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Neutral Hexa- and Pentacoordinate Silicon(IV) Complexes with SiO$_6$ and SiO$_4$N Skeletons

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The neutral heteroleptic hexacoordinate silicon(IV) complexes **4** and **5** (SiO$_6$ skeletons) and the neutral pentacoordinate silicon(IV) complexes **7**–**9** (SiO$_4$N skeletons) were synthesized, starting from the hexacoordinate precursor **2** and the pentacoordinate precursor **6**, respectively. In these reactions, two monoanionic cyanato-*N* ligands are replaced by one dianionic bidentate *O*,*O*-chelate ligand. Compounds **4**, **5**, and **7**–**9** were characterized by single-crystal X-ray diffraction and solid-state and solution NMR spectroscopy. The chiral silicon(IV) complexes **4**, **5**, **7**, and **8** were obtained as racemic mixtures, whereas **9** was isolated as a cocrystallizate consisting of the two diastereomers, (*C*,*S*)-**9** and (*A*,*S*)-**9** (ratio 1:1). The stereodynamics of **5** and **8** were studied by variable-temperature ^{1}H NMR experiments.

Introduction

The chemistry of hexacoordinate silicon(IV) complexes with SiO$_6$ skeletons is dominated by anionic and cationic species. The most prominent examples are the tris[benzene-1,2-diolato(2−)]silicate dianion and the tris[acetylacetonato-(1−)-*O*,*O*′]silicon cation.[1] We have also contributed to this field of chemistry and have determined the first crystal structures of compounds containing the tris[glycolato(2−)-O^1,O^2]silicate,[2] tris[benzilato(2−)-O^1,O^2]silicate,[2] tris[acetohydroximato(2−)]silicate,[3] tris[benzohydroximato(2−)]silicate,[3] or tris[salicylato(2−)-O^1,O^3]silicate[4] dianions as well as the tris[1-oxopyridin-2-olato(1−)]silicon cation.[5] In contrast to the well-established chemistry of anionic and cationic compounds with SiO$_6$ skeletons, the chemistry of neutral species with an SiO$_6$ core is significantly less explored. We have recently reported on the first crystal structure analysis of a neutral heteroleptic silicon(IV) complex with an SiO$_6$ skeleton, compound **1**.[6] However, the method used for the synthesis of **1** (reaction of tetramethoxysilane with 2 mol equiv of β-diketone and 1 mol equiv of 2-hydroxycarboxylic acid) could not be applied to the synthesis of related derivatives of **1** for selectivity or reactivity reasons. Therefore, we had to develop an alternative method for the synthesis of such compounds, which is described here.

Recently, we have reported on the neutral hexacoordinate silicon(IV) complexes **2** and **3**,[7,8] which contain two monodentate NCX$^-$ (X = O, S) ligands that should be accessible for substitution reactions, offering an alternative approach for the synthesis of neutral heteroleptic silicon(IV) complexes with SiO$_6$ skeletons. We report here on the reaction of **2** with glycolic acid and salicylic acid to give compounds **4** and **5**, respectively. When an analogous method is applied, the neutral pentacoordinate silicon(IV) complex **6**[9] could be used as the precursor for the synthesis of the neutral pentacoordinate silicon(IV) complexes **7**−**9** that contain an SiO$_4$N skeleton. Compounds **4**, **5**, and **7**−**9** were characterized by elemental analyses, solid-state and solution NMR spectroscopy, and single-crystal X-ray diffraction (**4** and **8** were investigated as the tetrahydrofuran solvates **4**·0.5THF and

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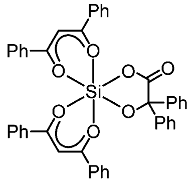
10.1021/ic700389r CCC: $37.00



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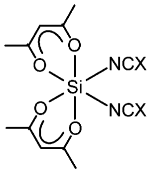

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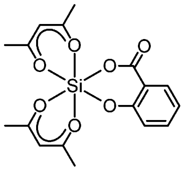
3: X = S



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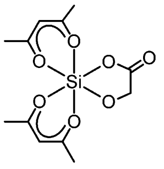

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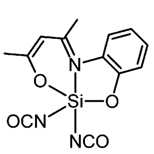

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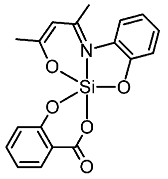

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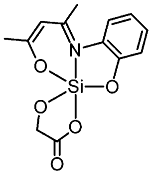

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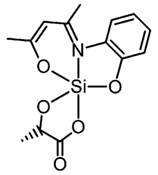

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8·0.5THF). Compounds **5** and **8** were additionally studied by variable-temperature (VT) ^{1}H NMR experiments to get some information about their stereodynamics. The studies presented in this paper are part of our systematic investigations on higher-coordinate silicon compounds (for recent publications, see ref 10; for reviews, see ref 11; for recent publications of other groups dealing with higher-coordinate silicon compounds, see ref 12). Preliminary results of the studies presented here have already been reported elsewhere.[13]

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 solution ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded at 23 °C on a Bruker DRX-300 (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz), a Bruker Avance 400 (^{1}H, 400.1 MHz), or a Bruker Avance 500 (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{29}Si, 99.4 MHz) NMR spectrometer using CD_2Cl_2 or $C_2D_2Cl_4$ as the solvent. Chemical shifts (ppm) were determined relative to internal $CHDCl_2$ (^{1}H, δ 5.32; CD_2Cl_2), C_2HDCl_4 (^{1}H, δ 5.91; $C_2D_2Cl_4$), CD_2Cl_2 (^{13}C, δ 53.8; CD_2Cl_2), or external tetramethylsilane (TMS) (^{29}Si, δ 0; CD_2Cl_2, $C_2D_2Cl_4$). Assignment of the ^{13}C NMR data was supported by DEPT 135 and ^{13}C−^{1}H correlation experiments. The thermocouple used with the probe for the VT ^{1}H NMR studies was calibrated for higher temperatures according to ref 14 using an 80% solution of ethane-1,2-diol in [D$_6$]DMSO. 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 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 precursor tetra(cyanato-*N*)silane [Si(NCO)$_4$] was synthesized according to ref 15.

