Donor-stabilized silyl cations
Part 7: Neutral hexacoordinate and ionic pentacoordinate silicon chelates with *N*-isopropylideneimino-acylimidato ligands[☆]

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Abstract

Silicon complexes with a new chelating donor group, the isopropylideneimino-acylimidato(*N,O*) moiety [OC(R)=NN=CMe$_2$], have been prepared (**9–12**, **15**), and their properties are compared with previously described silicon chelates (**1**, **2**, and **16**, respectively). The new ligand acts as a more powerful donor than the NNMe$_2$ ligand, based on three criteria: (a) the new complexes form directly as pentacoordinate siliconium salts **9–12**, i.e., the expected neutral hexacoordinate precursors ionize spontaneously; (b) comparison of crystallographic bond lengths with those of the NNMe$_2$ complexes shows consistently shorter N–Si coordination bonds and longer Si–halogen bonds in equally substituted new relative to the previously studied complexes; (c) while in the previous series **1**, the dihalo complexes **20–22**, **25**, resisted ionization at any temperature or solvent, the dibromo-isopropylideneimino complexes **19a** and **19b** ionize reversibly upon decrease of temperature in chloroform solution. Steric congestion forces the *trans*-dihalo configuration on the dichloro and bibromo complexes **18**, **19**. The ionization-resistant complexes **17**, **18** and the partly ionized **19** form stable ionic siliconium salts when their counterions are replaced by I$^-$, BPh$_4^-$, or by reaction with strong Lewis acids, AlCl$_3$ and AlBr$_3$.
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1. Introduction

The chemistry of hypercoordinate silicon complexes has been of considerable interest for some time [1]. Within the chemistry of silicon complexes, free and donor-stabilized silyl cations have been of particular recent interest [2,3]. We have reported on the formation of N→Si pentacoordinate siliconium salts as a result of ionization of neutral hexacoordinate precursors (Eq. (1)) [4]. The state of equilibrium (or relative stabilities of the ionic vs. the neutral species) was found to depend dramatically upon variations of the solvent, remote substituent R, ligand X, counterion, temperature, and steric bulk. It was of great interest to complete this study by investigating the effect of the donor strength upon the relative stabilities.

X = Me, Ph, PhCH$_2$
R = Me, Ph, PhCH$_2$, t-Bu
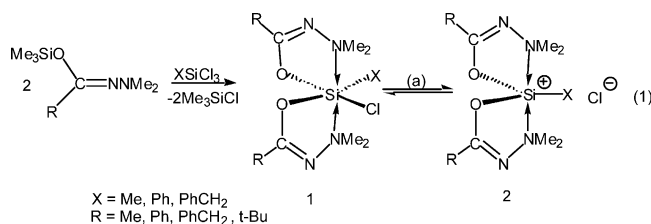
(a) At low temperature in CDCl$_3$, CD$_2$Cl$_2$ or CHCl$_2$F solution

$$\tag{1}$$

Table 1
^{1}H-, ^{13}C- and ^{29}Si-NMR spectral data for siliconium chlorides **9–12** and the siliconium triflate **13a** (CDCl$_3$ solution at 300 K)

Compound	$\delta(^{29}$Si) (ppm)	$\delta(^1$H) (ppm)			$\delta(^{13}$C) (ppm)	
		CMe	SiMe	CH$_2$ [a]	CMe	C=N
9a	−81.0	2.74; 2.80	1.08		23.8; 25.1	162.0; 181.9
13a	−81.1	2.74; 2.76	1.03		23.7; 24.8	162.4; 182.0
9b	−82.0	2.04; 2.40	0.61	3.57; 3.65 (15.2)	23.6; 24.2	166.5; 182.2
10a	−93.7	2.00; 2.53			23.7; 24.5	162.3; 183.5
10b	−94.3	1.59; 2.51		3.82; 3.88 (15.1)	24.0; 24.2	167.6; 184.2
11a	−80.2	2.93; 3.06			23.2; 25.3	160.9; 182.5
12a	−80.4	2.76; 2.82			24.4; 25.4	161.2; 182.0

[a] AB quartet: δ_A; δ_B ($^2J_{AB}$, Hz).

