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Neutral Hexacoordinate Silicon(IV) Complexes with a SiO_4NC or SiO_3N_2C Skeleton and Neutral Pentacoordinate Silicon(IV) Complexes Containing a Trianionic Tetradentate O,N,O,O Ligand

Jörg Weiß,^[a] Katharina Sinner,^[a] Johannes A. Baus,^[a] Christian Burschka,^[a] and Reinhold Tacke^{*[a]}

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A series of neutral hexacoordinate silicon(IV) complexes with a SiO_4NC or SiO_3N_2C skeleton was synthesized. Additionally, two neutral pentacoordinate silicon(IV) complexes with a SiO_3NC skeleton were synthesized. All compounds studied were structurally characterized by multinuclear NMR spectroscopy in the solid state and in solution and by single-crystal X-ray diffraction. The hexacoordinate compounds studied

contain a tridentate dianionic O,N,O or N,N,O ligand, a phenyl ligand, and a symmetrically substituted derivative of an acetylacetonato ligand of the formula type RC(O)–CH=C-(OSiMe₃)R (R = Me, Ph, CF₃). The two pentacoordinate complexes contain a tetradentate trianionic O,N,O,O ligand and a phenyl ligand.

Introduction

In a series of recent publications, we have reported on the synthesis of the neutral pentacoordinate silicon(IV) complexes 1-3 (S/O/NMe analogues) and their use in the preparation of further neutral pentacoordinate silicon(IV) complexes that contain other monoanionic monodentate ligands instead of the chlorido ligand.^[1] These studies were performed with a special focus on the comparison of the respective S/O/NMe analogues, some of which differ significantly in their chemical properties.





In addition, we have also reported on the transformation of **1** into the neutral hexacoordinate silicon(IV) complexes **4a** and **4b**.^[2] These syntheses represent two rare examples for the use of neutral pentacoordinate silicon(IV) complexes as starting materials for the preparation of neutral hexacoordinate silicon(IV) complexes.

In continuation of these studies, we have now synthesized the respective S/O and S/NMe analogues of **4a** and **4b**, compounds **5a**, **5b**, **6a**, and **6b**. Attempts to prepare the related S/O/NMe analogues **4c**, **5c**, and **6c** by using the same synthetic method failed. Instead, we obtained the neutral pentacoordinate silicon(IV) complexes **4c'**, **5c'**, and **6c'**. We report here on the syntheses of compounds **4c'**, **5a**, **5b**, **5c'**, **6a**, **6b**, and **6c'** and their characterization by NMR spectroscopic studies in the solid state and in solution and by crys-

[[]a] Universität Würzburg, Institut für Anorganische Chemie, Am Hubland, 97074 Würzburg, Germany E-mail: r.tacke@uni-wuerzburg.de http://www-anorganik.chemie.uni-wuerzburg.de/



tal structure analyses. These investigations were performed as part of our ongoing systematic studies on higher-coordinate silicon(IV) complexes.^[3–5]

Results and Discussion

Syntheses

Compounds **5a**, **5b**, **6a**, and **6b** were synthesized according to Scheme 1 by treatment of the chlorosilicon(IV) complexes **2** and **3** with the respective silylated acetylacetone derivatives of the formula type $RC(O)-CH=C(OSiMe_3)R$ (7: R = Me; **8**: R = Ph). All syntheses were carried out in acetonitrile at 20 °C, and compounds **5a**, **5b**, **6a**, and **6b** were isolated as crystalline solids (colors and yields: **5a**•0.5CH₃CN, yellow, 76%; **5b**•CH₃CN, orange, 85%; **6a**•CH₃CN, dark-red, 69%; **6b**•CH₃CN, dark-red, 44%).



Scheme 1. Synthesis of compounds 5a, 5b, 6a, and 6b.

Compound **5c**' was synthesized according to Scheme 2 by reaction of the chlorosilicon(IV) complex **2** with CF₃C(O)–CH=C(OSiMe₃)CF₃ (**9**) in diethyl ether at 20 °C and was isolated as a red crystalline solid in 78% yield.^[6] In contrast to the formation of **5a** and **5b** (\rightarrow hexacoordination), the reaction of **2** with **9** stops at the pentacoordinate stage (**5c**') (see "Crystal Structure Analyses").



Scheme 2. Synthesis of compound 5c'.

Compounds **4c**' and **6c**' were synthesized according to Scheme 3 by treatment of the chlorosilicon(IV) complexes **1** and **3**, respectively, with **9**. The syntheses were carried out in acetonitrile at 20 °C, and **4c**' and **6c**' were isolated, after crystallization from toluene, as colorless crystalline solids (yields: **4c**' \cdot 0.5C₆H₅CH₃, 63%; **6c**', 51%). Interestingly, the expected hexacoordinate silicon(IV) complexes **4c** and **6c** could not be obtained; instead, the pentacoordinate rearrangement products **4c**' and **6c**' were isolated. Treatment of **1** with PhC(O)–CH=C(OSiMe₃)CF₃ resulted in the forma-

tion of an analogous rearrangement product.^[2] The formation of 4c' and 6c' can be explained starting with the first step giving the expected products 4c and 6c, followed by cleavage of the Si-S and Si-N(amido) bond, respectively, and intramolecular formation of the new S-C or N-C bond. This rearrangement results in the formation of a new tetradentate trianionic O,N,O,O ligand in the silicon coordination sphere. The coordination of this ligand to the silicon atom leads to a tetracyclic ring system consisting of two six-membered rings, one seven-membered ring, and one nine-membered ring. The silicon atom and one of the two CF₃-bound carbon atoms represent the two bridgehead atoms of this tetracyclic ring system. The assumption that 4c and 6c are intermediates in the formation of 4c' and 6c', respectively, is supported by the color change observed for the two reaction mixtures. The solution of 1 in acetonitrile is yellow, and upon addition of the pale yellow reagent 9 initially an orange-colored mixture was formed. Likewise, the solution of 3 in acetonitrile is orange-colored, and upon addition of 9 a dark-red solution was observed. In both cases, after a short period of time, the reaction mixtures then turned to pale yellow solutions, and upon storage at -20 °C for one day colorless crystals of $4c' \cdot 0.5C_6H_5CH_3$ and 6c' were obtained.



Scheme 3. Synthesis of compounds 4c' and 6c'.

