14}N nuclei ($^{1}J(^{14}N,^{29}Si)$ = 28.0 Hz).

As also observed for *cis*-**2**,[4a] the N*C*S resonance signals in the ^{13}C NMR spectra of (*OC*-6-12)-**5** and *trans*-**8** show splittings due to $^{1}J(^{13}C,^{14}N)$ couplings; however, these splittings are not resolved in the ^{13}C NMR spectra of (*OC*-6-12)-**4** and (*OC*-6-2′2)-**7**. Because of the ^{14}N,^{29}Si couplings, the solution ($CDCl_3$, CD_2Cl_2) ^{29}Si NMR spectra of all compounds studied are characterized by broad, poorly resolved resonance signals, with chemical shifts similar to those obtained by the ^{29}Si VACP/MAS NMR experiments.

Geometry optimizations for (*OC*-6-2′2)-**7**, (*OC*-6-1′3)-**7**, (*OC*-6-32)-**7**, **9**α−ϵ, *trans*-**10**, and *cis*-**10** were performed at the RI-MP2 level[12] using a TZP basis set[13] and a TZVP auxiliary basis for the fit of the charge density.[14] The calculations were performed using the TURBOMOLE program system.[15] The structures of the respective calculated minima with selected calculated distances and angles can be found in the Supporting Information. As can be seen from these data, the calculated structures of (*OC*-6-2′2)-**7**, **9**α, and *trans*-**10** and the respective experimentally established structures are in reasonable agreement.[20]

Because of the presence of two identical unsymmetric bidentate ligands and two identical monodentate ligands in the chelate complexes (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, and (*OC*-6-12)-**6**, five stereoisomers have to be considered for these compounds. This is demonstrated in Figure 8 for the model compound **9** (isomers **9**α−ϵ). The three possible isomers of **7** ((*OC*-6-2′2)-**7**, (*OC*-6-1′3)-**7**, (*OC*-6-32)-**7**) and the two possible isomers of **10** (*trans*-**10**, *cis*-**10**) are also depicted in Figure 8.

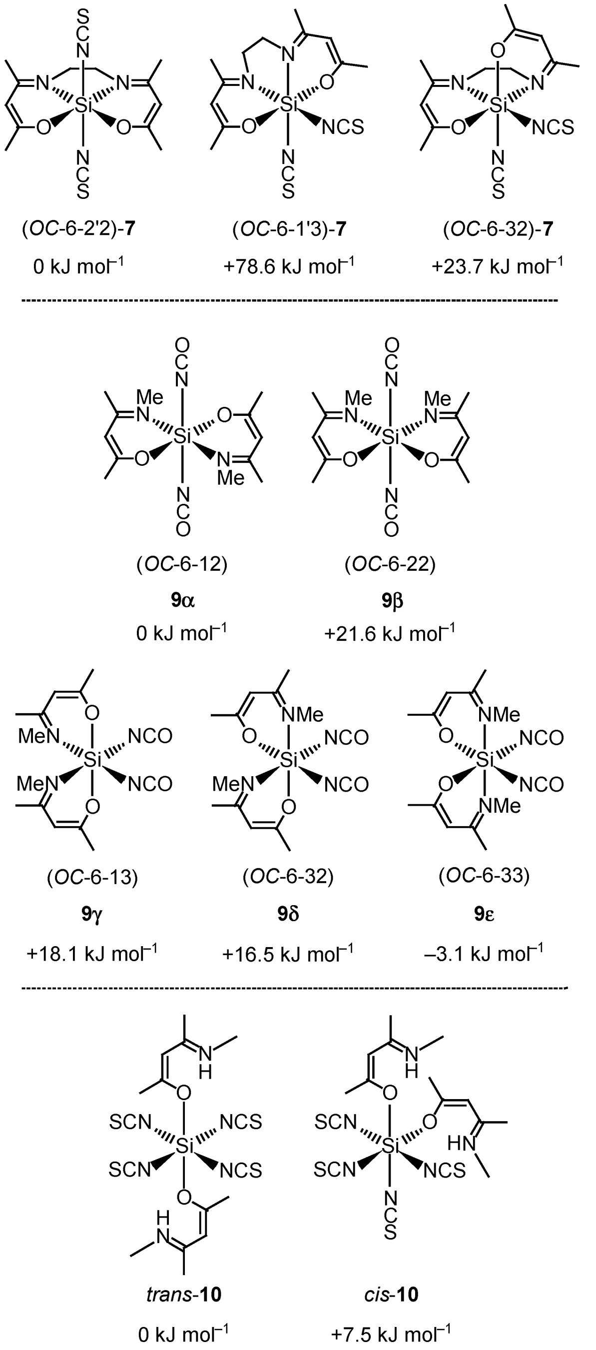

Figure 8. Configurations and calculated relative energies for the three possible stereoisomers of **7**, the five possible stereoisomers of **9**, and the two possible stereoisomers of **10**.