Pentacoordinate siliconium salts based on O→Si coordination (**3**) have previously been reported, providing the first indication that the donor strength plays a major role in favoring ionic pentacoordinate over neutral hexacoordinate species [5]. The stronger the ligand donor group, the more ionization to the donor-stabilized siliconium salt. In fact, in the O→Si coordinated bis-chelate series **3** only ionic species could be observed, without a detectable trace of hexacoordination. In a recent note, the introduction of a new chelating ligand based on *N*-isopropylidene hydrazides was described [6]. In the present study, we have prepared several new silicon chelates (**9–12**) based on the isopropylideneimino donor group (−N=CMe$_2$) and have studied their donor properties in comparison with the former chelates (**1 ⇌ 2** and **3**). In particular, we were interested in comparing the donor strengths of the two nitrogen-ligand systems (NMe$_2$ and N=CMe$_2$), and their effects on siliconium ion formation and stability. Three criteria for donor strength have been studied: the N–Si bond length, the ^{29}Si chemical shifts, and the ease of ionization.

nate bischelates (**9–12**, respectively, Eq. (2)) and the volatile Me$_3$SiCl byproduct.

4a, R = Ph
4b, R = PhCH$_2$

5, X = Me
6, X = Ph
7, X = C$_6$H$_{11}$
8, X = i-Bu

9a, R = Ph, X = Me
9b, R = PhCH$_2$, X = Me
10a, R = Ph, X = Ph
10b, R = PhCH$_2$, X = Ph
11a, R = Ph, X = C$_6$H$_{11}$
12a, R = Ph, X = i-Bu

$$(2)$$

The evidence for formation of **9–12** is found in the ^{29}Si-NMR chemical shifts, which are characteristic of pentacoordination (Table 1), and confirmed by a single crystal X-ray analysis obtained for **13a**, the triflate derivative of **9a** (Fig. 1). The solution ^{29}Si-NMR chemical shift of the triflate **13a** is exactly equal to that of the analogous chloride **9a**, confirming that the
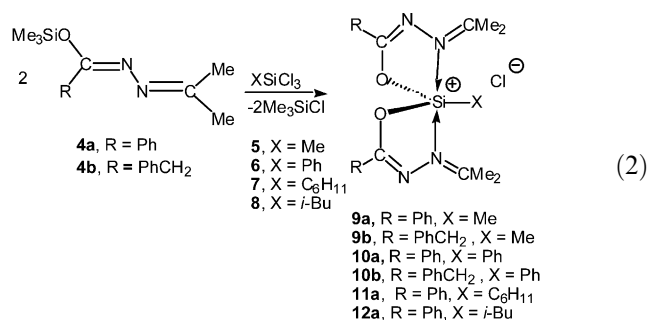

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2. Results and discussion

2.1. Complexes with one halogen ligand

N-Isopropylideneimino-*O*-(trimethylsilyl)acylimidates (**4**) react smoothly with trichlorosilanes (**5–8**), in a trans-silylation reaction producing ionic pentacoordi-
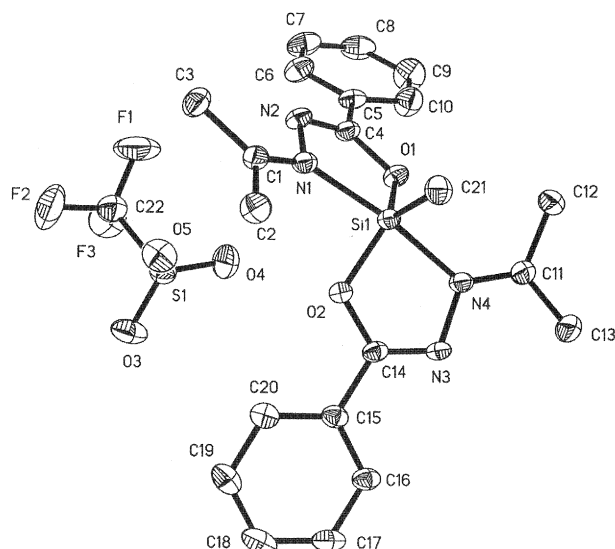

Fig. 1. Molecular structure of **13a** in the crystal.

cations of the two salts (chloride and triflate) are identical. Characterization of the other compounds of this series (9–12) was done by ^{1}H-, ^{13}C- and ^{29}Si-NMR spectral analogy (Table 1).