The different chemical behavior of compounds 4a, 4b, 5a, 5b, 6a, and 6b (no rearrangement) compared to that of 4c and 6c (rearrangement) can be explained by the presence of the CF_3 groups in the latter two compounds. The strongly electron-withdrawing CF_3 groups increase the electrophilicity of the carbon atoms next to the CF_3 groups, assisting the nucleophilic attack of the sulfur and nitrogen ligand atom of 4c and 6c, respectively, to give the rearrangement products 4c' and 6c'.

Crystal Structure Analyses

Compounds $4c' \cdot 0.5C_6H_5CH_3$, $5a \cdot 0.53CH_3CN$, $5b \cdot CH_3CN$, $5c' \cdot (C_2H_5)_2O$, 6a, $6b \cdot CH_3CN$, and 6c' were



Table 1. Crystallographic data f	for compounds 4c'	·0.5C ₆ H ₅ CH ₃ , 5a	•0.53CH ₃ CN, 5b•	CH ₃ CN, 5c'·($(C_2H_5)_2O$, 6a, 6b	·CH ₃ CN, and 6c'.
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	$\textbf{4c'} \cdot 0.5 C_6 H_5 C H_3$	5a•0.53CH ₃ CN	5b·CH ₃ CN	$5c' \cdot (C_2H_5)_2O$	6a	6b ⋅CH ₃ CN	6c'
Empirical formula	C ₂₂ H ₁₇ F ₆ NO ₃ SSi· 0.5C ₆ H ₅ CH ₃	C ₂₂ H ₂₃ NO ₄ Si· 0.53CH ₃ CN	C ₃₂ H ₂₇ NO ₄ Si· CH ₃ CN	C ₂₂ H ₁₇ F ₆ NO ₄ Si· (C ₂ H ₅) ₂ O	$C_{23}H_{26}N_2O_3Si$	C ₃₅ H ₃₃ N ₃ O ₃ Si• CH ₃ CN	C ₂₃ H ₂₀ F ₆ N ₂ O ₃ Si
$M_{\rm r}$	563.58	415.21	558.69	575.58	406.55	571.73	514.50
T[K]	173(2)	100(2)	100(2)	173(2)	173(2)	173(2)	173(2)
λ (Mo- K_{α}) [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group (no.)	$P\overline{1}(2)$	$P2_{1}(4)$	$P\overline{1}(2)$	$P2_1/c$ (14)	$P2_1/c$ (14)	$P\overline{1}(2)$	$P2_1/n$ (14)
a [Å]	11.8529(17)	11.7786(17)	10.0010(7)	10.8309(18)	8.4805(13)	10.119(2)	10.878(2)
b [Å]	12.2558(18)	23.476(3)	12.4225(9)	13.033(2)	15.143(3)	12.055(3)	13.1457(19)
c Å	18.634(3)	15.793(2)	12.8603(10)	19.248(3)	16.710(2)	13.764(3)	16.012(3)
a [°]	80.423(17)	90	111.202(2)	90	90	69.33(3)	90
β [°]	76.044(16)	90.205(7)	97.313(2)	90.327(19)	93.445(18)	83.80(3)	93.58(3)
v [°]	79.184(17)	90	102.624(2)	90	90	72.37(3)	90
V [Å ³]	2559.3(7)	4366.9(11)	1415.70(18)	2716.9(7)	2141.9(6)	1497.2(6)	2285.3(8)
Z	4	8	2	4	4	2	4
$\rho_{\rm calcd}$ [g cm ⁻³]	1.463	1.263	1.311	1.407	1.261	1.268	1.495
$\mu [\mathrm{mm}^{-1}]$	0.246	0.137	0.126	0.164	0.136	0.119	0.181
F(000)	1156	1757	588	1192	864	604	1056
Dimensions [mm]	$0.8 \times 0.5 \times 0.4$	$0.37 \times 0.31 \times 0.26$	$0.5 \times 0.4 \times 0.15$	$0.6 \times 0.5 \times 0.4$	$0.7 \times 0.3 \times 0.3$	$0.75 \times 0.55 \times 0.3$	$0.7 \times 0.5 \times 0.25$
2 <i>θ</i> [°]	5.14-52.04	2.58-56.55	3.48-61.00	5.26-52.04	5.52-52.04	4.80-52.04	5.96-52.04
Index ranges	$-14 \le h \le 14$	$-15 \le h \le 15$	$-14 \le h \le 14$	$-13 \le h \le 13$	$-10 \le h \le 10$	$-12 \le h \le 12$	$-13 \le h \le 13$
	$-15 \le k \le 15$.	$-31 \le k \le 31$.	$-17 \le k \le 17$.	$-16 \le k \le 16$.	$-18 \le k \le 18$.	$-14 \le k \le 14$.	$-15 \le k \le 16$.
	$-22 \le l \le 22$	$-21 \le l \le 20$	$-17 \le l \le 18$	$-23 \le l \le 23$	$-20 \le l \le 20$	$-16 \le l \le 16$	$-19 \le l \le 19$
No. reflns. coll.	27898	97045	57658	24547	23060	20042	24407
No. indep. reflns.	9407	21465	8553	5328	4031	5511	4463
Rint	0.0666	0.0459	0.0263	0.0412	0.0409	0.0417	0.0439
No. of restraints	0	64	0	36	0	0	0
No of param	681	1112	373	401	267	383	319
S[a]	1 105	1.104	1.012	1 053	1 044	1.039	1.067
Wt param <i>a</i> / <i>b</i> ^[b]	0 0730/1 4813	0.0553/2.3679	0.0538/0.6631	0.0679/1.3915	0.0434/0.7221	0 0523/0 2807	0.0605/0.5755
$R_{1}^{[c]}[I > 2\sigma(I)]$	0.0513	0.0456	0.0369	0.0464	0.0362	0.0354	0.0367
$wR_2^{[d]}$ (all data)	0 1471	0 1183	0.1039	0.1266	0.0947	0.0963	0.1034
Absol str. param		0.04(2)					
$\Delta \rho_{\text{max./min.}} [e \text{Å}^{-3}]$	+0.635/-0.401	+0.701/-0.313	+0.507/-0.300	+0.507/-0.371	+0.266/-0.254	+0.313/-0.240	+0.486/-0.313

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

structurally characterized by single-crystal X-ray diffraction. The crystal data and experimental parameters used for the crystal structure analyses are given in Table 1. Compounds $4c' \cdot 0.5C_6H_5CH_3$ and $5a \cdot 0.53CH_3CN$ crystallized with two and four silicon(IV) complexes, respectively, in the asymmetric unit. The molecular structures of 4c', 5a, 5b, 5c', 6a, 6b, and 6c' are shown in Figures 1, 2, 3, 4, 5, 6, and 7, respectively, with selected bond lengths and angles in the captions.

