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## Neutral Pentacoordinate Halogeno- and Pseudohalogenosilicon(IV) Complexes with a Tridentate Dianionic *O*,*N*,*O* or *N*,*N*,*O* Ligand: Synthesis and Structural Characterization in the Solid State and in Solution

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A series of neutral pentacoordinate silicon(IV) complexes with an  $SiFO_2NC$ ,  $SiBrO_2NC$ ,  $SiO_2NC_2$ ,  $SiO_2N_2C$ ,  $SiFON_2C$ ,  $SiBrON_2C$ ,  $SiON_2C_2$ , or  $SiON_3C$  skeleton was synthesized and structurally characterized by multinuclear NMR spectroscopy in the solid state and in solution and by single-crystal X-ray diffraction. The compounds studied contain a tridentate dianionic  $O_iN_iO$  or  $N_iN_iO$  ligand, a phenyl ligand, and a (pseudo)halogeno ligand (F, Br, CN, N<sub>3</sub>, NCS). The structures, NMR spectroscopic parameters, and chemical properties of these silicon(IV) complexes were compared with those of related compounds that contain an analogous

### Introduction

Higher-coordinate silicon compounds, with the first examples dating back to the beginning of the 19th century, have received considerable attention in recent years.<sup>[1,2]</sup> Most of the penta- and hexacoordinate silicon(IV) compounds reported in the literature contain hard ligand atoms such as fluorine, chlorine, oxygen, nitrogen, and carbon atoms.<sup>[1]</sup> Recently, quite new perspectives for the chemistry of higher-coordinate silicon have been generated by introducing soft chalcogen ligand atoms (sulfur, selenium, tellurium) into the coordination sphere of the hard silicon(IV) coordination center.<sup>[2b,2f,2m,3]</sup> In this context, we have recently reported on the syntheses, structures, and properties of the neutral pentacoordinate silicon(IV) complexes  $1a-1g.^{[2f,3f]}$  These compounds contain a tridentate *S*,*N*,*O* ligand, a phenyl ligand, and a (pseudo)halogeno ligand. To

tridentate dianionic S,N,O ligand instead of the O,N,O or N,N,O ligand (comparison of S/O/NMe analogues). In addition, two cationic pentacoordinate silicon(IV) complexes with an  $SiO_2N_2C$  and  $SiON_3C$  skeleton, respectively, were synthesized (isolated as iodides) and structurally characterized. These compounds contain a tridentate O,N,O or N,N,O ligand, a phenyl ligand, and an acetonitrile ligand. The experimental investigations reported in this article were complemented by computational studies to better understand the different properties of some of the S/O/NMe analogues studied.

get information about the effect of the soft sulfur ligand atom on the structure and properties of these compounds, we have been interested in the synthesis and characterization of the corresponding analogues 2a-2g and 3a-3g that contain a hard oxygen or nitrogen atom (NMe group) instead of the sulfur ligand atom. In a preliminary study, we have already demonstrated that the chlorosilicon(IV) complexes 2b and 3b (analogues of 1b) can be synthesized.<sup>[4]</sup> In extension of these investigations, we have now succeeded in synthesizing compounds 2a, 2c, 2e-2g, 3a, and 3c-3g. Interestingly, the synthesis of the iodosilicon(IV) complex 2d failed; instead, the ionic binuclear tetracoordinate silicon(IV) compound 2i was obtained. In addition, we succeeded in synthesizing the ionic pentacoordinate silicon(IV) complexes 2h and 3h, whereas the corresponding sulfur analogue 1h does not exist.

We report here on (i) the syntheses of compounds 2a, 2c, 2e–2i, 3a, and 3c–3h, (ii) their structural characterization in the solid state (crystal structure analysis, except for 3d; NMR spectroscopy, except for 2h, 3d, and 3h) and in solution (NMR spectroscopy), and (iii) a systematic comparison of the respective S/O/NMe analogues in question. The experimental investigations described herein were complemented by quantum-chemical studies to better understand the different properties of some of the S/O/NMe analogues studied.

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**Results and Discussion** 

### Syntheses

The fluorosilicon(IV) complex 2a was synthesized by treatment of the corresponding chlorosilicon(IV) complex 2b with ammonium fluoride in tetrahydrofuran (Scheme 1). The related (pseudo)halogenosilicon(IV) complexes 2c and 2e-2g were obtained by reaction of 2b with the corresponding (pseudo)halogenotrimethylsilane, Me<sub>3</sub>SiX (2c, X = Br; 2e, X = CN; 2f, X = N<sub>3</sub>; 2g, X = NCS), in acetonitrile (Scheme 1).



Scheme 1. Synthesis of compounds 2a, 2c, and 2e-2g.

The fluorosilicon(IV) complex **3a** was synthesized by treatment of the corresponding chlorosilicon(IV) complex **3b** with ammonium fluoride in tetrahydrofuran (Scheme 2). Alternatively, compound **3a** was obtained by reaction of **3b** with silver tetrafluoroborate/triethylamine in acetonitrile (Scheme 2). The related (pseudo)halogenosilicon(IV) complexes **3c** (isolated as **3c**·0.5C<sub>6</sub>H<sub>6</sub>) and **3e**–**3g** were synthesized by treatment of **3b** with the corresponding (pseudo)halogenotrimethylsilane, Me<sub>3</sub>SiX (**3c**, X = Br; **3e**, X = CN; **3f**,  $X = N_3$ ; **3g**, X = NCS), in acetonitrile or benzene (**3c** only) (Scheme 2). Attempts to synthesize the corresponding iodosilicon(IV) complex **3d** analogously to the synthesis of **3e–3g** by reaction of **3b** with iodotrimethylsilane in acetonitrile failed (see below); however, compound **3d** could be prepared by treatment of **3b** with iodotrimethylsilane in dichloromethane at -80 °C in an NMR tube, but upon warming of the solution to -20 °C, compound **3d** decomposed. All attempts to isolate **3d** below -20 °C failed.



Scheme 2. Synthesis of compounds 3a and 3c-3g.

Interestingly, treatment of the chlorosilicon(IV) complexes 2b and 3b with iodotrimethylsilane in acetonitrile did not yield the expected iodosilicon(IV) complexes 2d and 3d. Instead, the ionic complexes 2h (isolated as the solvate 2h·CH<sub>3</sub>CN) and 3h were obtained (Scheme 3), in which a neutral acetonitrile molecule is coordinated to the silicon coordination center; i.e., the resulting pentacoordinate silicon(IV) complexes are positively charged, with an iodide ion as the counterion. In this context, it is interesting to note that the analogous iodosilicon(IV) complex 1d (tridentate S.N.O ligand) can be easily synthesized by reaction of the corresponding chlorosilicon(IV) complex 1b with iodotrimethylsilane in acetonitrile.<sup>[2f]</sup> Thus, replacement of the soft sulfur ligand atom by the hard oxygen or nitrogen ligand atom  $(1b/1d \rightarrow 2b/2d, 3b/3d)$  affects the chemical properties of these analogues dramatically (in this context, see the section Computational Studies).

As already mentioned above, treatment of the pentacoordinate chlorosilicon(IV) complex **3b** (N,N,O ligand) with iodotrimethylsilane in dichloromethane at -80 °C yielded **3d**; however, all attempts to isolate **3d** failed so far. In contrast, reaction of the analogous chlorosilicon(IV) complex **2b** (O,N,O) with iodotrimethylsilane in dichloromethane at 20 °C afforded the ionic binuclear tetracoordinate silicon(IV) complex **2i** (Scheme 3), whereas this synthesis in dichloromethane at -80 °C failed. Neither the formation of **2d** nor the conversion of **2d** to **2i** could be observed.

Compounds 2a, 2c, 2e–2g, 2h·CH<sub>3</sub>CN, 2i, 3a,  $3c \cdot 0.5C_6H_6$ , 3e-3g, and 3h were isolated as yellow or orange-colored solids (yields: 2a, 57%; 2c, 61%; 2e, 64%; 2f, 79%; 2g, 88%; 2h·CH<sub>3</sub>CN, 44%; 2i, 58%; 3a, 49%/61%; 3c \cdot 0.5C\_6H\_6, 84%; 3e, 81%; 3f, 88%; 3g, 70%; 3h, 64%). Their identities were established by elemental analyses



Scheme 3. Synthesis of compounds 2h, 2i, and 3h.

(C, H, N), multinuclear NMR spectroscopic studies in the solid state (except for  $2h \cdot CH_3CN$  and 3h) and in solution, and crystal structure analyses (the crystal structure analysis of 3h was performed with the solvate  $3h \cdot 2CH_3CN$ ). Compound 3d was only characterized by NMR spectroscopy in solution.

#### **Crystal Structure Analyses**

Compounds 2a, 2c, 2e–2g, 2h·CH<sub>3</sub>CN, 2i, 3a,  $3c\cdot 0.5C_6H_6$ , 3e-3g, and  $3h\cdot 2CH_3CN$  were structurally characterized by single-crystal X-ray diffraction. The crystal data, the experimental parameters used for these studies, and the molecular structures of 2a, 2e–2g, 2i (cation), 3c, and 3e–3g are given in the Supporting Information. The molecular structures of compounds 2c, 2h (cation), 3a, and 3h (cation) are shown in Figures 1, 2, 3, and 4; selected bond lengths and angles are given in the respective captions.



Figure 1. Molecular structure of **2c** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–Br 2.3870(9), Si–O1 1.6843(19), Si–O2 1.694(2), Si–N 1.974(2), Si–C1 1.859(3); Br–Si–O1 87.76(7), Br–Si–O2 85.91(8), Br–Si–N 165.41(7), Br–Si–C1 98.34(8), O1–Si–O2 134.02(11), O1–Si–N 91.04(10), O1–Si–C1 112.69(11), O2–Si–N 84.49(10), O2–Si–C1 113.29(11), N–Si–C1 95.53(10).



Figure 2. Molecular structure of the cation of **2h** in the crystal of **2h**·CH<sub>3</sub>CN (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–O1 1.6761(16), Si–O2 1.6899(16), Si–N1 1.8969(19), Si–N2 1.934(2), Si–C1 1.858(2), N2–C2 1.136(3), C2–C3 1.442(3); O1–Si–O2 132.55(8), O1–Si–N1 87.05(8), O1–Si–N2 84.12(8), O1–Si–C1 115.26(9), O2–Si–N1 91.78(8), O2–Si–N2 83.71(8), O2–Si–C1 111.54(9), N1–Si–N2 163.12(8), N1–Si–C1 100.81(9), N2–Si–C1 95.97(9), Si–N2–C2 177.96(19), N2–C2–C3 178.7(3).