The exclusive formation of the ionic pentacoordinate salts 9–10 at room temperature was rather unexpected, in view of the previously reported transsilylations of dimethylamino analogs (Eq. (1)) which, at room temperature, led only to neutral hexacoordinate bischelates 1 [7]. One might expect the sp[3]-hybridized dimethylamino donor group in 1 to be a stronger donor than the sp[2]-hybridized isopropylideneimino group in 9–10. In contrast, the better ability of the isopropylideneimino complexes to release an anion and form stable siliconium ion salts was taken as evidence for the stronger donor property of this group, relative to the dimethylamino group. The isopropylideneimino complexes 9–12 are formed directly by transsilylation, in analogy to the O→Si coordinated 3. This is in contrast to the dimethylamino-coordinated 2, which are obtained by ionization of the hexacoordinate precursors 1 [4].

Additional and more direct evidence was sought in support of the idea that the isopropylideneimino is a stronger donor than the dimethylamino group in the present system. This was accomplished by comparison of the N→Si distances between complexes differing only in the donor groups: 13a with 14, and 15 with 16 (Table 2). The monochelate 15 was prepared (Eq. (3)), its crystal structure determined (Fig. 2) and compared with that of the dimethylamino analogs 16a and 16b [8] (Table 2).
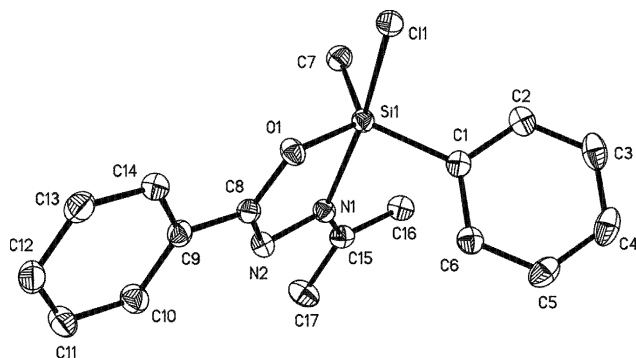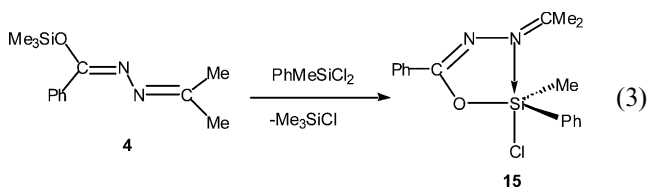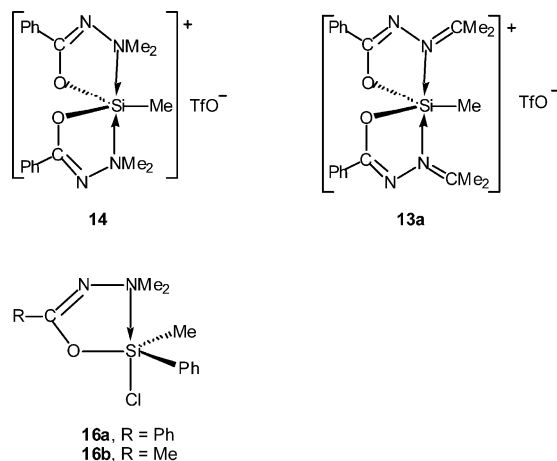

Fig. 2. Molecular structure of 15 in the crystal.

Indeed, it is striking to find (Table 2) that in 15 the N–Si distance is substantially shorter than in 16, indicating stronger coordination. The same trend is found in the comparison of 13a with 14 (Table 2), although in this case the difference in bond lengths is smaller. It must be concluded, based on the N–Si distances, that the isopropylideneimino is a stronger donor group than the dimethylamino in these complexes. This conclusion is further supported by comparison of the [29]Si chemical shifts (Table 2), which shows a substantial shift to high field in 15, relative to 16, and in 13a relative to 14, in accord with stronger coordination.