The calculated energies of the five isomers **9**α−ϵ differ only by a maximum of 24.7 kJ mol^{-1}, the (*OC*-6-12)-isomer **9**α (which corresponds to the experimentally established crystal structures) being energetically more stable than **9**β, **9**γ, and **9**δ (see legend of Figure 8). Only the (*OC*-6-33)-isomer **9**ϵ (with the NMe groups in *trans*-position as in **9**α) is somewhat more stable (3.1 kJ mol^{-1}) than the (*OC*-6-12)-isomer **9**α. For the isomers (*OC*-6-2′2)-**7**, (*OC*-6-1′3)-**7**, and (*OC*-6-32)-**7**, the maximum energy difference is significantly

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(20) A perfect agreement between the calculated and experimentally established structures cannot be expected since the latter are influenced by intermolecular interactions in the crystal.

higher (78.6 kJ mol^{-1}), the (*OC*-6-2′2)-configuration being more stable than the (*OC*-6-1′3)- and (*OC*-6-32)-**7**-configurations. This result is in accordance with the experimentally established structure of (*OC*-6-2′2)-**7** in the crystal. The calculated energy difference between *trans*-**10** and *cis*-**10** is low (7.5 kJ mol^{-1}), the *trans*-isomer being more stable than the *cis*-isomer.[21]

The isotropic ^{29}Si chemical shifts determined experimentally for (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, (*OC*-6-12)-**6**, (*OC*-6-2′2)-**7**, and *trans*-**8** were also accurately reproduced by quantum-chemical calculations, as can be seen from the computed ^{29}Si chemical shifts for (*OC*-6-2′2)-**7** (δ -200), **9**α (δ -198), and *trans*-**10** (δ -221). These studies were carried out at the HF/TZP level. It is interesting to note that the calculated ^{29}Si chemical shifts for (*OC*-6-2′2)-**7**, (*OC*-6-1′3)-**7**, (*OC*-6-32)-**7**, and **9**$\alpha-\epsilon$ are almost identical. Obviously, the different configurations of these complexes have no effect on the ^{29}Si chemical shift. The same holds true for the *trans*- and *cis*-configurations of **10** (the calculated ^{29}Si chemical shifts for (*OC*-6-2′2)-**7**, (*OC*-6-1′3)-**7**, (*OC*-6-32)-**7**, **9**$\alpha-\epsilon$, *trans*-**10**, and *cis*-**10** can be found in the Supporting Information).

Conclusions

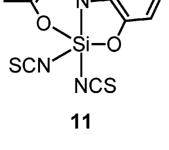
Treatment of tetra(cyanato-*N*)silane or tetra(thiocyanato-*N*)silane with acetylacetone yields the hexacoordinate silicon(IV) complexes *cis*-**1** and *cis*-**2**, respectively. In contrast, reaction of tetra(cyanato-*N*)silane or tetra(thiocyanato-*N*)silane with the 4-aminopent-3-en-2-ones Me−C(NRH)═CH−C(O)−Me (R = Bn, Ph, *i*-Pr) afforded the related hexacoordinate silicon(IV) complexes (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, and (*OC*-6-12)-**6**, with the two cyanato-*N* or thiocyanato-*N* ligands in *trans*-positions. (The latter compound was only obtained in the presence of 2 molar equiv of triethylamine.) From a formal point of view, these compounds can be regarded as derivatives of *cis*-**1** and *cis*-**2** (O/NR exchange; R = Bn, Ph, *i*-Pr), but their stereochemistry is totally different. From an energetical point of view, the existence of isomers with the two monodentate ligands in *cis*-position should also be possible as demonstrated by the computational studies of the five possible stereoisomers of the model compound **9** (calculated maximum energy difference between the *trans*-isomer **9**α and the *cis*-isomers **9**γ, **9**δ, and **9**ϵ: 18.1 kJ mol^{-1}). However, only products with the two cyanato-*N* or thiocyanato-*N* ligands in *trans*-positions ((*OC*-6-12)-configuration) were isolated. Further investigations are necessary to explain these experimental findings. The formation of (*OC*-6-2′2)-**7** upon reaction of tetra(thiocyanato-*N*)silane with 4,4′-(ethane-1,2-diyldiimino)bis[pent-3-en-2-one] is in good accordance with the results obtained in the computational studies: (*OC*-6-2′2)-**7** was found to be significantly more stable than the isomers (*OC*-6-1′3)-**7** and (*OC*-6-32)-**7** (maximum energy difference, 78.6 kJ mol^{-1}). In principle, the formation of *trans*-**8** upon reaction of tetra(thiocyanato-*N*)silane with 4-(isopropyl)pent-3-en-2-one correlates also with the computational studies (calculated energy difference between *trans*-**10** and *cis*-**10**, 7.5 kJ mol^{-1}); however, this energy difference is very small and, hence, the existence of *cis*-**10** should also be possible.[21]