Bis[acetylacetonato(1−)-*O,O′*]di(cyanato-*N*)silicon(IV) (2). This compound was synthesized according to ref 8.

Bis[acetylacetonato(1−)-*O,O′*][salicylato(2−)-*O*^{1},*O*^{3}]silicon(IV) (4). Salicylic acid (223 mg, 1.61 mmol) was added at 20 °C to a stirred solution of **2** (500 mg, 1.61 mmol) in THF (20 mL). The reaction mixture was stirred at 20 °C for 2 h, then carefully layered with *n*-pentane (20 mL), and kept undisturbed at 20 °C for 3 days. The resulting precipitate was isolated by filtration, washed with *n*-pentane (10 mL), and dried in vacuo (20 °C, 2 h, 0.01 mbar). Yield: 480 mg (1.32 mmol, 82%). Mp: >176 °C (dec). ^{1}H NMR

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(500.1 MHz, $\mathrm{CD_2Cl_2}$): δ 1.99 (s, 3 H, $\mathrm{C}H_3$), 2.09 (s, 3 H, $\mathrm{C}H_3$), 2.13 (s, 3 H, $\mathrm{C}H_3$), 2.14 (s, 3 H, $\mathrm{C}H_3$), 5.81 (s, 1 H, $\mathrm{C}H$), 5.84 (s, 1 H, $\mathrm{C}H$), 6.7−7.9 (m, 4 H, $\mathrm{C_6}H_4$). ^{13}C NMR (125.8 MHz, $\mathrm{CD_2Cl_2}$): δ 25.8 ($C\mathrm{H_3}$), 25.93 ($C\mathrm{H_3}$), 25.94 ($C\mathrm{H_3}$), 26.0 ($C\mathrm{H_3}$), 102.48 ($C\mathrm{H}$), 102.50 ($C\mathrm{H}$), 117.8, 118.9, 119.9, 130.9, 134.5, 159.2 ($C_6\mathrm{H_4}$), 165.7 ($\mathrm{C_6H_4}C\mathrm{(O)O}$), 191.7 ($\mathrm{CH_3}C\mathrm{(O)CH}$), 191.8 ($\mathrm{CH_3}C\mathrm{(O)CH}$), 192.6 ($\mathrm{CH_3}C\mathrm{(O)CH}$), 192.7 ($\mathrm{CH_3}C\mathrm{(O)CH}$). ^{29}Si NMR (99.4 MHz, $\mathrm{CD_2Cl_2}$): δ −190.3. ^{13}C VACP/MAS NMR: δ 24.9 ($C\mathrm{H_3}$), 25.9 (3 C, $C\mathrm{H_3}$), 100.7 ($C\mathrm{H}$), 104.7 ($C\mathrm{H}$), 116.9, 117.9, 121.7, 132.0, 135.2, 159.5 ($C_6\mathrm{H_4}$), 164.2 ($\mathrm{C_6H_4}C\mathrm{(O)O}$), 190.1 ($\mathrm{CH_3}C\mathrm{(O)CH}$), 190.6 ($\mathrm{CH_3}C\mathrm{(O)CH}$), 192.0 ($\mathrm{CH_3}C\mathrm{(O)CH}$), 193.0 ($\mathrm{CH_3}C\mathrm{(O)CH}$). ^{29}Si VACP/MAS NMR: δ −191.7. Anal. Calcd for $\mathrm{C_{17}H_{18}O_7Si}$ (362.41): C, 56.34; H, 5.01. Found: C, 56.1; H, 5.1.

Bis[acetylacetonato(1−)-*O,O′*][glycolato(2−)-*O*^{1},*O*^{2}]silicon(IV) (5). Glycolic acid (123 mg, 1.62 mmol) was added at 20 °C to a stirred solution of **2** (500 mg, 1.61 mmol) in THF (20 mL). The reaction mixture was stirred at 20 °C for 2 h, then carefully layered with *n*-pentane (20 mL), and kept undisturbed at 20 °C for 3 days. The resulting precipitate was isolated by filtration, washed with *n*-pentane (10 mL), and dried in vacuo (20 °C, 2 h, 0.01 mbar). Yield: 398 mg (1.33 mmol, 82%). Mp: >158 °C (dec). ^{1}H NMR (500.1 MHz, $\mathrm{CD_2Cl_2}$): δ 2.05 (s, 3 H, $\mathrm{C}H_3$), 2.07 (s, 3 H, $\mathrm{C}H_3$), 2.14 (s, 3 H, $\mathrm{C}H_3$), 2.16 (s, 3 H, $\mathrm{C}H_3$), 3.98 (δ_A) and 4.02 (δ_B), (2 H, $\mathrm{C}H_\mathrm{A}H_\mathrm{B}$, $^2J_\mathrm{AB}$ = 16.2 Hz), 5.79 (s, 1 H, $\mathrm{C}H$), 5.80 (s, 1 H, $\mathrm{C}H$). ^{13}C NMR (125.8 MHz, $\mathrm{CD_2Cl_2}$): δ 25.6 ($C\mathrm{H_3}$), 25.7 ($C\mathrm{H_3}$), 26.1 ($C\mathrm{H_3}$), 26.2 ($C\mathrm{H_3}$), 63.5 ($C\mathrm{H_2}$), 102.3 ($C\mathrm{H}$), 102.4 ($C\mathrm{H}$), 175.8 ($\mathrm{CH_2}C\mathrm{(O)O}$), 190.1 ($\mathrm{CH_3}C\mathrm{(O)CH}$), 191.1 ($\mathrm{CH_3}C\mathrm{(O)CH}$), 193.9 ($\mathrm{CH_3}C\mathrm{(O)CH}$), 194.1 ($\mathrm{CH_3}C\mathrm{(O)CH}$). ^{29}Si NMR (99.4 MHz, $\mathrm{CD_2Cl_2}$): δ −174.1. ^{13}C VACP/MAS NMR: δ 25.8 ($C\mathrm{H_3}$), 26.1 ($C\mathrm{H_3}$), 27.3 ($C\mathrm{H_3}$), 28.0 ($C\mathrm{H_3}$), 64.7 ($C\mathrm{H_2}$), 103.4 (2 C, $C\mathrm{H}$), 176.5 ($\mathrm{CH_2}C\mathrm{(O)O}$), 192.0 (2 C, $\mathrm{CH_3}C\mathrm{(O)CH}$), 194.4 ($\mathrm{CH_3}C\mathrm{(O)CH}$), 195.4 ($\mathrm{CH_3}C\mathrm{(O)CH}$). ^{29}Si VACP/MAS NMR: δ −174.2. Anal. Calcd for $\mathrm{C_{12}H_{16}O_7Si}$ (300.34): C, 47.99; H, 5.37. Found: C, 47.7; H, 5.2.