Table 2
Comparison of selected bond lengths (Å), angles (°), and ^{29}Si-NMR chemical shifts (ppm) for bis-isopropylideneimino- (13a, 15 and 26a) and mono-dimethylamino- (14, 16a and 16b) pentacoordinate silicon complexes

Parameter	13a	14	26a	15	16a	16b
Si–N	1.9337(17)	1.9665 (17)	1.912(2)	2.0824(13)	2.264(2)	2.216(2)
	1.9659(17)	1.9681 (19)	1.921(2)			
Si–O	1.6747(14)	1.6844 (15)	1.6648(16)	1.7012(11)	1.684(2)	1.703(2)
	1.6811(14)	1.6964 (14)	1.6682(17)			
Si–Cl			2.0501(9)	2.2230(5)	2.192(9)	2.216(2)
N–Si–N	166.44(7)	154.78(8)	170.13(9)			
O–Si–O	120.85(8)	136.27(8)	125.99(8)			
δ([29]Si)	−81.1	−60.9	−113.6	−52.9	−32.8	−29.0
Reference	This work	[4b]	This work	This work	[8a]	[8b]
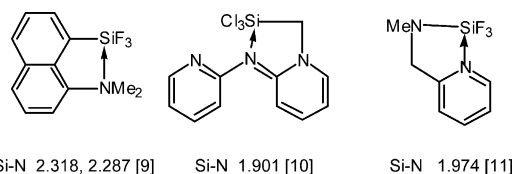
Scheme 1. Complexes with sp²- and sp³-hybridized nitrogen coordination to silicon; the sp² cases have shorter N→Si bonds.

Previous reports seem to agree with stronger coordination of sp² vs. sp³ hybridized nitrogen donors to silicon (Scheme 1) [9–11].

2.2. Complexes with two halo ligands

$$\text{(4)}$$
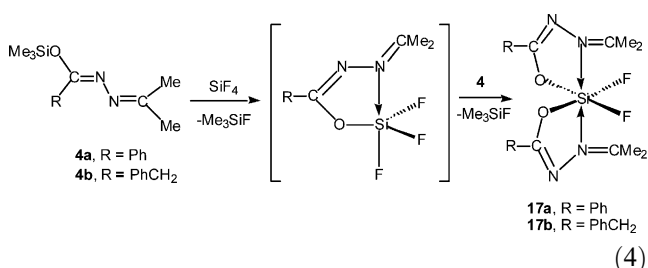
Transsilylation of **4a** and **4b** with tetrahalosilanes led to direct replacement of two halogens and formation of the dihalo-complexes **17a**, **19a** and **17b–19b** (Eqs. (4) and (5)) [6]. The pentacoordinate intermediate (Eq. (4)) could only be observed in the reaction of SiF$_4$ and **4a**, by NMR monitoring of the reaction progress. The intermediate was identified in the reaction mixture by its typical ^{29}Si quartet at δ −132.3 ppm, ($^1J_{Si-F}$ = 182 Hz), and reacted further to form **17a**. The crystal structures of **17a**, **18b**, **19b** and **20**, the dimethylamino analog of **17a**, have been determined, and are depicted in Figs. 3–6. The crystal structure of the related **19a** was reported previously [6]. The remarkable differences are apparent immediately from the figures: the difluoro complex (**17a**)

Fig. 3. Molecular structure of **17a** in the crystal.
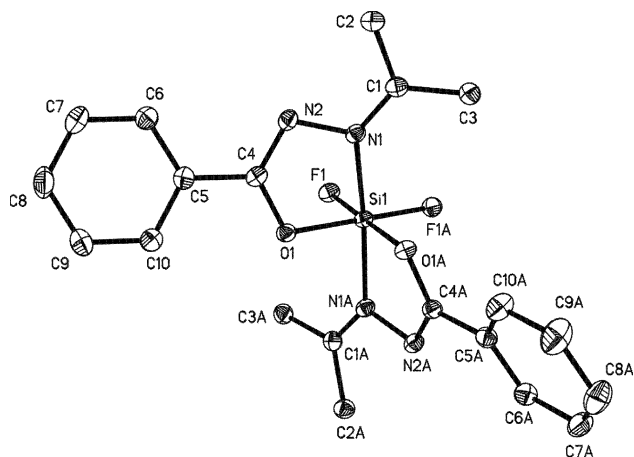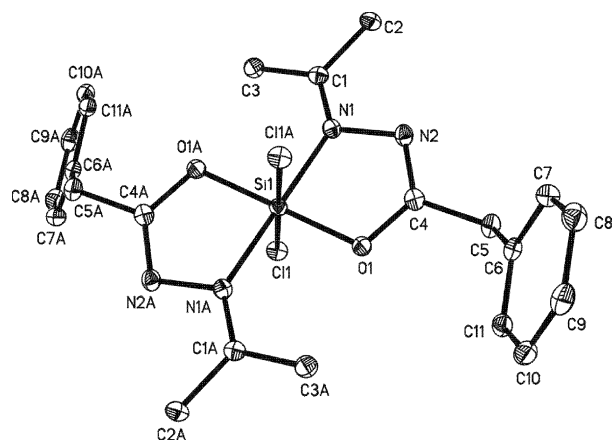