Figure 3. Molecular structure of **3a** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–F 1.6526(7), Si–O 1.7225(7), Si–N1 1.9603(8), Si–N2 1.7549(9), Si–C1 1.8860(9); F–Si–O 87.76(3), F–Si–N1 171.25(4), F–Si–N2 92.71(4), F–Si–C1 96.07(4), O–Si–N1 88.27(3), O–Si–N2 128.23(4), O–Si–C1 112.73(4), N1–Si–N2 83.64(4), N1–Si–C1 92.66(4), N2–Si–C1 118.66(4).

The silicon coordination polyhedra of the neutral pentacoordinate (pseudo)halogenosilicon(IV) complexes studied are strongly distorted trigonal bipyramids, with the imino nitrogen atom of the tridentate O,N,O and N,N,O ligand, respectively, and the monodentate (pseudo)halogeno ligand in the two axial positions. Analogous structures were also observed for the related silicon(IV) complexes **1a–1g** (S,N,Oligand),<sup>[2f,3f]</sup> **2b** (O,N,O),<sup>[4]</sup> and **3b** (N,N,O).<sup>[4]</sup> In the case of





Figure 4. Molecular structure of the cation of **3h** in the crystal of **3h**·2CH<sub>3</sub>CN (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–O 1.6770(19), Si–N1 1.9227(19), Si–N2 1.741(2), Si–N3 1.996(2), Si–C1 1.873(2), N3–C2 1.136(3), C2–C3 1.460(4); O–Si–N1 93.08(9), O–Si–N2 126.63(10), O–Si–N3 83.09(9), O–Si–C1 112.49(10), N1–Si–N2 86.18(9), N1–Si–N3 172.58(10), N1–Si–C1 96.83(9), N2–Si–N3 90.99(9), N2–Si–C1 120.58(11), N3–Si–C1 90.52(10), Si–N3–C2 168.6(2), N3–C2–C3 179.9(3).

1e, 2e, and 2f, the silicon coordination polyhedra are even better described as strongly distorted square pyramids (see below).

Table 1 shows the Berry distortions (transition trigonal bipyramid  $\rightarrow$  square pyramid) and the axial N–Si–X (X = F, Cl, Br, CN, N<sub>3</sub>, NCS) bond angles of the new compounds studied. The Berry distortions range from 29.8% to 57.3% (*O*,*N*,*O* ligand) and from 16.2% to 32.5% (*N*,*N*,*O*), respectively. The axial N–Si–X angles are in the range 161.14(5)–169.55(5)° (*O*,*N*,*O*) and 170.25(5)–175.27(5)° (*N*,*N*,*O*). The corresponding data of the related compounds

**1a**–**1g**,<sup>[2f,3f]</sup> **2b**,<sup>[4]</sup> and **3b**<sup>[4]</sup> are also summarized in Table 1. Comparison of all these data demonstrates that the degree of distortion of the trigonal-bipyramidal silicon coordination polyhedra of the respective S/O/NMe analogues differs significantly. The highest degree of distortion was observed for the series of compounds with the *O*,*N*,*O* ligand, followed by those with the *S*,*N*,*O* and *N*,*N*,*O* ligands; only **1a** and **1d** deviate from this rank order. With Berry distortions of >50%, the silicon coordination polyhedra of **1e** (57.3%), **2e** (52.1%), and **2f** (57.3%) can be alternatively described as strongly distorted square pyramids.

Contrary to the significantly different degrees of distortion (Table 1) observed for the respective S/O/NMe analogues, replacement of the sulfur ligand atom of 1a-1g by an oxygen or a methyl-bound nitrogen atom only slightly affects the analogous silicon-ligand bond lengths. As can be seen from Tables 2 and 3, most of the analogous Si-X  $(X = F, Cl, Br, CN, N_3, NCS), Si-O(enolato), Si-N(imino),$ and Si-C bond lengths of the respective S/O/NMe analogues are very similar. The greatest differences were observed for the Si-CN bond lengths of the S/O/NMe triple **1e/2e/3e** (Si–CN bond,  $\Delta_{\text{max}} = 0.166$  Å); all the other  $\Delta_{\text{max}}$ values are in the range 0.006-0.052 Å (Table 2 and Table 3). The Si-O(phenolato) bond lengths of 2a-2c and 2e-2g (O, N, O ligand) amount to 1.6788(10)–1.7013(12) Å ( $\Delta_{\text{max}}$ , 0.023 Å), and the Si-N(amido) bond lengths of 3a-3c and **3e–3g** (N,N,O ligand) are in the range 1.7432(13)– 1.7591(12) Å ( $\Delta_{\text{max}}$ , 0.016 Å); i.e., the different (pseudo)halogeno ligands do not significantly affect the Si-O(phenolato) and Si-N(amido) bond lengths.

The cationic pentacoordinate silicon(IV) complexes  $2h \cdot CH_3CN$  (*O*,*N*,*O* ligand) and  $3h \cdot 2CH_3CN$  (*N*,*N*,*O*), with their axial acetonitrile ligand, have similar structures as observed for the related neutral (pseudo)halogenosilicon(IV) complexes discussed above. The silicon coordination polyhedra are strongly distorted trigonal bipyramids (Berry dis-

Table 1. Berry distortions [%] and axial N–Si–X (X = F, Cl, Br, I, CN, N<sub>3</sub>, NCS) bond angles [°] of compounds 1a-1g, 2a-2c, 2e-2g, 3a-3c, and 3e-3g.

Compounds (ligands)	Berry distortions	N–Si–X	Compounds (ligands)	Berry distortions	N–Si–X	Compounds (ligands)	Berry distortions	N–Si–X
<b>1a</b> ( <i>S</i> , <i>N</i> , <i>O</i> , F)	19.0 <sup>[a]</sup>	168.46(3) <sup>[a]</sup>	<b>2a</b> ( <i>O</i> , <i>N</i> , <i>O</i> , F)	29.8	169.55(5)	<b>3a</b> ( <i>N</i> , <i>N</i> , <i>O</i> , F)	26.1	171.25(4)
<b>1b</b> ( <i>S</i> , <i>N</i> , <i>O</i> , Cl)	28.4 <sup>[b]</sup>	167.66(3) <sup>[b]</sup>	<b>2b</b> ( <i>O</i> , <i>N</i> , <i>O</i> , Cl)	41.2 <sup>[c]</sup>	166.02(2) <sup>[c]</sup>	<b>3b</b> ( <i>N</i> , <i>N</i> , <i>O</i> , Cl)	23.8 <sup>[c]</sup>	173.04(5) <sup>[c]</sup>
1c (S,N,O, Br) 1d (S,N,O, I)	$27.9^{[a]}$ $22.5^{[b]}$	167.41(3) <sup>[a]</sup> 167.96(7) <sup>[b]</sup>	<b>2c</b> ( <i>O</i> , <i>N</i> , <i>O</i> , Br) <b>2d</b> ( <i>O</i> , <i>N</i> , <i>O</i> , I)	42.6	165.41(7)	<b>3c</b> ( <i>N</i> , <i>N</i> , <i>O</i> , Br) <b>3d</b> ( <i>N</i> , <i>N</i> , <i>O</i> , I)	16.2	175.27(5)
1e $(S,N,O, CN)$	57.3 <sup>[a]</sup>	$161.73(5)^{[a]}$	<b>2e</b> ( <i>O</i> , <i>N</i> , <i>O</i> , CN)	52.1	163.23(6)	<b>3e</b> ( <i>N</i> , <i>N</i> , <i>O</i> , CN)	27.0	171.73(5)
1f $(S,N,O, N_3)$	42.6 <sup>[a]</sup>	164.41(6) <sup>[a]</sup>	<b>2f</b> ( <i>O</i> , <i>N</i> , <i>O</i> , N <sub>3</sub> )	57.3	161.14(5)	<b>3f</b> ( <i>N</i> , <i>N</i> , <i>O</i> , N <sub>3</sub> )	32.5	170.25(5)
1g $(S,N,O, NCS)$	29.8 <sup>[a]</sup>	168.30(7) <sup>[a]</sup>	<b>2g</b> ( <i>O</i> , <i>N</i> , <i>O</i> , NCS)	42.6	165.80(5)	<b>3g</b> ( <i>N</i> , <i>N</i> , <i>O</i> , NCS)	25.6	171.98(6)

[a] Data taken from ref.<sup>[2f]</sup> [b] Data taken from ref.<sup>[3f]</sup> [c] Data taken from ref.<sup>[4]</sup>

Table 2. Comparison of the Si-X (X = F, Cl, Br, I, CN, N<sub>3</sub>, NCS) bond lengths [Å] of 1a–1g, 2a–2c, 2e–2g, 3a–3c, and 3e–3g and maximum bond lengths differences  $\Delta_{max}$  [Å].

Compounds (ligands) and $\Delta_{max}$	Si-F	SiCl	Si–Br	Si–I	Si–CN	Si–N <sub>3</sub>	Si-NCS
<b>1a–1g</b> (S,N,O)	1.6687(5) <sup>[a]</sup>	2.1954(4) <sup>[b]</sup>	2.4051(4) <sup>[a]</sup>	2.7396(8) <sup>[b]</sup>	1.9563(16) <sup>[a]</sup>	1.8573(14) <sup>[a]</sup>	1.8729(17) <sup>[a]</sup>
<b>2a–2c</b> , <b>2e–2g</b> (O,N,O)	1.6462(11)	2.1913(3) <sup>[c]</sup>	2.3870(9)		2.0383(15)	1.8378(12)	1.8470(12)
<b>3a–3c</b> , <b>3e–3g</b> (N,N,O)	1.6526(7)	2.2098(6) <sup>[c]</sup>	2.4298(7)		1.8726(13)	1.8894(13)	1.8502(13)
Δ <sub>max</sub>	0.023	0.019	0.043		0.166	0.052	0.026

[a] Data taken from ref.<sup>[2f]</sup> [b] Data taken from ref.<sup>[3f]</sup> [c] Data taken from ref.<sup>[4]</sup>

Table 3. Comparison of the Si–O(enolato), Si–N(imino), and Si–C bond lengths [Å] of 1a–1g, 2a–2c, 2e–2g, 3a–3c, and 3e–3g and maximum bond lengths differences  $\Delta_{max}$  [Å].