Di(cyanato-*N*)[4-((2-hydroxyphenyl)imino)pent-2-en-2-olato(2−)-*N,O,O′*]silicon(IV) (6). This compound was synthesized according to ref 9.

[4-((2-Hydroxyphenyl)imino)pent-2-en-2-olato(2−)-*N,O,O′*][salicylato(2−)-*O*^{1},*O*^{3}]silicon(IV) (7). Compound **6** (400 mg, 1.33 mmol) was added at 20 °C to a stirred solution of salicylic acid (183 mg, 1.32 mmol) in THF (5 mL). The reaction mixture was stirred at 20 °C for 5 min and then kept undisturbed at 20 °C for 3 days. The resulting precipitate was isolated by filtration, washed with *n*-pentane (10 mL), and dried in vacuo (20 °C, 2 h, 0.01 mbar). Yield: 236 mg (668 μmol, 50%). Mp: >152 °C (dec). ^{1}H NMR (300.1 MHz, $\mathrm{CD_2Cl_2}$): δ 2.14 (s, 3 H, $\mathrm{C}H_3$), 2.66 (s, 3 H, $\mathrm{C}H_3$), 5.88 (s, 1 H, $\mathrm{C{-}C}H\mathrm{{=}C}$), 6.8−8.0 (m, 8 H, $\mathrm{C_6}H_4$). ^{13}C NMR (75.5 MHz, $\mathrm{CD_2Cl_2}$): δ 24.0 ($C\mathrm{H_3}$), 25.3 ($C\mathrm{H_3}$), 106.9 ($\mathrm{C{-}}C\mathrm{H{=}C}$), 115.9, 117.8, 120.1, 120.6, 121.4, 121.7, 129.0, 131.2, 132.0, 135.0, 149.8, 157.0 ($C_6\mathrm{H_4}$), 163.7 ($\mathrm{C_6H_4}C\mathrm{(O)O}$), 169.8 ($\mathrm{CH_3}C\mathrm{(N)CH}$ or $\mathrm{CH_3}C\mathrm{(O)CH}$), 171.0 ($\mathrm{CH_3}C\mathrm{(N)CH}$ or $\mathrm{CH_3}C\mathrm{(O)CH}$). ^{29}Si NMR (59.6 MHz, $\mathrm{CD_2Cl_2}$): δ −128.3. ^{13}C VACP/MAS NMR: δ 24.2 ($C\mathrm{H_3}$), 24.6 ($C\mathrm{H_3}$), 106.8 ($\mathrm{C{-}}C\mathrm{H{=}C}$), 115.7, 117.6, 120.2 (2 C), 121.8, 122.8, 129.7, 130.8 (2 C), 139.2, 148.2, 156.1 ($C_6\mathrm{H_4}$), 163.9 ($\mathrm{C_6H_4}C\mathrm{(O)O}$), 171.0 ($\mathrm{CH_3}C\mathrm{(N)CH}$ or $\mathrm{CH_3}C\mathrm{(O)CH}$), 173.2 ($\mathrm{CH_3}C\mathrm{(N)CH}$ or $\mathrm{CH_3}C\mathrm{(O)CH}$). ^{15}N VACP/MAS NMR: δ −180.7. ^{29}Si VACP/MAS NMR: δ −126.1. Anal. Calcd for $\mathrm{C_{18}H_{15}NO_5Si}$ (353.41): C, 61.18; H, 4.28; N, 3.96. Found: C, 60.8; H, 4.4; N, 4.0.