Surprisingly, treatment of tetra(thiocyanato-*N*)silane with 2 molar equiv of 4-(isopropylamino)pent-3-en-2-one does not afford the expected chelate complex (*OC*-6-12)-**6**; instead, the adduct *trans*-**8** was obtained. Adducts of this type can be regarded as intermediates in the formation of the chelate complexes (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, and (*OC*-6-12)-**5**. In fact, reaction of *trans*-**8** with triethylamine afforded the chelate complex (*OC*-6-12)-**6**. Treatment of tetra(thiocyanato-*N*)silane with 2 molar equiv each of 4-(isopropylamino)pent-3-en-2-one and triethylamine afforded (*OC*-6-12)-**6** as well.

The analysis of the O−C, N−C, and C−C bond lengths within the backbones of the *O*,*N*- (*O*,*N*,*N*,*O*-) chelate ligands of (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, (*OC*-6-12)-**6**, and (*OC*-6-2′2)-**7** reveals that the degree of delocalization of electron density is less pronounced than in the case of the *O*,*O*-chelate ligands of *cis*-**1** and *cis*-**2**. Thus, the *O*,*N*- (*O*,*N*,*N*,*O*-) chelate ligands are best described as ligands of the imino−enolato type. The organic ligands of *trans*-**8** represent ligands of the iminio−enolato type.

With the studies presented here, members of new classes of neutral hexacoordinate silicon(IV) complexes with an $Si\mathrm{O_2N_4}$ skeleton have been synthesized and structurally characterized. Tetra(cyanato-*N*)silane and tetra(thiocyanato-*N*)silane proved to be very useful precursors in the synthesis of these compounds. With these studies, a novel challenging field in the chemistry of higher-coordinate silicon has been entered. In this context, it is interesting to note that a neutral hexacoordinate silicon(IV) complex (Pc 4), with an $Si\mathrm{O_2N_4}$ skeleton and one tetradentate and two monodentate ligands, has recently entered phase I clinical trials,[22] indicating the potential usefulness of higher-coordinate silicon compounds for practical applications in medicine.

The successful synthesis of the neutral silicon(IV) complexes **11** (pentacoordination, $Si\mathrm{O_2N_3}$ skeleton) and **12** (hexacoordination, $Si\mathrm{O_4N_2}$ skeleton), starting from tetra(thiocyanato-*N*)silane and tetra(cyanato-*N*)silane, respectively, represents a further extension of our research activities in the field of higher-coordinate silicon compounds.[23]



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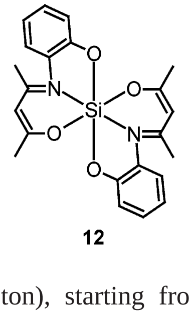

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[21] Because of the formation of a precipitate during the NMR measurements of *trans*-**8** in CD$_2$Cl$_2$, a possible *trans*/*cis*-isomerization process could not be studied in detail; however, there are some additional signals with low intensity in the ^{1}H NMR spectrum of *trans*-**8** that could point to the existence of *cis*-**8** in solution.

[22] Guo, M.; Kenney, M. E. *Book of Abstracts*, 37th Silicon Symposium, Philadelphia, PA, May 20−22, 2004; Abstract B18.

[23] Seiler, O.; Metz, S.; Penka, M.; Tacke, R. Manuscript in preparation.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, experimental details of the X-ray diffraction studies, and bond lengths and angles for (*OC*-6-12)-**3**, (*OC*-6-12)-**4**, (*OC*-6-12)-**5**, (*OC*-6-12)-**6**, (*OC*-6-2′2)-**7**, and *trans*-**8** in CIF format; structures of the respective calculated minima, selected calculated distances and angles, and calculated ^{29}Si chemical shifts for (*OC*-6-2′2)-**7**, (*OC*-6-1′3)-**7**, (*OC*-6-32)-**7**, **9**$\alpha-\epsilon$, *trans*-**10**, and *cis*-**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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