Compd. (ligands), $\Delta_{max}$	Si-O(enolato)	Si–N(imino)	Si–C
1a (S,N,O, F)	1.6967(6) <sup>[a]</sup>	2.0096(6) <sup>[a]</sup>	1.8745(7) <sup>[a]</sup>
<b>2a</b> ( <i>O</i> , <i>N</i> , <i>O</i> , F)	1.6861(12)	2.0052(14)	1.8661(15)
<b>3a</b> ( <i>N</i> , <i>N</i> , <i>O</i> , F)	1.7225(7)	1.9603(8)	1.8860(9)
$\Delta_{max}$ (subgroup)	0.036	0.049	0.020
<b>1b</b> ( <i>S</i> , <i>N</i> , <i>O</i> , Cl)	1.6850(8) <sup>[b]</sup>	2.0069(10) <sup>[b]</sup>	1.8593(11) <sup>[b]</sup>
<b>2b</b> ( <i>O</i> , <i>N</i> , <i>O</i> , Cl)	1.6802(7) <sup>[c]</sup>	1.9843(7) <sup>[c]</sup>	1.8547(8) <sup>[c]</sup>
<b>3b</b> ( <i>N</i> , <i>N</i> , <i>O</i> , Cl)	1.6858(14) <sup>[c]</sup>	$2.0044(14)^{[c]}$	1.8762(18) <sup>[c]</sup>
$\Delta_{max}$ (subgroup)	0.006	0.023	0.022
1c (S,N,O, Br)	1.6802(10) <sup>[a]</sup>	1.9851(12) <sup>[a]</sup>	1.8579(13) <sup>[a]</sup>
<b>2c</b> ( <i>O</i> , <i>N</i> , <i>O</i> , Br)	1.694(2)	1.974(2)	1.859(3)
<b>3c</b> ( <i>N</i> , <i>N</i> , <i>O</i> , Br)	1.6853(15)	1.9717(18)	1.879(2)
$\Delta_{max}$ (subgroup)	0.014	0.013	0.021
1d (S,N,O, I)	1.6655(19) <sup>[b]</sup>	1.936(2) <sup>[b]</sup>	1.851(3) <sup>[b]</sup>
1e ( <i>S</i> , <i>N</i> , <i>O</i> , CN)	1.6979(9) <sup>[a]</sup>	1.9451(13) <sup>[a]</sup>	1.8681(12) <sup>[a]</sup>
<b>2e</b> ( <i>O</i> , <i>N</i> , <i>O</i> , CN)	1.6886(11)	1.9736(13)	1.8659(15)
<b>3e</b> ( <i>N</i> , <i>N</i> , <i>O</i> , CN)	1.6958(11)	1.9918(11)	1.8726(13)
$\Delta_{max}$ (subgroup)	0.009	0.047	0.007
$1f(S,N,O,N_3)$	1.6768(10) <sup>[a]</sup>	2.0071(12) <sup>[a]</sup>	1.8507(14) <sup>[a]</sup>
$2f(O,N,O,N_3)$	1.6999(10)	2.0094(11)	1.8644(13)
<b>3f</b> $(N,N,O, N_3)$	1.6981(10)	1.9933(12)	1.8704(14)
$\Delta_{max}$ (subgroup)	0.023	0.016	0.020
<b>1g</b> ( <i>S</i> , <i>N</i> , <i>O</i> , NCS)	1.6788(13) <sup>[a]</sup>	1.9684(13) <sup>[a]</sup>	1.8697(16) <sup>[a]</sup>
<b>2g</b> ( <i>O</i> , <i>N</i> , <i>O</i> , NCS)	1.6888(10)	1.9670(11)	1.8535(13)
<b>3g</b> ( <i>N</i> , <i>N</i> , <i>O</i> , NCS)	1.6837(11)	1.9733(12)	1.8600(15)
$\Delta_{max}$ (subgroup)	0.010	0.006	0.016
$\overline{\Delta_{\max}}$ (all compounds)	0.057	0.074	0.035

[a] Data taken from ref.<sup>[2f]</sup> [b] Data taken from ref.<sup>[3f]</sup> [c] Data taken from ref.<sup>[4]</sup>

tortion: **2h**·CH<sub>3</sub>CN, 44.5%; **3h**·2CH<sub>3</sub>CN, 20.1%), with axial N–Si–N angles of 163.12(8)° and 172.58(10)°, respectively. The Si–N(acetonitrile) bond lengths amount to 1.934(2) Å and 1.996(2) Å. The Si–O(enolato) [1.6899(16), 1.6770(19) Å], Si–O(phenolato)/Si–N(amido) [1.6761(16)/ 1.741(2) Å], and Si–C [1.858(2), 1.873(2) Å] bond lengths of **2h**·CH<sub>3</sub>CN and **3h**·2CH<sub>3</sub>CN are very similar to the analogous bond lengths of the related neutral (pseudo)halogenosilicon(IV) complexes (see Tables 2 and 3). In contrast, the Si–N(imino) bond lengths of **2h**·CH<sub>3</sub>CN [1.8969(19) Å] and **3h**·2CH<sub>3</sub>CN [1.9227(19) Å] are somewhat shortened.

#### NMR Studies

Compounds 2a, 2c, 2e–2i, 3a, and 3c–3h were characterized by multinuclear NMR spectroscopy in the solid state (except for 2h·CH<sub>3</sub>CN, 3d, and 3h) and in solution (except for 2i). The NMR spectroscopic data obtained (Table 4 and Table 5) are in accordance with the experimentally established crystal structures of these compounds.

Analysis of Table 4 reveals that the <sup>15</sup>N (imino nitrogen atom) and <sup>29</sup>Si chemical shifts of the neutral pentacoordinate silicon(IV) complexes **1a–1g**, **2a–2c**, **2e–2g**, **3a–3c**, and **3e–3g** in the solid state depend on the nature of both the tridentate ligand (*S*,*N*,*O*, *O*,*N*,*O*, *N*,*N*,*O*) and the (pseudo)halogeno ligand. The <sup>15</sup>N chemical shifts of the imino nitrogen atom are in the range  $\delta = -173.2$  to -145.4/-140.4 ppm, and the <sup>29</sup>Si chemical shifts range from  $\delta = -116.4$  to -83 ppm. The <sup>29</sup>Si chemical shifts of **1a–1g**, **2a–2c**, **2e–2g**, **3a–3c**, and **3e–3g** determined by NMR spectroscopic studies in solution (solvent, CD<sub>2</sub>Cl<sub>2</sub>; Table 5) are very similar to those obtained in the solid state (Table 4), indicating that all these neutral pentacoordinate silicon(IV) complexes also exist in solution.

The solid-state <sup>29</sup>Si NMR spectra of **2a–2c** and **3a–3c** deserve a special discussion. As can be seen from Figure 5, a <sup>29</sup>Si,<sup>19</sup>F coupling was observed for the two fluorosilicon(IV) complexes **2a** and **3a**. For the related chloro- and bromosilicon(IV) complexes **2b**, **3b**, **2c**, and **3c**, broad and structured resonance signals were observed. This phenomenon can be explained by <sup>29</sup>Si,X couplings [X = <sup>35</sup>Cl (*I* = 3/2), <sup>37</sup>Cl (*I* = 3/2); <sup>79</sup>Br (*I* = 3/2), <sup>81</sup>Br (*I* = 3/2)] and the well known effect that MAS fails to completely eliminate the effect of dipolar coupling for spin-1/2 nuclei when coupled to quadrupole nuclei with a quadrupole frequency comparable to the Zeeman frequency of the nuclei.<sup>[5]</sup>

As already reported recently, for compounds **1a**, **1b**, and **1f** (*S*,*N*,*O* ligand) a dynamic equilibrium between the pentacoordinate species **A** and the tetracoordinate species **B** (existing as two diastereomers) in solution (solvent,  $CD_2Cl_2$ ) was detected (Scheme 4).<sup>[21]</sup> Interestingly, such kind of equilibrium could not be observed for the corresponding analogues **2a**, **2b**, and **2f** (*O*,*N*,*O* ligand) and **3a**, **3b**, and **3f** (*N*,*N*,*O*) (solvents:  $CD_2Cl_2$ ,  $CD_3CN$ ,  $C_6D_6$ ). The same holds true for the related compounds in the series **2** and **3** with other (pseudo)halogeno ligands. The special behavior

Table 4. <sup>15</sup> N (	(imino nitrogen atom)	and <sup>29</sup> Si chemical shifts of	compounds 1a-1	g, 2a-2c, 2e-2	g, 3a-3c, and 3e-3	g in the solid state

Compounds	$\delta^{15}N$ [ppm]	$\delta^{29}$ Si	Compounds	$\delta^{15}$ N	$\delta^{29}$ Si	Compounds	$\delta^{15}$ N	δ <sup>29</sup> Si
(ligands)		[ppm]	(ligands)	[ppm]	[ppm]	(ligands)	[ppm]	[ppm]
<b>1a</b> ( <i>S</i> , <i>N</i> , <i>O</i> , F)	$-151.5^{[a]}$	-89.1 <sup>[a]</sup>	<b>2a</b> ( <i>O</i> , <i>N</i> , <i>O</i> , F)	-160.4	-108.5	<b>3a</b> ( <i>N</i> , <i>N</i> , <i>O</i> , F)	-173.1	-111.5
<b>1b</b> ( <i>S</i> , <i>N</i> , <i>O</i> , Cl)	$-149.4^{[b]}$	-83 <sup>[b]</sup>	<b>2b</b> ( <i>O</i> , <i>N</i> , <i>O</i> , Cl)	-167.7 <sup>[c]</sup>	-97 <sup>[c,d]</sup>	<b>3b</b> ( <i>N</i> , <i>N</i> , <i>O</i> , Cl)	-161.5 <sup>[c]</sup>	-96 <sup>[c,d]</sup>
<b>1c</b> ( <i>S</i> , <i>N</i> , <i>O</i> , Br)	$-153.6^{[a]}$	-89 <sup>[a]</sup>	<b>2c</b> ( <i>O</i> , <i>N</i> , <i>O</i> , Br)	-171.7	-100 <sup>[d]</sup>	<b>3c</b> ( <i>N</i> , <i>N</i> , <i>O</i> , Br)	-165.4 <sup>[e]</sup>	-97 <sup>[d,e]</sup>
1d (S,N,O, I)	-163.8 <sup>[b]</sup>	-91 <sup>[b]</sup>	<b>2d</b> ( <i>O</i> , <i>N</i> , <i>O</i> , I)			<b>3d</b> ( <i>N</i> , <i>N</i> , <i>O</i> , I)		
1e ( <i>S</i> , <i>N</i> , <i>O</i> , CN)	-158.8 <sup>[a]</sup>	-100.8 <sup>[a]</sup>	<b>2e</b> ( <i>O</i> , <i>N</i> , <i>O</i> , CN)	-172.3	-113.7	<b>3e</b> ( <i>N</i> , <i>N</i> , <i>O</i> , CN)	-163.7	-107.1
<b>1f</b> ( <i>S</i> , <i>N</i> , <i>O</i> , N <sub>3</sub> )	$-145.4 \text{ or } -140.4 $ [a,f] $-157.6^{[a]}$	-87.1 <sup>[a]</sup>	<b>2f</b> ( <i>O</i> , <i>N</i> , <i>O</i> , N <sub>3</sub> )	-163.0	-106.0	<b>3f</b> ( <i>N</i> , <i>N</i> , <i>O</i> , N <sub>3</sub> )	-160.0	-101.6
<b>1g</b> ( <i>S</i> , <i>N</i> , <i>O</i> , NCS)		-98.8 <sup>[a]</sup>	<b>2g</b> ( <i>O</i> , <i>N</i> , <i>O</i> , NCS)	-173.2	-116.4	<b>3g</b> ( <i>N</i> , <i>N</i> , <i>O</i> , NCS)	-164.3	-110.4