[Glycolato(2−)-*O*^{1},*O*^{2}][4-((2-hydroxyphenyl)imino)pent-2-en-2-olato(2−)-*N,O,O′*]silicon(IV) (8). Compound **6** (400 mg, 1.33 mmol) was added at 20 °C to a stirred solution of glycolic acid (101 mg, 1.33 mmol) in THF (10 mL). The reaction mixture was stirred at 20 °C for 5 min and then kept undisturbed at 20 °C for 3 days. The resulting precipitate was isolated by filtration, washed with *n*-pentane (10 mL), and dried in vacuo (20 °C, 2 h, 0.01 mbar). Yield: 255 mg.[16] Mp: >135 °C (dec). ^{1}H NMR (300.1 MHz, $\mathrm{CD_2Cl_2}$): δ 1.82 (m, $\mathrm{OCH_2C}H_2$),[16] 2.23 (d, $^3J_\mathrm{HH}$ = 0.5 Hz, 3 H, $\mathrm{C}H_3$), 2.59 (s, 3 H, $\mathrm{C}H_3$), 3.68 (m, $\mathrm{OC}H_2\mathrm{CH_2}$),[16] 4.02 ($\delta_\mathrm{A}$) and 4.04 ($\delta_\mathrm{B}$) (2 H, $\mathrm{C}H_\mathrm{A}H_\mathrm{B}$, $^2J_\mathrm{AB}$ = 16.1 Hz), 5.88 (q, $^3J_\mathrm{HH}$ = 0.5 Hz, 1 H, $\mathrm{C{-}C}H\mathrm{{=}C}$), 7.0−7.5 (m, 4 H, $\mathrm{C_6}H_4$). ^{13}C NMR (75.5 MHz, $\mathrm{CD_2Cl_2}$): δ 24.0 ($C\mathrm{H_3}$), 24.7 ($C\mathrm{H_3}$), 25.9 ($\mathrm{OCH_2}C\mathrm{H_2}$),[16] 65.2 ($C\mathrm{H_2}$), 68.1 ($\mathrm{O}C\mathrm{H_2CH_2}$),[16] 106.9 ($\mathrm{C{-}}C\mathrm{H{=}C}$), 116.0, 120.4, 121.4, 129.2, 131.9, 149.8 ($C_6\mathrm{H_4}$), 169.8 ($\mathrm{CH_2}C\mathrm{(O)O}$, $\mathrm{CH_3}C\mathrm{(N)CH}$, or $\mathrm{CH_3}C\mathrm{(O)CH}$), 171.4 ($\mathrm{CH_2}C\mathrm{(O)O}$, $\mathrm{CH_3}C\mathrm{(N)CH}$, or $\mathrm{CH_3}C\mathrm{(O)CH}$), 172.5 ($\mathrm{CH_2}C\mathrm{(O)O}$, $\mathrm{CH_3}C\mathrm{(N)CH}$, or $\mathrm{CH_3}C\mathrm{(O)CH}$). ^{29}Si NMR (59.6 MHz, $\mathrm{CD_2Cl_2}$): δ −111.3. ^{13}C VACP/MAS NMR: δ 22.9 ($C\mathrm{H_3}$), 25.3 ($\mathrm{OCH_2}C\mathrm{H_2}$),[16] 25.5 ($C\mathrm{H_3}$), 64.8 ($C\mathrm{H_2}$), 65.8 ($\mathrm{O}C\mathrm{H_2CH_2}$),[16] 109.0 ($\mathrm{C{-}}C\mathrm{H{=}C}$), 115.5, 120.6, 121.4, 126.7, 131.6, 149.2 ($C_6\mathrm{H_4}$), 171.5 ($\mathrm{CH_2}C\mathrm{(O)O}$, $\mathrm{CH_3}C\mathrm{(N)CH}$, or $\mathrm{CH_3}C\mathrm{(O)CH}$), 171.8 ($\mathrm{CH_2}C\mathrm{(O)O}$, $\mathrm{CH_3}C\mathrm{(N)CH}$, or $\mathrm{CH_3}C\mathrm{(O)CH}$), 174.2 ($\mathrm{CH_2}C\mathrm{(O)O}$, $\mathrm{CH_3}C\mathrm{(N)CH}$, or $\mathrm{CH_3}C\mathrm{(O)CH}$). ^{15}N VACP/MAS NMR: δ −179.7. ^{29}Si VACP/MAS NMR: δ −111.0. Anal. Calcd for $\mathrm{C_{13}H_{13}NO_5Si}$ (291.34): C, 53.60; H, 4.50; N, 4.81. Found: C, 53.2; H, 5.1; N, 5.3.[16]

[4-((2-Hydroxyphenyl)imino)pent-2-en-2-olato(2−)-*N,O,O′*][(*S*)-lactato(2−)-*O*^{1},*O*^{2})]silicon(IV) (9). Tetra(cyanato-*N*)silane (541 mg, 2.76 mmol)[17] was added at −40 °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 allowed to warm to −20 °C over a time period of 1 h, then (*S*)-lactic acid (230 mg, 2.55 mmol) was added, and the reaction mixture was stirred for a further 2 min at this temperature and then kept undisturbed at −20 °C for 24 h. The resulting precipitate was isolated by filtration, washed with *n*-pentane (10 mL), and dried in vacuo (20 °C, 2 h, 0.01 mbar). Yield: 402 mg (1.32 mmol, 52%). Mp: 223−224 °C (dec). ^{13}C VACP/MAS NMR: δ 17.9 ($\mathrm{CH(}C\mathrm{H_3)C(O)O}$), 20.3 ($\mathrm{CH(}C\mathrm{H_3)C(O)O}$), 21.3 (2 C, $C\mathrm{H_3}$), 24.0 (2 C, $C\mathrm{H_3}$), 72.6 (2 C, $C\mathrm{H(CH_3)C(O)O}$), 107.3 ($\mathrm{C{-}}C\mathrm{H{=}C}$), 108.5 ($\mathrm{C{-}}C\mathrm{H{=}C}$), 116.4, 117.1, 119.1, 121.1 (2 C), 126.3, 128.3, 130.3 (2 C), 132.9, 148.9 (2 C) ($C_6\mathrm{H_4}$), 169.4 (2 C, $\mathrm{CH(CH_3)}C\mathrm{(O)O}$, $\mathrm{CH_3}C\mathrm{(N)CH}$, or $\mathrm{CH_3}C\mathrm{(O)CH}$), 171.6 (2 C, $\mathrm{CH(CH_3)}C\mathrm{(O)O}$, $\mathrm{CH_3}C\mathrm{(N)CH}$, or $\mathrm{CH_3}C\mathrm{(O)CH}$), 175.6 (2 C, $\mathrm{CH(CH_3)}C\mathrm{(O)O}$, $\mathrm{CH_3}C\mathrm{(N)CH}$, or $\mathrm{CH_3}C\mathrm{(O)CH}$). ^{15}N VACP/MAS NMR: δ −180.0 (2 N). ^{29}Si VACP/MAS NMR: δ −113.3, −114.3. Anal. Calcd for $\mathrm{C_{14}H_{15}NO_5Si}$ (305.36): C, 55.07; H, 4.95; N, 4.59. Found: C, 54.9; H, 5.0; N, 4.8.