The silicon coordination polyhedra of **5a**, **5b**, **6a**, and **6b** are best described as distorted octahedra. The maximum deviations from the ideal 180 and 90° angles range from 7.97(4) to 9.82(12)° and from 6.46(13) to 7.58(10)°, respectively. The tridentate O,N,O and N,N,O ligands show *mer* coordination, with O1–Si–O4 angles ranging from 170.18(12) to 172.03(4)° and O1–Si–N2 angles in the range 170.58(6)–172.09(5)°. The Si–O1 [1.765(2)–1.7896(13) Å] and Si–O3 [1.7802(12)–1.8064(13) Å] bond lengths of **5a**, **5b**, **6a**, and **6b** are similar, whereas differences were observed for the Si–O2 bond lengths. The Si–O2 bond distances of **5a/5b** [1.860(2)–1.902(2)/1.8602(7) Å; O,N,O ligand] are significantly shorter than those of **6a/6b** [1.9266(11)/1.9032(11) Å; N,N,O ligand]. The Si–O4 bond lengths of **5a** and **5b** are 1.745(2)–1.763(2) and 1.7612(7) Å,

respectively, and the corresponding Si–N(amido) distances of **6a** and **6b** range from 1.8172(14) to 1.8249(13) Å. The Si–N(imino) bond lengths of **5a**, **5b**, **6a**, and **6b** are in the range 1.9075(8)–1.957(3) Å, and the Si–C bond lengths are 1.924(3)–1.9383(16) Å. Generally, the structures of **5a**, **5b**, **6a**, and **6b** are very similar and compare well with those of **4a** and **4b**. Obviously, the three different tridentate *S*,*N*,*O*, *O*,*N*,*O*, and *N*,*N*,*O* ligands and the two different bidentate *O*,*O* ligands have only little impact on the structures of the S/O/NMe analogues **4a/5a/6a** and **4b/5b/6b**.

The silicon coordination polyhedron of **5c**' is best described as a slightly distorted square pyramid, with the carbon atom in the apical position and a Berry distortion^[8] (transition trigonal bipyramid \rightarrow square pyramid) of 94.0%. The O1–Si–O4 and O3–Si–N angles are 158.48(8) and 163.32(8)°, respectively. The three Si–O bond lengths (Si–O1, Si–O3, Si–O4) range from 1.7210(16) to 1.7803(16) Å, and the Si–N and Si–C distances are 1.8961(18) and 1.889(2) Å, respectively. The bond angles and lengths reported above and the long Si—O2 distance (2.333 Å) suggest pentacoordination of the silicon atom of **5c**'. Alternatively, the coordination mode might be discussed in terms of a [5+1] coordination, with a base-capped square pyramid as the coordination polyhedron. However,





Figure 1. Molecular structure of one of the two crystallographically independent molecules in the crystal of $4c' \cdot 0.5C_6H_5CH_3$ (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si1–O1 1.800(2), Si1–O2 1.739(2), Si1–O3 1.705(2), Si1–N1 1.828(2), Si1–C1 1.886(3); O1–Si1–O2 176.73(10); O1–Si1–O3 83.89(10), O1–Si1–N1 90.21(10), O1–Si1–C1 88.83(11), O2–Si1–O3 93.28(10), O2–Si1–N1 92.47(10), O2–Si1–C1 91.54(11), O3–Si1–N1 114.55(10), O3–Si1–C1 126.24(11), N1–Si1–C1 118.68(11). The structure of the second molecule is very similar and behaves, as a first approximation, as a mirror image.



Figure 2. Molecular structure of one of the four crystallographically independent molecules in the crystal of $5a \cdot 0.53$ CH₃CN (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si1–O1 1.770(2), Si1–O2 1.860(2), Si1–O3 1.805(2), Si1–O4 1.763(2), Si1–N1 1.928(3), Si1–C1 1.924(3); O1–Si1–O2 84.30(11), O1–Si1–O3 89.42(11), O1–Si1–O4 171.96(12), O1–Si1–N1 93.46(11), O1–Si1–C1 93.73(13), O2–Si1–O3 90.21(11), O2–Si1–O4 87.67(11), O2–Si1–N1 83.43(11), O2–Si1–C1 177.33(12), O3–Si1–O1 90.17(11), O3–Si1–N1 172.71(12), O3–Si1–C1 91.57(12), O4–Si1–N1 86.05(11), O4–Si1–C1 94.32(12), N1–Si1–C1 94.92(12). The structures of the three other molecules are very similar.



Figure 3. Molecular structure of **5b** in the crystal of **5b**·CH₃CN (probability level of displacement ellipsoids 50%). Selected bond lengths (Å) and angles (°): Si–O1 1.7857(7), Si–O2 1.8602(7), Si–O3 1.7837(7), Si–O4 1.7612(7), Si–N1 1.9075(8), Si–C1 1.9254(10); O1–Si–O2 84.10(3), O1–Si–O3 89.75(3), O1–Si–O4 172.03(4), O1–Si–N1 91.47(3), O1–Si–C1 93.41(4), O2–Si–O3 89.18(3), O2–Si–O4 88.16(3), O2–Si–N1 84.32(3), O2–Si–C1 177.34(4), O3–Si–O4 92.07(3), O3–Si–N1 173.23(4), O3–Si–C1 89.88(4), O4–Si–N1 85.84(3), O4–Si–C1 94.36(4), N1–Si–C1 96.70(4).



Figure 4. Molecular structure of **5**c' in the crystal of **5**c' \cdot (C₂H₅)₂O (occupation factor 63%;^[7] probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–OI 1.7382(16), Si–O3 1.7803(16), Si–O4 1.7210(16), Si–N 1.8961(18), Si–C1 1.889(2); O1–Si–O3 86.27(7), O1–Si–O4 158.48(8), O1–Si–N 92.43(8), O1–Si–C1 100.64(9), O3–Si–O4 88.58(7), O3–Si–N 163.32(8), O3–Si–C1 96.50(8), O4–Si–N 86.57(7), O4–Si–C1 100.70(9), N–Si–C1 100.07(9).