[a] Data taken from ref.<sup>[2f]</sup> [b] Data taken from ref.<sup>[3f]</sup> [c] Data taken from ref.<sup>[4]</sup> [d] Center of an asymmetric multiplet; see Figure 5. [e] Data for  $3.0.5C_6H_6$ . [f] Resonance signals could not be unambiguously assigned.



Table 5. <sup>29</sup>Si chemical shifts of compounds 1a-1g, 2a-2c, 2e-2g, 3a-3c, and 3e-3g in solution.

Compounds (ligands)	$\delta^{29}$ Si [ppm]	Compounds (ligands)	$\delta^{29}$ Si [ppm]	Compounds (ligands)	$\delta^{29}$ Si [ppm]
1a (S,N,O, F)	-88.1 <sup>[b]</sup>	<b>2a</b> ( <i>O</i> , <i>N</i> , <i>O</i> , F)	-109.3	<b>3a</b> ( <i>N</i> , <i>N</i> , <i>O</i> , F)	-108.1
<b>1b</b> ( <i>S</i> , <i>N</i> , <i>O</i> , Cl)	-82.1 <sup>[c]</sup>	<b>2b</b> ( <i>O</i> , <i>N</i> , <i>O</i> , Cl)	–95.5 <sup>[d]</sup>	<b>3b</b> ( <i>N</i> , <i>N</i> , <i>O</i> , Cl)	-94.8 <sup>[d]</sup>
<b>1c</b> ( <i>S</i> , <i>N</i> , <i>O</i> , Br)	-86.7 <sup>[b]</sup>	<b>2c</b> ( <i>O</i> , <i>N</i> , <i>O</i> , Br)	-98.0	<b>3c</b> ( <i>N</i> , <i>N</i> , <i>O</i> , Br)	-94.1
1d (S,N,O, I)	-92.5 <sup>[c]</sup>	<b>2d</b> (O,N,O, I)		<b>3d</b> (N,N,O, I)	-81.9
1e ( <i>S</i> , <i>N</i> , <i>O</i> , CN)	–99.9 <sup>[b]</sup>	<b>2e</b> ( <i>O</i> , <i>N</i> , <i>O</i> , CN)	-110.5	<b>3e</b> ( <i>N</i> , <i>N</i> , <i>O</i> , CN)	-106.7
$1f(S,N,O, N_3)$	-87.8 <sup>[b]</sup>	<b>2f</b> $(O, N, O, N_3)$	-105.5	<b>3f</b> $(N, N, O, N_3)$	-104.7
1g ( <i>S</i> , <i>N</i> , <i>O</i> , NCS)	-98.3 <sup>[b]</sup>	2g ( <i>O</i> , <i>N</i> , <i>O</i> , NCS)	-114.2	<b>3g</b> ( <i>N</i> , <i>N</i> , <i>O</i> , NCS)	-111.2

[a] Solvent, CD<sub>2</sub>Cl<sub>2</sub>. [b] Data taken from ref.<sup>[2f]</sup> [c] Data taken from ref.<sup>[3f]</sup> [d] Data taken from ref.<sup>[4]</sup>



Figure 5. <sup>29</sup>Si VACP/MAS NMR spectra of A) **2a** (X = F; O,N,O), B) **3a** (X = F; N,N,O), C) **2b** (X = Cl; O,N,O), D) **3b** (X = Cl; N,N,O), E) **2c** (X = Br; O,N,O), and F) **3c** (X = Br; N,N,O).

of 1a, 1b, and 1f with their S,N,O ligand (compared with their corresponding analogues containing the O,N,O or N,N,O ligand) can be understood in terms of a more favored cleavage of the Si–S bond of 1a, 1b, and 1f compared

to the cleavage of the stronger Si–O (2a, 2b, 2f) and Si–N bond (3a, 3b, 3f) (in this context, see the section Computational Studies).



Scheme 4. Dynamic equilibrium of 1a, 1b, and 1f between penta-(A) and tetracoordination (B) in solution.

The <sup>29</sup>Si chemical shifts of the cationic pentacoordinate silicon(IV) complexes **2h** and **3h** were only determined in solution (solvent,  $CD_3CN$ ). When using  $CD_2Cl_2$  as the solvent, both compounds decompose. Attempts to characterize **2h**·CH<sub>3</sub>CN and **3h** by solid-state NMR spectroscopy gave unsatisfactory results (NMR spectra of very poor quality).

#### **Computational Studies**

We have conducted computational studies to understand two of the experimental observations described above using relativistic density functional theory (DFT). The first objective was to understand why the pentacoordinate silicon(IV) complex **1b** (X = S) is experimentally observed to be in equilibrium with the tetracoordinate silicon(IV) species **1b**'/ **1b**'', whereas such an equilibrium is not observed for the analogous pentacoordinate silicon(IV) complexes **2b** (X = O) and **3b** (X = NMe) (Scheme 5).



Scheme 5. Equilibrium between penta- and tetracoordination.

The second objective was to understand why the neutral pentacoordinate iodosilicon(IV) complexes 2d (X = O) and 3d (X = NMe) undergo an iodo/acetonitrile exchange, leading to the cationic pentacoordinate silicon(IV) complexes 2h and 3h, whereas the analogue 1d (X = S) does not show such a ligand exchange in acetonitrile and keeps the iodo ligand (Scheme 6).



Scheme 6. Iodo/acetonitrile ligand exchange.

All calculations were performed using the Amsterdam Density Functional (ADF) program,<sup>[6]</sup> using density functional theory at BP86/TZ2P for geometry optimization and energies.<sup>[7]</sup> Relativistic effects were taken into account using the zeroth-order regular approximation (ZORA).<sup>[8]</sup> In all cases, solvation in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) or acetonitrile (CH<sub>3</sub>CN) was simulated using the conductor-like screening model (COSMO).<sup>[9]</sup> All stationary points were verified to be minima through vibrational analysis. Gibbs free energies were computed using electronic energies augmented with the COSMO free energies of solvation plus the gas-phase internal energy and entropy corrections of the solute. The bonding mechanism was analyzed within the framework of quantitative Kohn-Sham molecular orbital (MO) theory in combination with a quantitative energy decomposition analysis (EDA). In this EDA approach, the bond energy  $\Delta E$  is first decomposed into the preparation energy  $\Delta E_{\text{prep}}$  needed to deform the constituting molecular fragments from their own equilibrium structure to the geometry they adopt in the overall complex plus the interaction energy  $\Delta E_{int}$  between these deformed fragments, i.e.,  $\Delta E = \Delta E_{\text{prep}} + \Delta E_{\text{int}}$ . The interaction energy  $\Delta E_{\text{int}}$  is furthermore decomposed into classical electrostatic attraction  $\Delta V_{\text{elstat}}$ , Pauli repulsion  $\Delta E_{\text{Pauli}}$  between occupied orbitals, and stabilizing orbital interactions  $\Delta E_{oi}$ , such as HOMO-LUMO interaction (for details, see ref.<sup>[10]</sup>). Atomic charges were computed using the Voronoi deformation density (VDD) method.<sup>[11]</sup>

The results of the COSMO-ZORA-BP86/TZ2P calculations concerning the equilibrium between penta- and tetracoordination (Scheme 5) are summarized in Tables 6 and 7 and in Figure 6. Note that the experiments concerning this issue were carried out in CH<sub>2</sub>Cl<sub>2</sub>, and our computations therefore also simulate solvation in CH<sub>2</sub>Cl<sub>2</sub> using the COSMO model. The different behavior between **1b**, on one hand, and **2b** and **3b**, on the other hand, can not be explained by thermodynamic factors (see Table 6). The formation of the respective tetracoordinate species **b**'/**b**'' is in all cases endothermic, with the diastereomers **b**' being only slightly (by up to ca. 1 kcal/mol) more stable than **b**''. In line with the experimental observation, the formation of the tetracoordinate species **1b**' (X = S) and **2b**' (X = O) is relatively favorable ( $\Delta G = 8.4$  kcal/mol, in CH<sub>2</sub>Cl<sub>2</sub>) and prohibitively unfavorable ( $\Delta G = 21.6$  kcal/mol, in CH<sub>2</sub>Cl<sub>2</sub>), respectively. However, the formation of the tetracoordinate species **3b**' (X = NMe) is associated with the same Gibbs free energy of reaction ( $\Delta G = 8.4$  kcal/mol, in CH<sub>2</sub>Cl<sub>2</sub>) as that of **1b**', whereas the latter species is experimentally observed and the former is not.

Table 6. Computed relative Gibbs free energies  $\Delta G$  [kcal/mol] for the reactions associated with Scheme 5.<sup>[a]</sup>

Medium	System	$\Delta G$			
		b	I	b′	b′′
Gas phase	1 (X = S)	0	16.7	3.0	4.0
1	2(X = O)	0	26.1	15.9	17.2
	3 (X = NMe)	0	28.4	5.9	6.2
CH <sub>2</sub> Cl <sub>2</sub>	1 (X = S)	0	15.9	8.4	8.9
2 2	2(X = O)	0	25.9	21.6	22.8
	3 (X = NMe)	0	30.7	8.4	8.4

[a] Computed at ZORA-BP86/TZ2P using COSMO to estimate solvent effects by CH<sub>2</sub>Cl<sub>2</sub>.