(a) Isomer I.[18] ^{1}H NMR (500.1 MHz, $\mathrm{CD_2Cl_2}$): δ 1.25 (d, $^3J_\mathrm{HH}$ = 6.9 Hz, 3 H, $\mathrm{CH(C}H_3\mathrm{)C(O)O}$), 2.23 (s, 3 H, $\mathrm{C}H_3$), 2.59 (s, 3 H, $\mathrm{C}H_3$), 4.18 (q, $^3J_\mathrm{HH}$ = 6.9 Hz, 1 H, $\mathrm{C}H\mathrm{(CH_3)C(O)O}$), 5.89 (s, 1 H, $\mathrm{C{-}C}H\mathrm{{=}C}$), 7.0−7.5 (m, 4 H, $\mathrm{C_6}H_4$). ^{13}C NMR (125.8 MHz, $\mathrm{CD_2Cl_2}$): δ 20.1 ($\mathrm{CH(}C\mathrm{H_3)C(O)O}$), 24.0 ($C\mathrm{H_3}$), 24.7 ($C\mathrm{H_3}$), 71.8 ($C\mathrm{H(CH_3)C(O)O}$), 106.9 ($\mathrm{C{-}}C\mathrm{H{=}C}$), 116.0, 120.4, 121.4, 129.1, 131.9, 150.0 ($C_6\mathrm{H_4}$), 169.7 ($\mathrm{CH(CH_3)}C\mathrm{(O)O}$, $\mathrm{CH_3}C\mathrm{(N)CH}$, or $\mathrm{CH_3}C\mathrm{(O)CH}$), 171.0 ($\mathrm{CH(CH_3)}C\mathrm{(O)O}$, $\mathrm{CH_3}C\mathrm{(N)CH}$, or $\mathrm{CH_3}C\mathrm{(O)CH}$), 175.2 ($\mathrm{CH(CH_3)}C\mathrm{(O)O}$, $\mathrm{CH_3}C\mathrm{(N)CH}$, or $\mathrm{CH_3}C\mathrm{(O)CH}$). ^{29}Si NMR (99.4 MHz, $\mathrm{CD_2Cl_2}$): δ −113.6.

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(16) Because of a partial loss of the solvating THF upon drying of the crystalline solvate in vacuo, the yield could not be determined exactly. This partial loss of THF is also reflected in the NMR spectra and in the poor results of the elemental analysis.

(17) The use of a small excess of $\mathrm{Si(NCO)_4}$ resulted in a better yield compared with the use of stoichometric amounts of $\mathrm{Si(NCO)_4}$.

(18) In solution ($\mathrm{CD_2Cl_2}$), two diastereomers were observed (ratio 5:4 isomer I/isomer II). The assignment of the NMR data for the two isomers is based on the integration of the ^{1}H NMR resonance signals and ^{13}C−^{1}H correlation experiments.

(b) Isomer II.[18] ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ 1.19 (d, $^{3}J_{HH}$ = 6.9 Hz, 3 H, $CH(C\mathit{H}_3)C(O)O$), 2.23 (s, 3 H, $C\mathit{H}_3$), 2.59 (s, 3 H, $C\mathit{H}_3$), 4.20 (q, $^{3}J_{HH}$ = 6.9 Hz, 1 H, $C\mathit{H}(CH_3)C(O)O$), 5.88 (s, 1 H, $C{-}C\mathit{H}{=}C$), 7.0−7.5 (m, 4 H, $C_6\mathit{H}_4$). ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ 20.0 ($CH(\mathit{C}H_3)C(O)O$), 24.0 ($\mathit{C}H_3$), 24.8 ($\mathit{C}H_3$), 72.0 ($\mathit{C}H(CH_3)C(O)O$), 106.9 ($C{-}\mathit{C}H{=}C$), 115.9, 120.4, 121.3, 129.1, 131.9, 149.8 (C_6H_4), 169.7 ($CH(CH_3)\mathit{C}(O)O$, $CH_3\mathit{C}(N)CH$, or $CH_3\mathit{C}(O)CH$), 171.4 ($CH(CH_3)\mathit{C}(O)O$, $CH_3\mathit{C}(N)CH$, or $CH_3\mathit{C}(O)CH$), 175.2 ($CH(CH_3)\mathit{C}(O)O$, $CH_3\mathit{C}(N)CH$, or $CH_3\mathit{C}(O)CH$). ^{29}Si NMR (99.4 MHz, CD_2Cl_2): δ −113.7.

Crystal Structure Analyses. Suitable single crystals of **4**·0.5THF, **5**, **7**, **8**·0.5THF, and **9** were isolated directly from the respective reaction mixtures. The crystals were mounted in an inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (**5**, **8**·0.5THF, and **9**, Stoe IPDS diffractometer, graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å; **4**·0.5THF and **7**, Bruker APEX-CCD diffractometer, graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å). All structures were solved by direct methods.[19] The non-H atoms were refined anisotropically.[20] A riding model was employed in the refinement of the C*H* hydrogen atoms. 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-642885 (**4**·0.5THF), CCDC-642886 (**5**), CCDC-642887 (**7**), CCDC-642888 (**8**·0.5THF), and CCDC-642889 (**9**). Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax, (+44)-1223/336033; e-mail, deposit@ccdc.cam.ac.uk].