Figure 5. Molecular structure of **6a** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–O1 1.7896(13), Si–O2 1.9266(11), Si–O3 1.7802(12), Si–N1 1.9275(14), Si–N2 1.8172(14), Si–C1 1.9383(16); O1–Si–O2 82.87(5), O1–Si–O3 88.10(6), O1–Si–N1 92.10(6), O1–Si–N2 170.58(6), O1–Si–C1 92.71(6), O2–Si–O3 90.16(5), O2–Si–N1 83.53(5), O2–Si–N2 87.95(6), O2–Si–C1 175.09(6), O3–Si–N1 173.61(5), O3–Si–N2 94.05(6), O3–Si–C1 91.81(6), N1–Si–N2 84.74(6), N1–Si–C1 94.56(6), N2–Si–C1 96.39(6).



Figure 6. Molecular structure of **6b** in the crystal of **6b**·CH₃CN (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–O1 1.7839(11), Si–O2 1.9032(11), Si–O3 1.8064(13), Si–N1 1.9099(14), Si–N2 1.8249(13), Si–C1 1.9346(15); O1–Si–O2 83.60(5), O1–Si–O3 88.07(6), O1–Si–N1 92.02(6), O1–Si–N2 172.09(5), O1–Si–C1 93.33(6), O2–Si–O3 87.67(5), O2–Si–N1 82.82(5), O2–Si–N2 88.96(5), O2–Si–C1 176.93(5), O3–Si–N1 170.42(5), O3–Si–N2 94.33(6), O3–Si–C1 92.17(6), N1–Si–N2 84.37(6), N1–Si–C1 97.39(6), N2–Si–C1 94.11(6).



Figure 7. Molecular structure of **6c**' in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–O1 1.8013(12), Si–O2 1.7257(12), Si–O3 1.6994(12), Si–N1 1.8267(14), Si–C1 1.8940(17); O1–Si–O2 178.55(5), O1–Si–O3 84.59(6), O1–Si–N1 89.55(6), O1–Si–C1 89.52(6), O2–Si–O3 94.28(6), O2–Si–N1 90.04(6), O2–Si–C1 91.84(6), O3–Si–N1 112.08(6), O3–Si–C1 120.51(7), N1–Si–C1 127.04(7).

there is no clear experimental evidence for a long-range interaction between the silicon coordination center and the oxygen atom O2 (in this context, see also the section "NMR Spectroscopic Studies"). Nevertheless, the molecular structures of the hexacoordinate compounds **5a** and **5b** and the pentacoordinate compound **5c'** are related to each other since the Si–O2 bonds of **5a** [1.860(2) Å] and **5b** [1.8602(7) Å] are significantly longer than the Si–O1 bonds of these compounds [**5a** 1.770(2) Å, **5b** 1.7857(7) Å]. This indicates a pronounced localization of the negative charge of the acetylacetonato ligand at one of the two oxygen atoms of **5a** and **5b**, and compound **5c'** appears to be a rather striking case of this charge localization, leading to a much stronger Si–O2 bond weakening or even an almost complete loss of bonding interaction (Si-O2 2.333 Å).

The silicon coordination polyhedra of **4c**' and **6c**' are best described as slightly distorted trigonal bipyramids, with the oxygen atoms O1 and O2 in the axial positions. The Berry distortions^[8] are 14.4/16.1 and 11.9%, respectively. The maximum deviations from the ideal 180° angles are 3.61(10) (**4c**') and 1.45(5)° (**6c**'), and the maximum deviations from the ideal 120° angles are 6.86(11) (**4c**') and 7.92(6)° (**6c**'). The axial Si–O bond distances of **4c**' and **6c**' [1.7257(12)–1.8013(12) Å] are somewhat longer than those of the equatorial ones [1.6994(12)–1.708(2) Å]. The Si–N distances are 1.828(2)/1.838(2) (**4c**') and 1.8267(14) Å (**6c**'), and Si–C bond lengths range from 1.886(3)/1.877(3) (**4c**') to 1.8940(17) Å (**6c**'). Generally, the structural features of the S/NMe analogues **4c**' and **6c**' are very similar.



NMR Spectroscopic Studies

Compounds $4c' \cdot 0.5C_6H_5CH_3$, $5a \cdot 0.5CH_3CN$, $5b \cdot CH_3CN$, $5c' \cdot (C_2H_5)_2O$, 6a, $6b \cdot CH_3CN$, and 6c' were studied by NMR spectroscopy in the solid state (¹⁵N, ²⁹Si) and in solution (solvent: CD_2Cl_2 ; ¹H, ¹³C, ¹⁹F, ²⁹Si). The isotropic ²⁹Si chemical shifts in the solid state clearly indicate the presence of pentacoordinate (4c'-6c') or hexacoordinate (5a, 5b, 6a, 6b) silicon atoms (Table 2). These chemical shifts are very similar to those obtained in solution (Table 2), indicating that all compounds studied exist in solution as well.

Table 2. Isotropic ²⁹Si chemical shifts of **4c'**, **5a**, **5b**, **5c'**, **6a**, **6b**, and **6c'** in the solid state (T = 22 °C) and in solution (solvent: CD₂Cl₂; T = 23 °C).

Compound	δ^{29} Si (solid state) [ppm]	δ^{29} Si (solution) [ppm]
4c'	-124.5 ^[a]	-125.3
5a	$-168.1, -167.2, -166.1, -165.8^{[b]}$	-165.1
5b	-164.3 ^[c]	-164.2
5c'	$-134.4^{[d]}$	-133.2
6a	-163.4	-162.0
6b	-161.5 ^[e]	-161.1
6c'	-127.7	-124.2

[a] Solvate $4c' \cdot 0.5C_6H_5CH_3$. [b] Solvate $5a \cdot 0.5CH_3CN$; four crystallographically independent molecules. [c] Solvate $5b \cdot CH_3CN$. [d] Solvate $5c' \cdot (C_2H_5)_2O$. [e] Solvate $6b \cdot CH_3CN$.