Table 7. Analysis of the heterolytic Si–X bonding mechanism associated with Scheme 7 [kcal/mol unless stated otherwise].<sup>[a]</sup>

Medium	Energy	1M	2M	3M
Gas phase	ε <sub>HOMO</sub> of PhX <sup>−</sup>	0.364 eV	0.612 eV	1.177 eV
_	$\Delta Q(X)$ in PhX <sup>-</sup>	–0.582 a.u.	–0.550 a.u.	–0.411 a.u.
	$\Delta Q(Si)$ in $[Si]^+$ fragment	0.430 a.u.	0.437 a.u.	0.456 a.u.
	d(Si–X)	2.30 Å	1.74 Å	1.78 Å
	$\Delta E_{\text{Pauli}}$	154.1	195.0	248.8
	$\Delta V_{\rm elstat}$	-179.4	-224.9	-263.9
	$\Delta E_{\rm oi}$	-114.3	-140.4	-179.1
	$\Delta E_{\rm int}$	-139.6	-170.3	-194.2
	$\Delta E_{\rm prep}$	35.9	47.0	73.9
	$\Delta E$	-103.7	-123.3	-120.3
	$\Delta G$	-90.6	-108.1	-102.9
CH <sub>2</sub> Cl <sub>2</sub>	$\Delta G$	-7.3	-20.6	-21.1

[a] Computed at ZORA-BP86/TZ2P using COSMO to estimate solvent effects by  $\rm CH_2Cl_2.$ 

The experimental trend, however, can be understood, if we take into account the intermediate species I potentially involved in the equilibrium shown in Scheme 5. In I, the Si–X bond of **b** has already been heterolytically broken, and the new X–C bond in **b**' (or **b**'') is not yet formed. The intermediate **1I** (X = S) is comparatively low in energy, at  $\Delta G = 15.9$  kcal/mol (in CH<sub>2</sub>Cl<sub>2</sub>), whereas it is prohibitively high for both **2I** (X = O) and **3I** (X = NMe), at 25.9 and 30.7 kcal/mol (in CH<sub>2</sub>Cl<sub>2</sub>), respectively (see Table 6).







Figure 6.  $X^-$  lone-pair orbitals (HOMO-1 and HOMO) and LUMO of the cationic silicon-containing fragment for the true intermediate **11** (X = S) (upper) and for the separate fragments of the model system **1M** (X = S) shown in Scheme 7 (below).

The fact that the formation of intermediate **1I** is relatively favorable compared to the intermediates **2I** and **3I** can be directly traced to the strength of the Si–X bond and electron-donating capacity or basicity of the X<sup>-</sup> group. Thus, for the related model system **M** shown in Scheme 7, we computed heterolytic bond free energies  $\Delta G$  in CH<sub>2</sub>Cl<sub>2</sub> of -7.3, -20.6, and -21.1 kcal/mol for the Si–S, Si–O, and Si–N bonds, respectively (see Table 7). In the gas phase, the corresponding bond free energies are much stronger (due to the absence of differential solvation of the charged fragments) but essentially the same trend emerges, that is, the Si–S bond is substantially weaker than the Si–O and Si–N bonds.



Scheme 7. Heterolytic Si–X dissociation (X = S, O, NMe) of the model system M leading to separated charged fragments.

The gas-phase bond analyses show that the trend in  $\Delta E$  essentially derives from two factors: (i) the increasing energy of the PhX<sup>-</sup> lone-pair orbitals along X = S, O, and NMe and (ii) the introduction of an extra substituent on X in the case of X = NMe. The orbital interactions are dominated by the donor-acceptor interaction between the HOMO-1 and the HOMO of PhX<sup>-</sup> (X = S, O, NMe), which has mainly X<sup>-</sup> lone-pair character, and the LUMO of the cationic silicon-containing fragment, which has a large 3*p*-derived amplitude on the silicon atom. In Figure 6,

the corresponding orbitals, as they emerge from our Kohn-Sham MO analyses, are depicted for both, the two separate fragments of the model system 1M(X = S) used in the bond analyses (Table 7) as well as the true intermediate 1I (X = S). The corresponding orbitals for 2M and 2I (X = O) as well as for 3M and 3I (X = NMe) (not depicted) are similar in character. Importantly, however, the aforementioned rank order of the lone-pair orbital energies is S<O<NMe (see  $\varepsilon_{HOMO}$  in Table 7). Consequently, the HOMO-LUMO gap diminishes, which leads to an increasingly stabilizing orbital interaction  $\Delta E_{oi}$  and thus interaction energy  $\Delta E_{int}$ along the series (see Table 7). Interestingly, this trend in interaction is also directly related to the basicity (proton affinity), alkyl cation affinity, and nucleophilicity of RX- reagents.<sup>[12]</sup> The electrostatic attraction  $\Delta V_{elstat}$  also becomes more stabilizing along X = S, O, and NMe (see Table 7). This is not the result of an increase in the partial negative charge on X, which is relatively constant and in fact even slightly decreases. The trend in  $\Delta V_{\text{elstat}}$  follows from the substantial shortening of the Si–X bond from X = S to X = Oand the increasing steric contact between the fragments from X = O to X = NMe (vide infra). The overall bond energy  $\Delta E$  follows the trend of the increasingly stabilizing interaction energy  $\Delta E_{int}$  from X = S to X = O but not from X = O to X = NMe. Here, we see the effect of introducing a methyl substituent at X. The concomitant increase in steric repulsion shows up not only in a higher Pauli repulsion  $\Delta E_{\text{Pauli}}$  (and a more stabilizing electrostatic attraction) but, in particular, in a substantially more destabilizing  $\Delta E_{\text{prep}}$ (see Table 7). The latter effect is simply the result of a partial alleviation of the initial Pauli repulsion in the case of X = NMe by deforming the molecular fragments as to avoid steric contact, inter alia, by bending away the methyl substituent. Note that the Si–N bond (1.74 Å) is also somewhat longer than the Si-O bond (1.78 Å; see Table 7).

The results of the COSMO-ZORA-BP86/TZ2P calculations concerning the iodo/acetonitrile ligand exchange reaction associated with Scheme 6 are summarized in Table 8. This issue turns out to be a more subtle phenomenon. As can be seen from Table 8, the intrinsic behavior of this reaction system is to have no exchange of the iodo ligand at all because this reaction goes with charge separation, which is highly unfavorable in the gas phase, with Gibbs free energies of reaction of 81.7–83.9 kcal/mol. Also, there is no pronounced trend for the respective S/O/NMe analogues, only a slight preference for the iodo/acetonitrile exchange in the case of 2d (X = O). This does not match the qualitative trend observed in the experiment in which the ligand exchange occurs for 2d (X = O) and 3d (X = NMe) but not for 1d (X = S).

Table 8. Computed relative Gibbs free energies  $\Delta G$  [kcal/mol] for the reactions associated with Scheme 6.<sup>[a]</sup>

Medium	System	$\Delta G$		
		d	h	
Gas phase	1 (X = S)	0	83.3	
	2(X = O)	0	81.7	
	3 (X = NMe)	0	83.9	
CH <sub>3</sub> CN	1 (X = S)	0	6.5	
5	2(X = O)	0	4.1	
	3 (X = NMe)	0	3.7	

[a] Computed at ZORA-BP86/TZ2P using COSMO to estimate solvent effects by CH<sub>3</sub>CN.

As can be seen from Table 8, solvation in acetonitrile strongly stabilizes the situation of charge separation, that is, after the iodo ligand has been exchanged for an acetonitrile ligand. As a result, ligand exchange in acetonitrile as the solvent is only slightly endothermic, with reaction Gibbs free energies of 3.7-6.5 kcal/mol (Table 8). Absolute energy differences are thus not much larger than in the gas phase but on a relative scale they differ now significantly. Importantly, the qualitative trend after the incorporation of the large solvent effects is now in the right order, namely: exchange should occur more readily for 2 (X = O) and 3 (X = NMe) than for 1 (X = S), in accordance with the experiment.

### Conclusions

With the synthesis of compounds 2a, 2c, 2e–2g, 3a, 3c, and 3e–3g, a series of novel neutral pentacoordinate silicon(IV) complexes has been made available. These compounds contain an  $SiFO_2NC$ ,  $SiBrO_2NC$ ,  $SiO_2NC_2$ ,  $SiO_2N_2C$ ,  $SiFON_2C$ ,  $SiBrON_2C$ ,  $SiON_2C_2$ , or  $SiON_3C$ skeleton. The (pseudo)halogenosilicon(IV) complexes 2a, 2c, 2e–2g, 3a, 3c, and 3e–3g were synthesized from the corresponding chlorosilicon(IV) complexes 2b ( $SiCIO_2NC$ skeleton) and 3b ( $SiCION_2C$ ), respectively. All these compounds contain a tridentate dianionic O,N,O (series 2) or N,N,O ligand (series 3), a phenyl ligand, and a (pseudo)halogeno ligand (F, Cl, Br, CN, N<sub>3</sub>, NCS). They represent analogues of the already known silicon(IV) complexes 1a-1c and 1e-1g that contain a tridentate *S*,*N*,*O* ligand, with a soft sulfur ligand atom instead of a hard oxygen (series 2) or nitrogen ligand atom (series 3). The silicon(IV) complexes of series 2 and 3 are stable both in the solid state and in solution (solvent,  $CD_2Cl_2$ ).