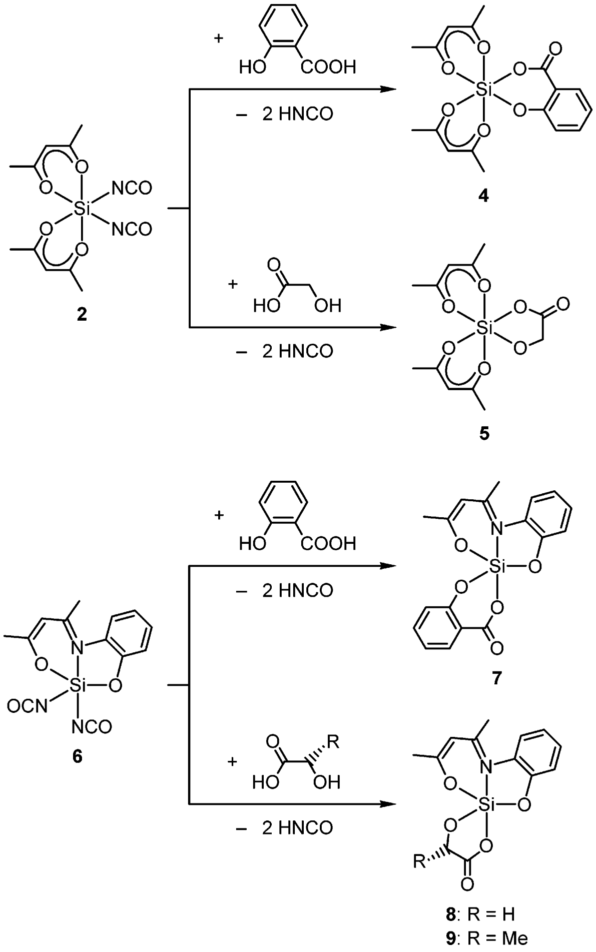
Results and Discussion

Compounds **4** and **5** were synthesized according to Scheme 1 by treatment of **2** with 1 mol equiv of salicylic acid and glycolic acid, respectively. Compounds **7**−**9** were obtained analogously by the reaction of **6** with 1 mol equiv of salicylic acid, glycolic acid, and (*S*)-lactic acid, respectively.[21] Compounds **5** (yield 82%), **7** (yield 50%), and **9** (yield 52%) were isolated as crystalline solids, and **4** and **8** were obtained as the crystalline tetrahydrofuran solvates **4**·0.5THF and **8**·0.5THF. Drying of these solvates in vacuo yielded solvent-free **4** (yield 82%), whereas in the case of **8**·0.5THF, only partial loss of THF was observed.[16]

The identities of compounds **4**, **5**, and **7**−**9** were established by elemental analyses (C, H, N), solid-state VACP/MAS NMR (^{13}C, ^{15}N, and ^{29}Si), and solution NMR studies (^{1}H, ^{13}C, and ^{29}Si), as well as single-crystal X-ray diffraction studies of **4**·0.5THF, **5**, **7**, **8**·0.5THF, and **9**. In addition, compounds **5** and **8** were studied by VT ^{1}H NMR experiments.

Quite surprisingly, compound **9** was obtained as a cocrystallizate consisting of the two diastereomers, (*C*,*S*)-**9** and (*A*,*S*)-**9** (ratio 1:1). Cocrystallization of diastereomers is a phenomenon that has not often been reported in the literature (in this context, see ref 22). All of the other chiral compounds were isolated as racemic mixtures.

Scheme 1



The crystal data and experimental parameters used for the crystal structure analyses of **4**·0.5THF, **5**, **7**, **8**·0.5THF, and **9** are given in the Supporting Information. The molecular structures of the silicon(IV) complexes **4**, **7**, and **9** in the crystal are shown in Figures 1−3; selected bond distances and angles of **4**·0.5THF, **5**, **7**, **8**·0.5THF, and **9** are given in the respective figure legends.

The Si-coordination polyhedra of compounds **4** and **5** can be described as distorted octahedra, with maximum deviations from the ideal 90° angles of 7.58(6)° (**4**) and 5.57(6)° (**5**) and maximum deviations from the ideal 180° angles of 6.79(7)° (**4**) and 3.36(7)° (**5**). The Si−O distances of **4** and **5** amount to 1.7116(14)−1.8010(13) and 1.7020(14)−1.8165(12) Å, respectively. These structural features are similar to those observed for compound **1**,[6] with one remarkable difference: In contrast to **1** and **5**, where the Si−O(alcoholato) distances of the benzilato(2−) or glycolato(2−) ligands are significantly shorter than the Si−O(carboxylato) distances, the difference between the two Si−O distances of the salicylato(2−) ligand is relatively small. In addition, the O−Si−O angles in the five-membered (**1** and **5**) and six-

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

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

(21) In the case of compound **9**, the starting material, **6**, was not isolated after it has been synthesized; it was treated with (*S*)-lactic acid in a one-pot synthesis.

(22) Brunner, H.; Zwack, T.; Zabel, M. *Organometallics* **2003**, *22*, 1741−1750.

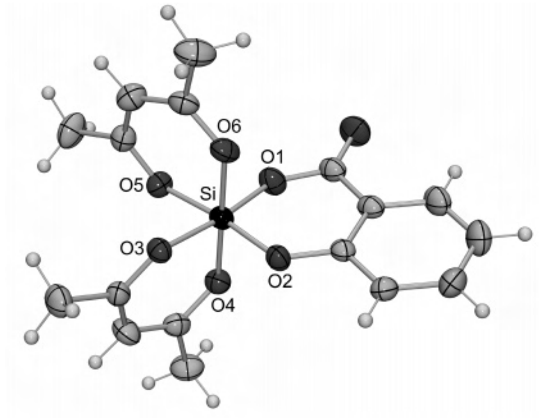

Figure 1. Molecular structure of **4** in the crystal of **4**·0.5THF (probability level of displacement ellipsoids 50%). Selected bond lengths (Å) and angles (deg): Si−O1 1.7259(13), Si−O2 1.7116(14), Si−O3 1.7902(13), Si−O4 1.7922(13), Si−O5 1.8010(13), Si−O6 1.7935(13); O1−Si−O2 97.58(6), O1−Si−O3 173.21(7), O1−Si−O4 89.47(6), O1−Si−O5 87.28(6), O1−Si−O6 90.95(7), O2−Si−O3 88.60(6), O2−Si−O4 90.56(6), O2−Si−O5 174.13(6), O2−Si−O6 89.79(6), O3−Si−O4 93.31(6), O3−Si−O5 86.73(6), O3−Si−O6 86.23(6), O4−Si−O5 86.17(6), O4−Si−O6 179.41(6), O5−Si−O6 93.44(6). Selected bond lengths (Å) and angles (deg) for **5** (analogous numbering scheme): Si−O1 1.7719(13), Si−O2 1.7020(14), Si−O3 1.7777(13), Si−O4 1.8043(12), Si−O5 1.7930(14), Si−O6 1.8165(12); O1−Si−O2 90.77(6), O1−Si−O3 177.29(7), O1−Si−O4 88.53(6), O1−Si−O5 88.58(7), O1−Si−O6 90.80(6), O2−Si−O3 90.78(7), O2−Si−O4 92.97(7), O2−Si−O5 177.34(7), O2−Si−O6 90.33(6), O3−Si−O4 93.62(5), O3−Si−O5 89.97(7), O3−Si−O6 86.96(6), O4−Si−O5 84.43(6), O4−Si−O6 176.64(7), O5−Si−O6 92.26(6).