The solution ¹H and ¹³C NMR spectroscopic studies (solvent: CD_2Cl_2) revealed a major difference between the S/O/NMe analogues 4a/5a/6a and 4b/5b/6b. Compounds 6a and **6b** (NMe series) showed a dynamic behavior at room temperature [one set of resonance signals each for the two RC(O) groups of the bidentate O,O ligands], whereas this kind of behavior was not observed for 4a and 4b (S series)^[2] and **5a** and **5b** (O series). This observation can be correlated with the longer Si-O2 bond distances (see "Crystal Structure Analyses") in the NMe series [6a 1.9266(11) Å, **6b** 1.9032(11) Å] compared to those in the O series [5a 1.860(2) Å, 5b 1.8602(7) Å] and the S series [4a 1.8505(16) Å, 4b 1.8492(10) Å].^[2] These longer Si-O2 distances in 6a and 6b may reflect a weaker bonding of the acetylacetonato ligand to the silicon coordination center and could explain the higher mobility of the bidentate O,Oligands of 6a and 6b.

Compound **5c**' also shows a dynamic behavior in solution (solvent: CD_2Cl_2). At room temperature, only one ¹⁹F and one ¹³C resonance signal for the two CF₃ groups were observed, and the ¹³C NMR signal for the two oxygenbound carbon atoms of the CF₃C(O)=CH–C(O)CF₃⁻ ligand could not be detected. In contrast, the ¹H, ¹³C, and ¹⁹F NMR spectra of compounds **4c**' and **6c**' do not indicate any dynamic behavior.

Conclusions

The neutral pentacoordinate chlorosilicon(IV) complexes 1-3 have been demonstrated to be suitable starting materials for the synthesis of neutral hexacoordinate silicon(IV)

complexes with $SiSO_3NC$ (4a, 4b), SiO_4NC (5a, 5b), or SiO_3N_2 skeletons (6a, 6b). The silicon complexes 4a and 4b have already been described earlier, whereas 5a, 5b, 6a, and 6b represent new types of hexacoordinate silicon(IV) complexes. The S/O/NMe analogues 4a/5a/6a and 4b/5b/6b show an analogous stereochemistry in the solid state. The silicon coordination polyhedron is a distorted octahedron, with the tridentate *S*,*N*,*O*, *O*,*N*,*O*, or *N*,*N*,*O* ligand in *mer* positions. For compounds 6a and 6b (NMe series), a dynamic behavior in solution was observed (dynamic of the *O*,*O* ligand), whereas 4a and 4b (S series) and 5a and 5b (O series) do not show such behavior.

Compounds 1-3 have also been demonstrated to be valuable precursors for the preparation of neutral pentacoordinate silicon(IV) complexes, compounds 4c'-6c'. Compounds 4a-6a, 4b-6b, and 4c'-6c' were all obtained by treatment of 1-3 with the corresponding silvlated acetylacetone derivatives RC(O)-CH=C(OSiMe₃)R (R = Me, Ph, CF₃; elimination of Me₃SiCl). In these reactions, the nature of the R group of the silvlated acetylacetone derivative controls the product formation. In the case of $R = CF_3$, the expected hexacoordinate products 4c-6c could not be observed; instead, the pentacoordinate compound 4c'-6c'were obtained. Compound 5c' contains a square-pyramidal silicon coordination polyhedron, whereas 4c' and 6c' contain a trigonal-bipyramidal structure. This is another interesting example of the striking differences of S/O/NMe analogues derived from 1-3 (in this context, see also ref.^[1,2]). The formation of 4c' and 6c' represents a remarkable example of the generation of a new tetradentate trianionic O, N, O, O ligand in the silicon coordination sphere, probably by rearrangement of the potential intermediates 4c and 6c. As a result, tetracyclic ring systems consisting of two sixmembered rings, one seven-membered ring, and one ninemembered ring are built up.

In conclusion, the results reported here again emphasize the high synthetic potential of the S/O/NMe analogues 1-3 for the chemistry of penta- and hexacoordinate silicon(IV) complexes.

Experimental Section

General Procedures: All syntheses were carried out under dry argon. The organic solvents used were dried and purified according to standard procedures and stored under argon. The solution-state ¹H, ¹³C, ¹⁹F, and ²⁹Si NMR spectra were recorded at 23 °C by using a Bruker Avance 400 (19F, 376.5 MHz) or Bruker Avance 500 NMR spectrometer (¹H, 500.1 MHz; ¹³C, 125.8 MHz; ²⁹Si, 99.4 MHz). CD₂Cl₂ served as the solvent. Chemical shifts were determined relative to internal CHDCl₂ (¹H, δ = 5.32 ppm), CD₂Cl₂ (¹³C, δ = 53.8 ppm), or external TMS (²⁹Si, δ = 0 ppm). Assignment of the ¹³C NMR spectroscopic data was supported by DEPT 135 and 13C, 1H correlation experiments. Solid-state 15N and 29Si VACP/ MAS NMR spectra were recorded at 22 °C by using a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO₂ (diameter, 7 mm) containing about 300 mg of sample [15N, 40.6 MHz; $^{29}\mathrm{Si},~79.5$ MHz; external standard, TMS ($^{29}\mathrm{Si},~\delta$ = 0 ppm) or glycine (¹⁵N, δ = -342.0 ppm); spinning rate, 5 kHz; con-



3.6 µs; repetition time, 4–7 s].

tact time, 3 ms (15 N) or 5 ms (29 Si); 90° ¹H transmitter pulse length, to 20 °C (fo