Comparison of the respective S/O/NMe analogues of the series 1–3 revealed insight into the impact of the soft sulfur ligand atom (compared to the hard oxygen and nitrogen ligand atoms) on (i) the molecular structure in the crystal, (ii) the NMR spectroscopic parameters in the solid state and in solution, and (iii) the chemical reactivity. All compounds studied have a strongly distorted trigonal-bipyramidal structure, with the N(imino) ligand atom and the (pseudo)halogeno ligand in the two axial positions. However, the degree of distortion of the trigonal-bipyramidal silicon coordination polyhedra differs significantly and depends on the tridentate ligand, with the highest degree of distortion observed for series 2 (O,N,O ligand), followed by series 1 (S,N,O) and series 3 (N,N,O). There are only a few exceptions from this general trend. Striking differences between the respective S/O/NMe analogues were also observed in terms of chemical reactivity. While some compounds of series 1 (1a, 1b, and 1f; S,N,O ligand) isomerize upon dissolution in organic solvents (equilibrium between the pentacoordinate silicon complex and two isomeric tetracoordinate species), no such kind of isomerization could be observed for the respective analogues of series 2(O,N,O)and 3 (N,N,O). Quantum-chemical calculations show that this can be ascribed to the smaller energy demand associated with heterolytic dissociation of the relatively weak Si-S bond. The higher stability of the Si-O and Si-N bonds with respect to heterolytic dissociation could be traced to the higher energy of the O and N lone-pair orbitals, which is also responsible for the higher basicity and alkyl cation affinity of oxygen and nitrogen bases.<sup>[12]</sup> Another difference between the S/O/NMe analogues concerns the iodosilicon(IV) complexes 1d, 2d, and 3d. The pentacoordinate iodosilicon(IV) complex 1d (S,N,O ligand) could be synthesized from the corresponding chlorosilicon(IV) complex 3b as a stable crystalline product, whereas the analogous iodosilicon(IV) complex 2d (O,N,O) could not be prepared at all, and the analogue 3d(N,N,O) could only be generated at low temperature in solution and decomposed upon heating. Obviously, the soft iodo ligand is tolerated in the presence of the soft sulfur ligand atom (1d), whereas the combination of the hard oxygen (2d) or nitrogen ligand atom (3d) with the soft iodo ligand is significantly less favored. Instead of the neutral pentacoordinate iodosilicon(IV) complexes 2d and 3d, the monocationic pentacoordinate silicon(IV) complexes 2h and 3h (with an iodide counterion each) and the dicationic tetracoordinate dinuclear silicon(IV) complex 2i (with two iodide counterions) were obtained. That is, replacement of the soft sulfur ligand atom of 1d by a hard oxygen (2d) or nitrogen ligand atom (3d) leads to a dramatic decrease in stability. This is not what one would expect if it is assumed that hard ligand atoms (such as oxygen and nitrogen) should favor pentacoordination of the hard silicon(IV) coordination center (expected rank order of stability: O > N > S). Obviously, this concept is too simple to explain the experimental results obtained in this study.

### **Experimental Section**

General Procedures: All syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. Melting points were determined with a Büchi Melting Point B-540 apparatus using samples in sealed capillaries. The solution-state <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, and <sup>29</sup>Si NMR spectra were recorded at 23 °C by using a Bruker DRX-300 (1H, 300.1 MHz; 13C, 75.5 MHz; 19F, 282.4 MHz; 29Si, 59.6 MHz) or a Bruker Avance 500 NMR spectrometer (1H, 500.1 MHz; <sup>13</sup>C, 125.8 MHz; <sup>29</sup>Si, 99.4 MHz). CD<sub>2</sub>Cl<sub>2</sub> or CD<sub>3</sub>CN served as the solvent. Chemical shifts (ppm) were determined relative to internal CHDCl<sub>2</sub> (<sup>1</sup>H,  $\delta = 5.32$  ppm; CD<sub>2</sub>Cl<sub>2</sub>), CHD<sub>2</sub>CN (<sup>1</sup>H,  $\delta$  = 1.93 ppm; CD<sub>3</sub>CN), CD<sub>2</sub>Cl<sub>2</sub> (<sup>13</sup>C,  $\delta$  = 53.8 ppm; CD<sub>2</sub>Cl<sub>2</sub>), CD<sub>3</sub>CN (<sup>13</sup>C,  $\delta$  = 1.3 ppm; CD<sub>3</sub>CN), or external TMS (<sup>29</sup>Si,  $\delta$  = 0 ppm; CD<sub>2</sub>Cl<sub>2</sub>, CD<sub>3</sub>CN). Assignment of the <sup>13</sup>C NMR spectroscopic data was supported by DEPT 135 experiments and <sup>13</sup>C,<sup>1</sup>H correlation experiments. Solid-state <sup>13</sup>C, <sup>15</sup>N, and <sup>29</sup>Si VACP/MAS NMR spectra were recorded at 22 °C by using a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO<sub>2</sub> (diameter, 7 mm) containing ca. 300 mg of sample (13C, 100.6 MHz; 15N, 40.6 MHz; <sup>29</sup>Si, 79.5 MHz; external standard, TMS (<sup>13</sup>C, <sup>29</sup>Si;  $\delta$  = 0 ppm) or glycine (<sup>15</sup>N,  $\delta = -342.0$  ppm); spinning rate, 5–7 kHz; contact time, 1 ms (<sup>13</sup>C), 3 ms (<sup>15</sup>N), or 5 ms (<sup>29</sup>Si); 90° <sup>1</sup>H transmitter pulse length,  $3.6 \,\mu s$ ; repetition time,  $4 \,s$ ).

Synthesis of 2a: Freshly sublimed ammonium fluoride (119 mg, 3.18 mmol) was added in a single portion at 20 °C to a stirred solution of 2b (1.00 g, 3.03 mmol) in tetrahydrofuran (20 mL), and the reaction mixture was then stirred at 20 °C for 48 h. The resulting solid was filtered off, washed with tetrahydrofuran (5 mL), and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, toluene (8 mL) was added to the residue, and the resulting suspension was heated until a clear solution was obtained. This solution was allowed to cool to 20 °C and was then kept undisturbed at this temperature for 4 h and at -20 °C for a further 16 h. The resulting precipitate was isolated by filtration, washed with n-pentane (8 mL), and dried in vacuo (0.01 mbar, 20 °C, 4 h) to give 2a in 57% yield (538 mg, 1.72 mmol) as a yellow solid; m.p. >160 °C (decomp.). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500.1 MHz):  $\delta$ = 2.18 [d,  ${}^{4}J({}^{1}H, {}^{1}H)$  = 0.5 Hz, 3 H, CCH<sub>3</sub>], 2.52 (s, 3 H, CCH<sub>3</sub>), 5.66-5.69 (m, 1 H, CCHC), 6.92-6.97, 7.10-7.13, 7.19-7.24, 7.27-7.32, 7.35–7.40, and 7.44–7.48 ppm (m, 9 H,  $C_6H_5$ ,  $C_6H_4$ ). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.8 MHz):  $\delta$  = 24.3 (CCH<sub>3</sub>), 24.9 (CCH<sub>3</sub>), 106.2 [d,  ${}^{4}J({}^{13}C, {}^{19}F) = 0.5$  Hz, CCHC], 115.8 [d,  $J({}^{13}C, {}^{19}F) = 0.8$  Hz], 120.5, 120.7, 127.9 (2 C) [d,  ${}^{4}J({}^{13}C, {}^{19}F) = 0.7$  Hz], 128.8, 130.1 [d,  $J({}^{13}C, {}^{19}F) = 0.6 \text{ Hz}], 132.7, 134.5 (2 \text{ C}) [d, {}^{3}J({}^{13}C, {}^{19}F) = 3.5 \text{ Hz}],$ 135.5 [d,  ${}^{2}J({}^{13}C, {}^{19}F) = 32.5$  Hz], and 151.8 [d,  $J({}^{13}C, {}^{19}F) = 7.7$  Hz] (C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>), 168.9 (NCCH<sub>3</sub> or OCCH<sub>3</sub>), 172.3 ppm [d, J(<sup>13</sup>C, <sup>19</sup>F) = 7.9 Hz, NCCH<sub>3</sub> or OCCH<sub>3</sub>]. <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 282.4 MHz):  $\delta$ = -118.1 ppm. <sup>29</sup>Si NMR (CD<sub>2</sub>Cl<sub>2</sub>, 99.4 MHz):  $\delta$  = -109.3 ppm [d,  ${}^{1}J({}^{29}\text{Si}, {}^{19}\text{F}) = 204.8 \text{ Hz}]. {}^{13}\text{C} \text{ VACP/MAS NMR}: \delta = 23.8 (CCH_3),$ 24.6 (CCH<sub>3</sub>), 106.9 (CCHC), 116.6, 119.0 (2 C), 121.0, 128.7 (2 C), 129.8, 131.5 (3 C), 136.6, and 151.4 (C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>), 166.8 (NCCH<sub>3</sub> or OCCH<sub>3</sub>), 167.8 ppm (NCCH<sub>3</sub> or OCCH<sub>3</sub>). <sup>15</sup>N VACP/MAS NMR:  $\delta = -160.4$  ppm. <sup>29</sup>Si VACP/MAS NMR:  $\delta = -108.5$  ppm  $[d, {}^{1}J({}^{29}Si, {}^{19}F) = 206 \text{ Hz}]. C_{17}H_{16}FNO_{2}Si (313.40): calcd. C 65.15,$ H 5.15, N 4.47; found C 64.8, H 5.4, N 4.5.

Synthesis of 2b: Compound 2b was synthesized according to ref.<sup>[4]</sup>



Synthesis of 2c: Bromotrimethylsilane (306 mg, 2.00 mmol) was added in a single portion at 20 °C to a stirred suspension of 2b (547 mg, 1.66 mmol) in acetonitrile (10 mL). The reaction mixture was heated to 95 °C and then concentrated to a volume of ca. 6 mL by distillation at ambient pressure. The remaining solution was slowly cooled to 20 °C (formation of crystals) and then kept undisturbed at this temperature for 1 h and at -20 °C for a further 3 h. The resulting precipitate was isolated by filtration, washed with diethyl ether (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 5 h) to give 2c in 61% yield (383 mg, 1.02 mmol) as a yellow crystalline solid; m.p. >120 °C (decomp.). For analytical data, see the Supporting Information.

Synthesis of 2e: Cyanotrimethylsilane (339 mg, 3.42 mmol) was added in a single portion at 20 °C to a stirred suspension of 2b (950 mg, 2.88 mmol) in acetonitrile (20 mL), and the reaction mixture was then stirred at 20 °C for 1.5 h. The volatile components of the reaction mixture were removed in vacuo, acetonitrile (8 mL) was added to the residue, and the resulting suspension was heated until a clear solution was obtained. This solution was allowed to cool to 20 °C and then kept undisturbed at this temperature for 1 h and at -20 °C for a further 16 h. The resulting precipitate was isolated by filtration, washed with diethyl ether (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 3 h) to give **2e** in 64% yield (593 mg, 1.85 mmol) as a red to orange-colored crystalline solid; m.p. >155 °C (decomp.). For analytical data, see the Supporting Information.