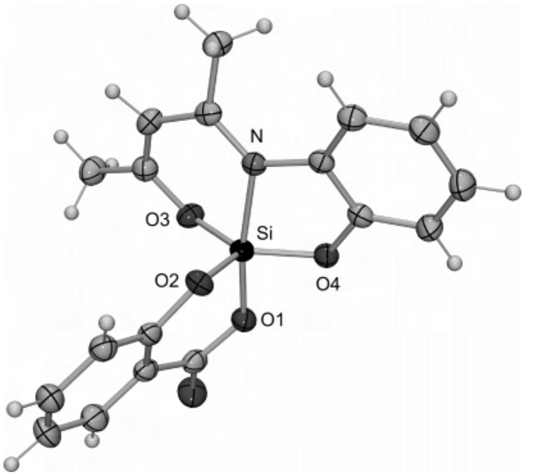

Figure 2. Molecular structure of **7** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths (Å) and angles (deg): Si−O1 1.7200(12), Si−O2 1.6569(13), Si−O3 1.6748(13), Si−O4 1.6741(13), Si−N 1.9352(14); O1−Si−O2 98.66(6), O1−Si−O3 89.34(6), O1−Si−O4 86.90(6), O1−Si−N 169.87(6), O2−Si−O3 111.28(6), O2−Si−O4 116.40(7), O2−Si−N 90.55(6), O3−Si−O4 132.19(7), O3−Si−N 91.26(6), O4−Si−N 85.20(6). Selected bond lengths (Å) and angles (deg) for **8**·0.5THF (analogous numbering scheme): Si−O1 1.7702(18), Si−O2 1.6561(18), Si−O3 1.6854(18), Si−O4 1.6745(18), Si−N 1.905(2); O1−Si−O2 91.26(9), O1−Si−O3 89.68(9), O1−Si−O4 89.79(9), O1−Si−N 176.80(9), O2−Si−O3 116.60(9), O2−Si−O4 119.98(10), O2−Si−N 90.40(9), O3−Si−O4 123.42(10), O3−Si−N 92.02(9), O4−Si−N 87.01(9).

membered (**4**) chelate rings differ significantly [O1−Si−O2: **1**, 90.31(5)°; **4**, 97.58(6)°; **5**, 90.77(6)°].

The Si-coordination polyhedra of **7**−**9** are distorted trigonal bipyramids, with the oxygen atoms of the tridentate ligands and the alcoholato oxygen atom of the bidentate ligands in the equatorial positions [(*TBPY*-5−15)-isomers].

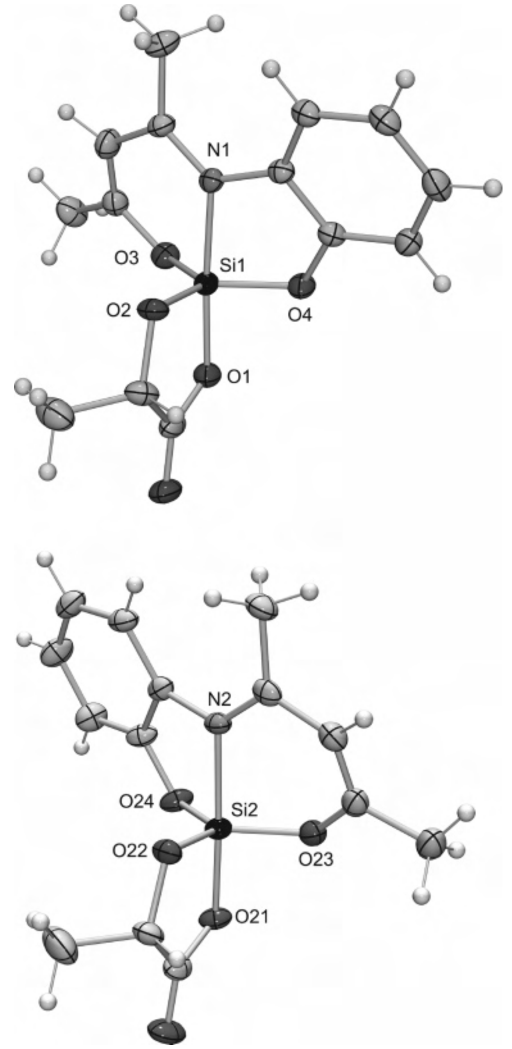

Figure 3. Molecular structures of (*C*,*S*)-**9** (above) and (*A*,*S*)-**9** (below) in the crystal of **9** (probability level of displacement ellipsoids 50%). Selected bond lengths (Å) and angles (deg) for (*C*,*S*)-**9**: Si1−O1 1.766(2), Si1−O2 1.6578(19), Si1−O3 1.6765(18), Si1−O4 1.6804(17), Si1−N1 1.915(3); O1−Si1−O2 92.16(10), O1−Si1−O3 89.56(10), O1−Si1−O4 90.11(9), O1−Si1−N1 176.67(9), O2−Si1−O3 120.64(9), O2−Si1−O4 116.61(9), O2−Si1−N1 89.87(10), O3−Si1−O4 122.72(10), O3−Si1−N1 91.67(10), O4−Si1−N1 86.63(10). Selected bond lengths (Å) and angles (deg) for (*A*,*S*)-**9**: Si2−O21 1.755(2), Si2−O22 1.6474(18), Si2−O23 1.6762(19), Si2−O24 1.6885(17), Si2−N2 1.935(3); O21−Si2−O22 92.47(10), O21−Si2−O23 91.09(10), O21−Si2−O24 88.79(9), O21−Si2−N2 175.22(9), O22−Si2−O23 116.49(9), O22−Si2−O24 120.32(10), O22−Si2−N2 89.94(10), O23−Si2−O24 123.14(10), O23−Si2−N2 91.53(10), O24−Si2−N2 86.43(10).