4c'·0.5C₆H₅CH₃: 1,1,1,5,5,5-Hexafluoro-4-(trimethylsilyloxy)pent-3-en-2-one (2.07 g, 7.39 mmol) was added in a single portion at 20 °C to a stirred mixture of 1 (2.13 g, 6.16 mmol) and acetonitrile (50 mL), and the reaction mixture was then stirred at this temperature for 1 h. All volatile components were removed in vacuo, toluene (20 mL) was added to the residue, and the resulting mixture was heated until a clear solution was obtained, which was cooled slowly to -20 °C and then kept undisturbed at this temperature for 17 h. The resulting precipitate was isolated by filtration, washed with n-pentane (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give $4c' \cdot 0.5C_6H_5CH_3$ in 63% yield (2.19 g, 3.89 mmol) as a colorless crystalline solid. ¹H NMR (CD₂Cl₂): $\delta = 1.78$ (s, 3 H, CCH₃), 2.29 (s, 3 H, CCH₃), 2.35 (m, 1.5 H, C₆H₅CH₃), 5.79 (s, 1 H, CCHC), 5.87 (s, 1 H, CCHC), 6.94-6.99, 7.13-7.20, 7.23-7.30, 7.31-7.36, 7.36-7.40, 7.64-7.68, 7.69-7.73 (m, 11.5 H, SC₆H₄N, SiC_6H_5 , $C_6H_5CH_3$) ppm. ¹³C NMR (CD₂Cl₂): δ = 21.5 (0.5 C, $C_6H_5CH_3$), 24.9 (CCH₃), 25.0 (CCH₃), 83.7 [q, ²J(¹³C, ¹⁹F) = 32.5 Hz, CCF_3], 102.6 (CCHC), 102.9 [q, ${}^{3}J({}^{13}C, {}^{19}F) = 1.9$ Hz, CCHC], 119.7 [q, ${}^{1}J({}^{13}C, {}^{19}F) = 273.9$ Hz, CF_{3}], 124.3 [q, ${}^{1}J({}^{13}C, {}^{19}F) = 283.5 \text{ Hz}, CF_{3}, 146.9 [q, {}^{2}J({}^{13}C, {}^{19}F) = 36.8 \text{ Hz},$ CCF₃], 125.6 (0.5 C), 126.8, 127.5 (2 C), 128.5, 128.7, 129.2, 129.3, 130.0, 131.4, 137.2 (2 C), 137.4, 137.6, 138.3 (0.5 C), 147.8 (SC₆H₄N, SiC₆H₅, C₆H₅CH₃), 177.3 [C(N)CH₃], 187.9 [C(O)CH₃] ppm. ¹⁹F NMR (CD₂Cl₂): $\delta = -81.6$ (CF₃), -75.3 (CF₃) ppm. ²⁹Si NMR (CD₂Cl₂): δ = -125.3 ppm. ¹⁵N VACP/MAS NMR:^[9] δ = -205.3 ppm. ²⁹Si VACP/MAS NMR:^[9] δ = -124.5 ppm. C_{25.5}H₂₁F₆NO₃SSi (563.59): calcd. C 54.34, H 3.76, N 2.49, S 5.69; found C 54.75, H 3.70, N 2.93, S 5.45.

4-(Trimethylsilyloxy)pent-3-en-2-one 5a·0.5CH₂CN: (700 mg. 4.06 mmol) was added in a single portion at 20 °C to a stirred mixture of 2 (820 mg, 2.49 mmol) and acetonitrile (10 mL), and the reaction mixture was stirred at this temperature for 2 h and then heated until a clear solution was obtained, which was cooled slowly to 20 °C and kept undisturbed at this temperature for 21 h and then at -20 °C for a further 3 d. The resulting precipitate was isolated by filtration, washed with n-pentane (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give 5a·0.5CH₃CN in 76% yield (782 mg, 1.89 mmol) as a yellow crystalline solid. ¹H NMR (CD₂Cl₂): δ = 1.91 (s, 3 H, CCH₃), 1.95 (br. s, 3 H, CCH₃), 1.96 (s, 1.5 H, CH₃CN), 2.13 (s, 3 H, CCH₃), 2.35 (s, 3 H, CCH₃), 5.19 (s, 1 H, CCHC), 5.79 (s, 1 H, CCHC), 6.62-6.70, 6.96-7.01, 7.04-7.11, 7.12–7.16, 7.46–7.51 (m, 9 H, OC_6H_4N , SiC_6H_5) ppm. ¹³C NMR $(CD_2Cl_2): \delta = 1.9 (CH_3CN), 24.0 (CCH_3), 24.7 (CCH_3), 25.8$ (CCH₃), 26.0 (CCH₃), 102.0 (CCHC), 102.4 (CCHC), 116.9 (CH₃CN), 115.2, 117.2, 121.1, 126.1, 126.4 (2 C), 127.8, 133.1, 134.6 (2 C), 153.2, 155.8 (OC₆H₄N, SiC₆H₅), 167.8 [C(N)CH₃], 176.5 [C(O)CH₃], 189.7 [CO(CH₃), O,O ligand], 192.5 [CO(CH₃), *O*,*O* ligand] ppm. ²⁹Si NMR (CD₂Cl₂): δ = -165.1 ppm. ¹⁵N VACP/ MAS NMR: $\delta = -179.7, -177.7, -175.5, -174.8$ ppm (four crystallographically independent molecules), CH₃CN not detected. ²⁹Si VACP/MAS NMR: $\delta = -168.1, -167.2, -166.1, -165.8$ ppm (four crystallographically independent molecules). C₂₃H_{24.5}N_{1.5}O₄Si (414.04): calcd. C 66.72, H 5.96, N 5.07; found C 66.30, H 6.02, N 4.74.

5b·CH₃CN: 1,3-Diphenyl-3-(trimethylsilyloxy)prop-2-en-1-one (494 mg, 1.67 mmol) was added in a single portion at 20 °C to a stirred mixture of **2** (542 mg, 1.64 mmol) and acetonitrile (15 mL), and the reaction mixture was then stirred at this temperature for 15 min. Acetonitrile (10 mL) was added, and the mixture was heated until a clear solution was obtained, which was cooled slowly

to 20 °C (formation of crystals) and kept undisturbed at this temperature for 3 h and then at -20 °C for a further 15 h. The resulting precipitate was isolated by filtration, washed with n-pentane (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 4 h) to give 5b·CH₃CN in 85% yield (781 mg, 1.40 mmol) as an orange-colored crystalline solid. ¹H NMR (CD₂Cl₂): δ = 1.88 (s, 3 H, CCH₃), 1.97 (s, 3 H, CH₃CN), 2.45 (s, 3 H, CCH₃), 5.25 (s, 1 H, CCHC), 7.12 (s, 1 H, CCHC), 6.63-6.74, 7.11-7.29, 7.37-7.75, 8.00-8.06 (m, 19 H, OC₆ H_4 N, SiC₆ H_5 , CC₆ H_5) ppm. ¹³C NMR (CD₂Cl₂): δ = 2.0 (CH₃CN), 23.9 (CCH₃), 24.8 (CCH₃), 94.8 (CCHC), 102.6 (CCHC), 117.4 (CH₃CN), 115.4, 121.0, 126.2, 126.5 (2 C), 127.8, 128.4 (2 C), 128.6 (2 C), 128.9 (2 C), 129.0, 129.1 (2 C), 133.3, 133.4, 133.5, 134.7 (2 C), 135.8, 136.5, 153.0, 156.3 (OC₆H₄N, SiC₆H₅, CC₆H₅), 168.0 [C(N)CH₃], 177.2 [C(O)CH₃], 182.8 $[C(O)C_6H_5]$, 184.7 $[C(O)C_6H_5]$ ppm. ²⁹Si NMR (CD₂Cl₂): δ = -164.2 ppm. ¹⁵N VACP/MAS NMR: $\delta = -177.3$ [C(N)CH₃], -126.1(CH₃CN) ppm. ²⁹Si VACP/MAS NMR: δ = -164.3 ppm. C₃₄H₃₀N₂O₄Si (558.71): calcd. C 73.09, H 5.41, N 5.01; found C 73.01, H 5.39, N 4.76.