Synthesis of 2f: Azidotrimethylsilane (324 mg, 2.81 mmol) was added in a single portion at 20 °C to a stirred suspension of 2b (773 mg, 2.34 mmol) in acetonitrile (10 mL). The reaction mixture was heated to 90 °C and then concentrated to a volume of ca. 7 mL by distillation at ambient pressure. The remaining solution was slowly cooled to 20 °C and then kept undisturbed at this temperature for 24 h and at -20 °C for a further 3 h. The resulting precipitate was isolated by filtration, washed with diethyl ether (15 mL), and dried in vacuo (0.01 mbar, 20 °C, 3 h) to give 2f in 79% yield (623 mg, 1.85 mmol) as a yellow crystalline solid; m.p. >120 °C (decomp.). For analytical data, see the Supporting Information.

Synthesis of 2g: (Thiocyanato-*N*)trimethylsilane (560 mg, 4.27 mmol) was added in a single portion at 20 °C to a stirred suspension of **2b** (1.41 g, 4.27 mmol) in acetonitrile (20 mL), and the reaction mixture was then stirred at 20 °C for 2 h. The volatile components of the reaction mixture were removed in vacuo, acetonitrile (18 mL) was added to the residue, and the resulting suspension was heated until a clear solution was obtained. This solution was allowed to cool to 20 °C for a further 16 h. The resulting precipitate was isolated by filtration, washed with *n*-pentane (20 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **2g** in 88% yield (1.32 g, 3.74 mmol) as a yellow crystalline solid; m.p. >216 °C (decomp.). For analytical data, see the Supporting Information.

Synthesis of 2h·CH<sub>3</sub>CN: Iodotrimethylsilane (350 mg, 1.75 mmol) was added in a single portion at 20 °C to a stirred suspension of 2b (503 mg, 1.52 mmol) in acetonitrile (5 mL), and the resulting mixture was stirred at 20 °C for 1 h. The volatile components of the reaction mixture were removed in vacuo, acetonitrile (4 mL) was added to the residue, and the resulting suspension was heated until a clear solution was obtained. This solution was allowed to cool to 20 °C and then kept undisturbed at this temperature for 1 h and at 4 °C for a further 24 h. The resulting precipitate was isolated by filtration, washed with *n*-pentane (6 mL), and dried in vacuo (0.01 mbar, 20 °C, 3 h) to give 2h·CH<sub>3</sub>CN in 44% yield (339 mg, 673 µmol) as a yellow crystalline solid; m.p. >85 °C (decomp.). <sup>1</sup>H

NMR (CD<sub>3</sub>CN, 500.1 MHz):<sup>[13]</sup>  $\delta$  = 1.95 (s, 6 H, N=CCH<sub>3</sub>), 2.32 [d, <sup>4</sup>*J*(<sup>1</sup>H, <sup>1</sup>H) = 0.5 Hz, 3 H, CCH<sub>3</sub>], 2.59 (s, 3 H, CCH<sub>3</sub>), 6.14 [q, <sup>4</sup>*J*(<sup>1</sup>H, <sup>1</sup>H) = 0.5 Hz, 1 H, CCHC], 7.09–7.16, 7.19–7.24, 7.30–7.48, and 7.62–7.67 ppm (m, 9 H, C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 125.8 MHz):<sup>[13]</sup>  $\delta$  = 1.75 (2 C) (N=CCH<sub>3</sub>), 23.9 (CCH<sub>3</sub>), 25.1 (CCH<sub>3</sub>), 109.0 (CCHC), 132.0 (2 C) (br., N=CCH<sub>3</sub>), 116.3, 122.3, 123.4, 129.2 (2 C), 130.8, 132.0, 132.3, 132.5, 133.5 (2 C), and 149.7 (C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>), 172.4 (NCCH<sub>3</sub> or OCCH<sub>3</sub>), 174.3 ppm (NCCH<sub>3</sub> or OCCH<sub>3</sub>). <sup>29</sup>Si NMR (CD<sub>3</sub>CN, 99.4 MHz):<sup>[13]</sup>  $\delta$  = –103.2 ppm. C<sub>21</sub>H<sub>22</sub>IN<sub>3</sub>O<sub>2</sub>Si (503.41): calcd. C 50.10, H 4.40, N 8.35; found C 49.8, H 4.5, N 8.5.

Synthesis of 2i: Iodotrimethylsilane (374 mg, 1.87 mmol) was added in a single portion at 20 °C to a stirred suspension of 2b (515 mg, 1.56 mmol) in dichloromethane (7 mL), and the resulting mixture was stirred for 10 min and then kept undisturbed at 20 °C for 20 h excluding light. The resulting precipitate was isolated by filtration, washed with diethyl ether (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 3 h) to give 2i in 58% yield (383 mg, 455 µmol) as a yellow crystalline solid; m.p. >190 °C (decomp.). <sup>13</sup>C VACP/MAS NMR:  $\delta = 23.9$  (CCH<sub>3</sub>), 27.4 (CCH<sub>3</sub>), 112.1 (CCHC), 119.3, 121.2, 125.0, 129.5 (3 C), 132.0, 134.0 (3 C), 135.9, and 146.4 (C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>), 178.3 (NCCH<sub>3</sub> or OCCH<sub>3</sub>), 189.3 ppm (NCCH<sub>3</sub> or OCCH<sub>3</sub>). <sup>15</sup>N VACP/MAS NMR:  $\delta = -208.3$  ppm. <sup>29</sup>Si VACP/MAS NMR:  $\delta =$ -56.9 ppm. C<sub>34</sub>H<sub>32</sub>I<sub>2</sub>N<sub>2</sub>O<sub>4</sub>Si<sub>2</sub> (842.62): calcd. C 48.46, H 3.83, N 3.32; found C 48.1, H 3.8, N 3.4.

Synthesis of 3a. Method A: Freshly sublimed ammonium fluoride (95.6 mg, 2.58 mmol) was added in a single portion at 20 °C to a stirred solution of 3b (883 mg, 2.58 mmol) in tetrahydrofuran (20 mL), and the reaction mixture was then stirred at 20 °C for 20 h. The resulting solid was filtered off, washed with tetrahydrofuran (5 mL), and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, acetonitrile (9 mL) was added to the residue, and the resulting suspension was heated until a clear solution was obtained. This solution was allowed to cool to 20 °C and then kept undisturbed at this temperature for 3 h and at -20 °C for a further 24 h. The resulting precipitate was isolated by filtration, washed with diethyl ether (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 4 h) to give 3a in 49% yield (410 mg, 1.26 mmol) as a yellow solid; m.p. >143 °C (decomp.). <sup>1</sup>H NMR (500.1 MHz,  $CD_2Cl_2$ ):  $\delta = 2.16 [d, {}^{4}J({}^{1}H, {}^{1}H) = 0.6 Hz, 3 H,$ CCH<sub>3</sub>], 2.47 (s, 3 H, CCH<sub>3</sub>), 3.14 (s, 3 H, NCH<sub>3</sub>), 5.60 (m, 1 H, CCHC), 6.72-6.77, 6.82-6.86, 7.13-7.29, and 7.36-7.39 ppm (m, 9 H, C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 24.1  $(CCH_3)$ , 25.1  $(CCH_3)$ , 33.0 [d,  ${}^{3}J({}^{13}C, {}^{19}F) = 12.4$  Hz, NCH<sub>3</sub>], 106.1 [d,  ${}^{4}J({}^{13}C, {}^{19}F) = 0.8$  Hz, CCHC], 110.8 [d,  $J({}^{13}C, {}^{19}F) = 2.8$  Hz], 116.4, 120.1, 127.6 (2 C) [d,  ${}^{4}J({}^{13}C, {}^{19}F) = 0.8$  Hz], 128.4, 129.3 [d,  $J({}^{13}C, {}^{19}F) = 1.0 \text{ Hz}$ ], 131.0, 134.0 (2 C) [d,  ${}^{3}J({}^{13}C, {}^{19}F) = 3.9 \text{ Hz}$ ], 138.8 [d,  ${}^{2}J({}^{13}C, {}^{19}F) = 36.1$  Hz], and 146.1 [d,  $J({}^{13}C, {}^{19}F) = 3.6$  Hz] (C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>), 166.8 (NCCH<sub>3</sub> or OCCH<sub>3</sub>), 170.2 ppm [d, J(<sup>13</sup>C, <sup>19</sup>F) = 7.8 Hz, NCCH<sub>3</sub> or OCCH<sub>3</sub>]. <sup>19</sup>F NMR (282.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ = -112.4 ppm. <sup>29</sup>Si NMR (99.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = -108.1 ppm [d,  ${}^{1}J({}^{29}\text{Si}, {}^{19}\text{F}) = 222 \text{ Hz}]. {}^{13}\text{C} \text{ VACP/MAS NMR}: \delta = 24.9 (CCH_3),$ 26.3 (CCH<sub>3</sub>), 33.1 (NCH<sub>3</sub>), 107.9 (CCHC), 109.6, 116.1, 118.9, 127.2 (3 C), 129.7, 131.7, 133.5, 136.0, 141.4, and 145.4 (C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>), 169.2 (NCCH<sub>3</sub> or OCCH<sub>3</sub>), 170.2 ppm (NCCH<sub>3</sub> or OCCH<sub>3</sub>). <sup>15</sup>N VACP/MAS NMR:  $\delta$  = -306.2 (NCH<sub>3</sub>), -173.1 ppm (NCCH<sub>3</sub>). <sup>29</sup>Si VACP/MAS NMR:  $\delta = -111.5$  ppm [d, <sup>1</sup>J(<sup>29</sup>Si, <sup>19</sup>F) = 227 Hz].  $C_{18}H_{19}FN_2OSi$  (326.45): calcd. C 66.23, H 5.87, N 8.58; found C 65.73, H 5.85, N 8.76.

**Methode B:** Silver tetrafluoroborate (895 mg, 4.60 mmol) was added in a single portion at 20 °C with exclusion of light to a stirred solution of **3b** (1.58 g, 4.61 mmol) in tetrahydrofuran

(30 mL) and triethylamine (465 mg, 4.60 mmol), and the reaction mixture was then stirred at 20 °C for 1 h. The resulting solid was filtered off, washed with tetrahydrofuran (5 mL), and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, acetonitrile (11 mL) was added to the residue, and the resulting suspension was heated until a clear solution was obtained. This solution was allowed to cool to 20 °C and was then kept undisturbed at this temperature for 2 h and at -20 °C for a further 19 h. The resulting precipitate was isolated by filtration, washed with diethyl ether (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 5 h) to give **3a** in 61% yield (918 mg, 2.81 mmol) as a yellow crystalline solid. The analytical data of the product match with those obtained for the product synthesized according to method A.