The structures of the two isomers of **9** (Figure 3) are very similar; they differ only slightly in their bond lengths and angles. The equatorial Si−O distances of **7**−**9** are very similar and range from 1.6561(18) to 1.6885(17) Å. The axial Si−O distances are significantly longer and amount to 1.7200(12) Å (**7**), 1.7702(18) Å (**8**), 1.766(2) Å (*C*,*S*-**9**), and 1.755(2) Å (*A*,*S*-**9**). The Si−N distances range from 1.905(2) to 1.9352(14) Å and are significantly shorter than the corresponding Si−N bond in the precursor **6** [1.9668(16) Å].[6] The O3−Si−O4 angle spanned by the tridentate ligand in **7** shows a value of 132.19(7)° and is similar to the corresponding O−Si−O angle in **6** [133.64(7)°].[9] In compounds **8** and **9**, the O3−Si−O4 angle is somewhat smaller [**8**, 123.42(10)°; (*C*,*S*)-**9**, 122.72(10)°; (*A*,*S*-**9**), 123.14(10)°].[9]

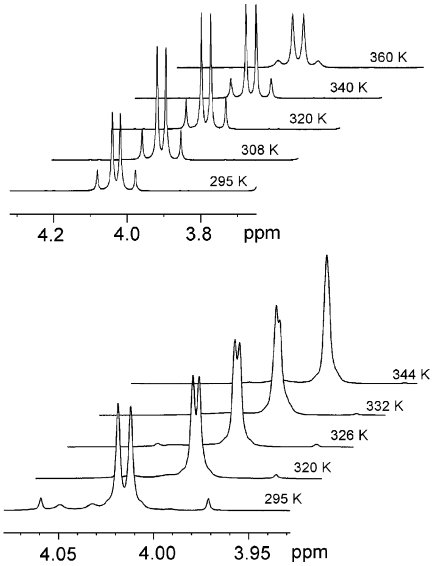

Figure 4. Temperature dependence of the ^{1}H NMR signals for the diastereotopic $OCH_2C(O)O$ protons of **5** and **8**. Top: partial ^{1}H NMR spectrum of **5** (solution in $C_2D_2Cl_4$, 400.1 MHz) upon heating from 295 to 360 K. Bottom: partial ^{1}H NMR spectrum of **8** (solution in $C_2D_2Cl_4$, 400.1 MHz) upon heating from 295 to 344 K. The ^{1}H NMR spectra of **5** and **8** are completely reversible upon cooling.

The isotropic ^{29}Si NMR chemical shifts obtained in the solid-state VACP/MAS NMR studies of compounds **4**, **5**, and **7**−**9** clearly indicate the presence of higher-coordinate silicon atoms (**4**, δ −191.7; **5**, δ −174.2; **7**, δ −126.1; **8**, δ −111.0; **9**, δ −113.3, −114.3) and match with the ^{29}Si NMR chemical shifts obtained in solution (solvent, CD_2Cl_2; **4**, δ −190.3; **5**, δ −174.1; **7**, δ −128.3; **8**, δ −111.3; **9**, δ −113.6, −113.7). The solid-state NMR spectra (^{13}C, ^{15}N, and ^{29}Si) of all compounds studied are compatible with the structures determined by single-crystal X-ray diffraction. In the case of **9**, the solid-state NMR spectra clearly indicate the presence of two isomers (1:1 ratio) in the crystal.

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **4**, **5**, **8**, and **9** in solution (CD_2Cl_2) show only one set of resonance signals each (and one set for each diastereomer of **9**)[18] and are compatible with the spectra obtained in the solid state, indicating that the higher-coordinate silicon(IV) complexes exist in solution as well. This holds also true for a freshly prepared solution of **7**; however, after a few hours at room temperature, new sets of resonance signals are observed in the ^{1}H and ^{13}C NMR spectra and two new signals in the ^{29}Si NMR spectrum at δ −188.8 and δ −164.7. These values fit well with those observed for the tris[salicylato(2−)]silicate dianion[4] and for the neutral silicon(IV) complex containing two of the tridentate ligands,[9] indicating a decomposition of **7** in solution.

To obtain some information about their stereodynamics in solution, the chiral compounds **5** and **8** were additionally studied by VT ^{1}H NMR experiments, using the diastereotopic CH_2 protons of their glycolato(2−) ligands (AB spin systems) as the probe (solvent, $C_2D_2Cl_4$). Figure 4 shows the reversible temperature dependence of the respective ^{1}H NMR signals of **5** (top) and **8** (bottom). The coalescence phenomenon in the spectra of the pentacoordinate silicon compound **8** (coalescence temperature at ca. 48 °C) indicates a dynamic process that might be described in terms of a racemization of the SiO_4N skeleton. The spectra of the hexacoordinate silicon compound **5** do not show such a phenomenon, indicating configurational stability on the NMR time scale in the temperature range studied.

Conclusion

With the synthesis of the neutral silicon(IV) complexes **4**, **5**, and **7**−**9** (**4** and **8** were isolated as the solvates **4**·0.5THF and **8**·0.5THF), the potential of the di(cyanato-*N*)silicon(IV) complexes **2**[8] and **6**[9] for the synthesis of neutral penta- and hexacoordinate silicon(IV) complexes has been demonstrated. These results clearly show the high synthetic potential of tetra(cyanato-*N*)silane [$Si(NCO)_4$], which is the precursor of **2** and **6**. Because of the fact that the four cyanato-*N* groups of $Si(NCO)_4$ can be substituted subsequently by different chelate ligands [$Si(NCO)_4 \rightarrow$ **2** $\rightarrow$ **4**, **5**; $Si(NCO)_4 \rightarrow$ **8** $\rightarrow$ **7**−**9**] with high selectivity (which is normally not possible with $SiCl_4$ as the starting material), tetra(cyanato-*N*)silane is a very useful precursor for the synthesis of novel penta- and hexacoordinate silicon(IV) complexes with two different types of bidentate or bidentate/tridentate chelate ligands.

Supporting Information Available: Crystal and structure refinement data, tables of atomic coordinates and equivalent isotropic displacement parameters, experimental details of the X-ray diffraction studies, and bond lengths and angles for **4**·0.5THF, **5**, **7**, **8**·0.5THF, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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