1,1,1,5,5,5-Hexafluoro-4-(trimethylsilyloxy)pent-3-en-2-one 5c': (1.66 g, 5.92 mmol) was added in a single portion at 20 °C to a stirred mixture of 2 (1.63 g, 4.94 mmol) and diethyl ether (50 mL), and the reaction mixture was then stirred at this temperature for 3 d. All volatile components were removed in vacuo, diethyl ether (15 mL) was added to the residue, and the resulting solution was kept undisturbed at -20 °C for 3 d. The resulting precipitate was isolated by filtration and dried in vacuo (0.01 mbar, 20 °C, 1 h) to give 5c' in 78% yield (1.92 g, 3.83 mmol) as a red crystalline solid.^[10] ¹H NMR (CD₂Cl₂): $\delta = 2.01$ [d, ⁴*J*(¹H, ¹³C) = 0.4 Hz, 3 H, CCH_3], 2.50 (s, 3 H, CCH_3), 5.46 [q, ${}^4J({}^1H, {}^{13}C) = 0.4$ Hz, 1 H, CCHC], 6.41 (s, 1 H, CCHC), 6.78-6.83, 6.83-6.86, 7.09-7.14, 7.17-7.25, 7.29-7.30, 7.42-7.46 (m, 9 H, OC₆H₄N, SiC₆H₅) ppm. ¹³C NMR (CD₂Cl₂): δ = 24.3 (CCH₃), 24.8 (CCH₃), 93.6 (CCHC), 104.3 (CCHC), 117.6 (q, ${}^{1}J({}^{13}C, {}^{19}F) = 283.8 \text{ Hz}, 2 \text{ C}, CF_3$], 115.3, 119.2, 120.9, 127.4 (2 C), 128.6, 128.8, 132.1, 134.1 (2 C), 142.2, 153.1 (OC₆H₄N, SiC₆H₅), 171.1 [C(N)CH₃], 176.3 [C(O)CH₃] ppm, $C(O)CF_3$ not detected. ¹⁹F NMR (CD₂Cl₂): $\delta = -76.9$ ppm. ²⁹Si NMR (CD₂Cl₂): δ = -133.2 ppm. ¹⁵N VACP/MAS NMR: δ = -187.3 ppm. ²⁹Si VACP/MAS NMR: δ = -134.4 ppm. C₂₂H₁₇F₆NO₄Si (501.46): calcd. C 52.69, H 3.42, N 2.79; found C 53.02, H 3.40, N 2.97.

6a: 4-(Trimethylsilyloxy)pent-3-en-2-one (889 mg, 5.16 mmol) was added in a single portion at 20 °C to a stirred mixture of 3 (1.11 g, 3.24 mmol) and acetonitrile (13 mL), and the reaction mixture was then stirred at this temperature for 2 h. All volatile components were removed in vacuo, acetonitrile (10 mL) was added to the residue, and the mixture was heated until a clear solution was obtained, which was cooled slowly to 20 °C and then kept undisturbed at this temperature for 21 h and then at -20 °C for a further 3 d. The resulting precipitate was isolated by filtration, washed with n-pentane (8 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give 6a in 69% yield (910 mg, 2.24 mmol) as a dark-red crystalline solid. ¹H NMR (CD₂Cl₂): δ = 1.84 (s, 3 H, CCH₃), 2.00 (s, 6 H, CCH₃), 2.28 (s, 3 H, CCH₃), 2.53 (s, 3 H, NCH₃), 5.11 (s, 1 H, CCHC), 5.69 (s, 1 H, CCHC), 6.26-6.36, 6.91-6.95, 7.01-7.09, 7.39–7.44 (m, 9 H, NC₆ H_4 N, SiC₆ H_5) ppm. ¹³C NMR (CD₂Cl₂): δ = 23.7 (CCH₃), 24.6 (CCH₃), 25.9 (2 C, CCH₃), 31.4 (NCH₃), 101.9 (CCHC), 102.7 (CCHC), 107.6, 112.2, 120.7, 125.8, 126.2 (2 C), 127.7, 130.9, 134.8 (2 C), 149.7, 153.8 (NC₆H₄N, SiC₆H₅), 167.7 [C(N)CH₃], 177.1 [C(O)CH₃] ppm, C(O)CH₃ (O,O ligand) not detected. ²⁹Si NMR (CD₂Cl₂): δ = -162.0 ppm. ¹⁵N VACP/MAS NMR: δ = -284.6 (NCH₃), -174.9 [C(N)CH₃] ppm. ²⁹Si VACP/

481



FULL PAPER

MAS NMR: $\delta = -163.4$ ppm. $C_{23}H_{26}N_2O_3Si$ (406.56): calcd. C 67.95, H 6.45, N 6.89; found C 67.84, H 6.24, N 6.86.