Synthesis of 3b: Compound 3b was synthesized according to ref.<sup>[4]</sup>

Synthesis of 3c.0.5C<sub>6</sub>H<sub>6</sub>: Bromotrimethylsilane (1.69 g, 11.0 mmol) was added in a single portion at 20 °C to a stirred suspension of 3b (3.16 g, 9.22 mmol) in benzene (30 mL). The reaction mixture was slowly heated from 20 °C to 85 °C within 5 h and then concentrated to a volume of ca. 30 mL by distillation at ambient pressure. The remaining solution was cooled to 20 °C, and bromotrimethylsilane (1.69 g, 11.0 mmol) was added again in a single portion. The reaction mixture was heated slowly from 20 °C to 85 °C within 5 h, and the volatile components were removed by distillation at ambient pressure. Subsequently, benzene (20 mL) was added to the residue, and the resulting suspension was heated until a clear solution was obtained. This solution was allowed to cool to 20 °C and then kept undisturbed at this temperature for 24 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  $3c \cdot 0.5C_6H_6$  in 84% yield (3.00 g, 7.74 mmol) as an orange-colored crystalline solid; m.p. >170 °C (decomp.). For analytical data, see the Supporting Information.

**Synthesis of 3d:** In an NMR tube, iodotrimethylsilane (58 mg, 290 μmol) was added in a single portion at -80 °C to a solution of **3b** (33 mg, 96 μmol) in [D<sub>2</sub>]dichloromethane (750 μL), and the resulting mixture was studied immediately by NMR spectroscopy. <sup>1</sup>H NMR (500.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -80 °C):  $\delta = 2.47$  (s, 3 H, CCH<sub>3</sub>), 2.65 (s, 3 H, CCH<sub>3</sub>), 3.24 (s, 3 H, NCH<sub>3</sub>), 6.43 (s, 1 H, CCHC), 6.92–6.98, 7.02–7.07, 7.25–7.29, 7.30–7.36, 7.37–7.42, and 7.44–7.50 (m, 9 H, C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 23.8$  (CCH<sub>3</sub>), 25.0 (CCH<sub>3</sub>), 32.7 (NCH<sub>3</sub>), 108.3 (CCHC), 111.2, 118.6, 120.3, 128.1 (2 C), 128.5, 129.4, 130.5, 131.6, 132.4 (2 C), and 142.3 (C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>), 169.9 (NCCH<sub>3</sub> or OCCH<sub>3</sub>), 171.4 ppm (NCCH<sub>3</sub> or OCCH<sub>3</sub>). <sup>29</sup>Si NMR (99.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -81.9$  ppm.

Synthesis of 3e: Cyanotrimethylsilane (210 mg, 2.12 mmol) was added in a single portion at 20 °C to a stirred suspension of 3b (662 mg, 1.93 mmol) in acetonitrile (15 mL), and the reaction mixture was then stirred at 20 °C for 24 h. The volatile components of the reaction mixture were removed in vacuo, acetonitrile (3 mL) was added to the residue, and the resulting suspension was heated until a clear solution was obtained. This solution was allowed to cool to 20 °C and then kept undisturbed at this temperature for 3 h and at -20 °C for a further 24 h. The resulting precipitate was isolated by filtration, washed with *n*-pentane (5 mL), and dried in vacuo (0.01 mbar, 20 °C, 4 h) to give 3e in 81% yield (521 mg, 1.56 mmol) as an orange-colored crystalline solid; m.p. >137 °C (decomp.). For analytical data, see the Supporting Information.

**Synthesis of 3f:** Azidotrimethylsilane (117 mg, 1.02 mmol) was added in a single portion at 20 °C to a stirred suspension of **3b** (348 mg, 1.01 mmol) in acetonitrile (10 mL), and the reaction mixture was then stirred at 20 °C for 2 h. The volatile components of

the reaction mixture were removed in vacuo, acetonitrile (10 mL) was added to the residue, and the resulting suspension was heated until a clear solution was obtained. This solution was allowed to cool to 20 °C and then kept undisturbed at this temperature for 2 h and at -20 °C for a further 24 h. The resulting precipitate was isolated by filtration, washed with *n*-pentane (8 mL), and dried in vacuo (0.01 mbar, 20 °C, 5 h) to give **3f** in 88% yield (310 mg, 887 µmol) as an orange-colored crystalline solid; m.p. >172 °C (decomp.). For analytical data, see the Supporting Information.

(Thiocyanato-N)trimethylsilane **Synthesis** of 3g: (567 mg, 4.32 mmol) was added in a single portion at 20 °C to a stirred suspension of **3b** (1.48 g, 4.32 mmol) in acetonitrile (30 mL), and the reaction mixture was then stirred at 20 °C for 16 h. The volatile components of the reaction mixture were removed in vacuo, acetonitrile (12 mL) was added to the residue, and the resulting suspension was heated until a clear solution was obtained. This solution was allowed to cool to 20 °C and then kept undisturbed at this temperature for 24 h and at -20 °C for a further 16 h. The resulting precipitate was isolated by filtration, washed with diethyl ether (9 mL), and dried in vacuo (0.01 mbar, 20 °C, 4 h) to give 3g in 70% yield (1.10 g, 3.01 mmol) as a yellow crystalline solid; m.p. >165 °C (decomp.). For analytical data, see the Supporting Information

Synthesis of 3h: Iodotrimethylsilane (1.47 g, 7.35 mmol) was added in a single portion at 20 °C to a stirred suspension of 3b (2.51 g, 7.32 mmol) in acetonitrile (50 mL), and the resulting mixture was stirred at 20 °C for 1 h and then kept undisturbed at -20 °C for 24 h. The resulting precipitate was isolated by filtration, washed with *n*-pentane (20 mL), and dried in vacuo (0.01 mbar, 20 °C, 6 h) to give **3h** in 64% yield (2.24 g, 4.71 mmol) as an orange-colored solid; m.p. >107 °C (decomp.). <sup>1</sup>H NMR (500.1 MHz, CD<sub>3</sub>CN):<sup>[13]</sup>  $\delta = 1.95$  (s, 3 H, N=CCH<sub>3</sub>), 2.34 [d, <sup>4</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 0.6 Hz, 3 H, CCH<sub>3</sub>], 2.50 (s, 3 H, CCH<sub>3</sub>), 2.28 (s, 3 H, NCH<sub>3</sub>), 6.06 [d, <sup>4</sup>*J*(<sup>1</sup>H, <sup>1</sup>H) = 0.6 Hz, 1 H, CCHC], 6.88-6.92, 7.07-7.11, 7.25-7.29, 7.34-7.38, and 7.46–7.49 ppm (m, 9 H,  $C_6H_5$ ,  $C_6H_4$ ). <sup>13</sup>C NMR (125.8 MHz,  $CD_3CN$ :<sup>[13]</sup>  $\delta = 1.79$  (N=CCH<sub>3</sub>), 23.8 (CCH<sub>3</sub>), 24.9 (CCH<sub>3</sub>), 33.8  $(NCH_3)$ , 108.5 (CCHC), 118.2  $(N \equiv CCH_3)$ , 113.1, 119.7, 121.7, 129.0 (2 C), 130.0, 130.4, 131.5, 132.6 (2 C), 135.2, and 144.0 (C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>), 171.0 (NCCH<sub>3</sub> or OCCH<sub>3</sub>), 171.9 ppm (NCCH<sub>3</sub> or OCCH<sub>3</sub>). <sup>29</sup>Si NMR (99.4 MHz, CD<sub>3</sub>CN):<sup>[13]</sup>  $\delta$  = -96.4 ppm. C<sub>20</sub>H<sub>22</sub>IN<sub>3</sub>OSi (475.40): calcd. C 50.53, H 4.66, N 8.84; found C 50.9, H 4.8, N 9.0.

Crystal Structure Analyses: Suitable single crystals of compounds 2a, 2c, 2e-2g, 2h·CH<sub>3</sub>CN, 2i, 3a, 3c·0.5C<sub>6</sub>H<sub>6</sub>, 3e-3g, and 3h·2CH<sub>3</sub>CN were isolated directly from the respective reaction mixtures. The crystals were mounted in inert oil (perfluoropolyalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (3a and 3g: Bruker Nonius KAPPA APEX II diffractometer, Montel mirror, Mo-Ka radiation,  $\lambda = 0.71073$  Å; **2a**, **2c**, **2e–2g**, **2h**·CH<sub>3</sub>CN, **2i**, **3c**·0.5C<sub>6</sub>H<sub>6</sub>, **3e**– 3f, and 3h·2CH<sub>3</sub>CN: Stoe IPDS diffractometer, graphite-monochromated Mo- $K_{\alpha}$  radiation,  $\lambda = 0.71073$  Å). All structures were solved by direct methods.<sup>[14]</sup> For compound 2h·CH<sub>3</sub>CN the PLA-TON routine "SQUEEZE" was used to account for regions of disordered solvent in the structure.<sup>[15]</sup> In all the structures, the nonhydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the CH hydrogen atoms.<sup>[14]</sup> According to the X-ray data, the cyano ligand in 2e is disordered (in this context, see also ref.<sup>[16]</sup>). Best refinement results are obtained when 70% of the coordinating atom is nitrogen and 30% is carbon  $(R_1 = 0.039)$ . Although the <sup>15</sup>N NMR spectroscopic data do not indicate any N coordination (Si-NC), the refinement with 100% C coordination (Si–CN) results in a higher residual of  $R_1 = 0.045$ .



CCDC-873533 (for 2a), -873534 (for 2c), -874092 (for 2e), -873535 (for 2f), -873536 (for 2g), -873537 (for 2h·CH<sub>3</sub>CN), -873538 (for 2i), -873539 (for 3a), -873540 (for 3c· $0.5C_6H_6$ ), -873541 (for 3e), -873542 (for 3f), -873543 (for 3g), and -873544 (for 3h·2CH<sub>3</sub>CN) 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.

Supporting Information (see footnote on the first page of this article): Crystallographic data for compounds 2a, 2c, 2e–2g, 2h·CH<sub>3</sub>CN, 2i, 3a, 3c· $0.5C_6H_6$ , 3e–3g, and 3h·2CH<sub>3</sub>CN. Molecular structures of 2a, 2e–2g, 2i (cation), and 3c· $0.5C_6H_6$ , 3e–3g. NMR spectroscopic data and elemental analyses for compounds 2c, 2e–2g, 3c· $0.5C_6H_6$ , and 3e–3g. Cartesian coordinates and total energies for 1b, 2b, 3b, 1b', 1b'', 2b', 2b'', 3b', 3b'', 1d, 1h, 2d, 2h, 3d, and 3h.

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