6b·CH₃CN: 1,3-Diphenyl-3-(trimethylsilyloxy)prop-2-en-1-one (739 mg, 2.49 mmol) was added in a single portion at 20 °C to a mixture of 3 (564 mg, 1.64 mmol) and acetonitrile (8 mL), and the reaction mixture was then stirred at this temperature for 1 h. All volatile components were removed in vacuo, acetonitrile (13 mL) was added to the residue, and the mixture was heated until a clear solution was obtained, which was cooled slowly to 20 °C (formation of crystals) and then kept undisturbed at this temperature for 30 h. The resulting precipitate was isolated by filtration, washed with *n*-pentane (8 mL), and dried in vacuo (0.01 mbar, 20 °C, 3 h) to give 6b·CH₃CN in 44% yield (412 mg, 721 µmol) as a dark-red crystalline solid. ¹H NMR (CD₂Cl₂): δ = 1.81 (s, 3 H, CCH₃), 1.97 (s, 3 H, CH₃CN), 2.37 (s, 3 H, CCH₃), 2.47 (s, 3 H, NCH₃), 5.13 (s, 1 H, CCHC), 7.00 (s, 1 H, CCHC), 6.90-6.97, 7.09-7.20, 7.48-7.66, 7.96–8.02 (m, 19 H, NC₆H₄N, SiC₆H₅, CC₆H₅) ppm. ¹³C NMR (CD₂Cl₂): δ = 2.1 (CH₃CN), 23.5 (CCH₃), 24.7 (CCH₃), 31.6 (NCH₃), 94.7 (CCHC), 102.9 (CCHC), 116.5 (CH₃CN), 107.9, 110.6, 112.4, 120.6, 125.9, 126.3 (2 C), 127.5 (2 C), 127.8 (2 C), 128.4, 128.7, 129.1 (2 C), 131.4, 132.9, 133.2 (2 C), 135.1 (2 C), 135.8, 150.3, 153.3 (NC₆H₄N, SiC₆H₅, CC₆H₅), 167.7 [C(N)CH₃], 177.6 [C(O)CH₃], 186.1 (2 C, C(O)C₆H₅] ppm. ²⁹Si NMR (CD₂Cl₂): δ = -161.1 ppm. ¹⁵N VACP/MAS NMR: δ = -290.9 (NCH₃), -175.3 [C(N)CH₃], -126.4 (CH₃CN) ppm. ²⁹Si VACP/ MAS NMR: $\delta = -161.5$ ppm. $C_{35}H_{33}N_3O_3Si$ (571.75): calcd. C 73.53, H 5.82, N 7.35; found C 73.58, H 5.83, N 6.95.

6c': 1,1,1,5,5,5-Hexafluoro-4-(trimethylsilyloxy)pent-3-en-2-one (1.99 g, 7.10 mmol) was added in a single portion at 20 °C to a stirred mixture of 3 (1.62 g, 4.72 mmol) and acetonitrile (50 mL), and the reaction mixture was then stirred at this temperature for 1 h. All volatile components were removed in vacuo, toluene (15 mL) was added to the residue, and the resulting mixture was heated until a clear solution was obtained, which was kept undisturbed at 20 °C for 16 h. The resulting precipitate was isolated by filtration, washed with n-pentane (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 1 h) to give 6c' in 51% yield (1.25 g, 2.43 mmol) as a colorless crystalline solid. ¹H NMR (CD₂Cl₂): $\delta = 1.69$ (s, 3 H, CCH₃), 2.24 (s, 3 H, CCH₃), 2.96 [q, ${}^{5}J({}^{1}H, {}^{19}F) = 2.3$ Hz, 3 H, NCH₃], 5.80 (s, 1 H, CCHC), 5.91 (s, 1 H, CCHC), 6.80-6.84, 7.04-7.10, 7.22-7.27, 7.28-7.38, 7.71-7.75 (m, 9 H, NC₆H₄N, SiC₆ H_5) ppm. ¹³C NMR (CD₂Cl₂): δ = 24.2 (CCH₃), 24.8 (CCH₃), 35.0 [q, ${}^{4}J({}^{13}C, {}^{19}F) = 2.3 \text{ Hz}, \text{ NCH}_{3}$], 86.5 [q, ${}^{2}J({}^{13}C, {}^{19}F) =$ 28.6 Hz, CCF_3], 101.1 [q, ${}^{3}J({}^{13}C, {}^{19}F) = 3.7$ Hz, CCHC], 102.6 (CCHC), 120.0 [q, ${}^{1}J({}^{13}C, {}^{19}F) = 273.6 \text{ Hz}, CF_{3}$], 125.1 [q, ${}^{1}J({}^{13}C, {}^{19}F) = 297.7 \text{ Hz}, CF_{3}, 146.8 [q, {}^{2}J({}^{13}C, {}^{19}F) = 35.2 \text{ Hz},$ CCF₃], 124.5, 125.1, 125.9, 127.4 (2 C), 128.9, 129.7, 137.1 (2 C), 138.5, 141.1, 143.3 (NC₆H₄N, SiC₆H₅), 176.9 [C(N)CH₃], 187.3 $[C(O)CH_3]$ ppm. ¹⁹F NMR (CD₂Cl₂): $\delta = -77.3$ (CF₃), -75.1 (CF₃) ppm. ²⁹Si NMR (CD₂Cl₂): δ = -124.2 ppm. ¹⁵N VACP/MAS NMR: $\delta = -321.8$ (NCH₃), -203.4 [C(N)CH₃] ppm. ²⁹Si VACP/ MAS NMR: $\delta = -127.7$ ppm. $C_{23}H_{20}F_6N_2O_3Si$ (514.50): calcd. C 53.69, H 3.92, N 5.44; found C 53.80, H 3.78, N 5.44.

7: This compound was synthesized according to ref.^[11]

8: This compound was synthesized according to ref.^[12]

9: This compound was synthesized according to ref.^[13]

Crystal Structure Analyses: Suitable single crystals of $4c' \cdot 0.5C_7H_8$, $5a \cdot 0.53CH_3CN$, $5b \cdot CH_3CN$, $5c' \cdot (C_2H_5)_2O$, 6a, $6b \cdot CH_3CN$, and 6c' were mounted in inert oil (perfluoropolyalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer {Stoe IPDS [$4c' \cdot 0.5C_7H_8$, $5c' \cdot (C_2H_5)_2O$, 6a,

6b·CH₃CN, and **6c**'; graphite-monochromated Mo- K_a radiation, $\lambda = 0.71073$ Å] or Bruker Nonius KAPPA APEX II (**5a**·0.53CH₃CN and **5b**·CH₃CN; Montel mirror, Mo- K_a radiation, $\lambda = 0.71073$ Å)}. All structures were solved by direct methods (SHELXS-97^[14]) and refined by full-matrix least-squares methods on F^2 for all unique reflections (SHELXL-97^[14]). SHELXLE was used as refinement GUI.^[15] For the *CH* hydrogen atoms, a riding model was employed. CCDC-9606664 (**4c**'-0.5C₇H₈), CCDC-960665 (**5a**·0.53CH₃CN), CCDC-9606666 (**5b**·CH₃CN), CCDC-960667 [**5c**'·(C₂H₅)₂O], CCDC-960668 (**6a**), CCDC-960669 (**6b**·CH₃CN), and CCDC-960670 (**6c**') contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

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