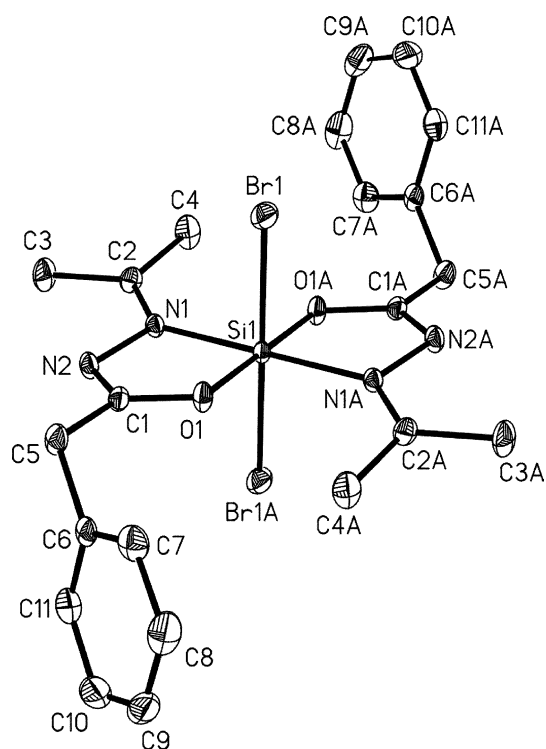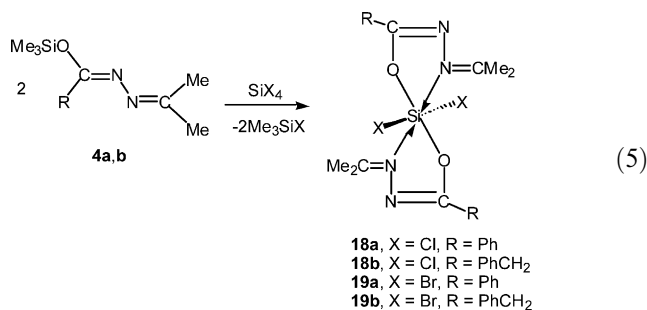Fig. 4. Molecular structure of **18b** in the crystal.

Fig. 5. Molecular structure of **19b** in the crystal.

crystallized in the *cis* geometry, while the dichloro (**18b**) and the dibromo (**19a**) [6], and **19b** complexes preferred the *trans* geometry.
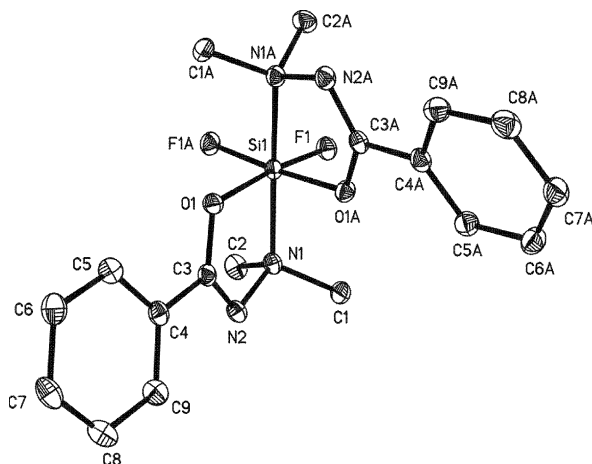

$$\text{(5)}$$

18a, X = Cl, R = Ph
18b, X = Cl, R = PhCH$_2$
19a, X = Br, R = Ph
19b, X = Br, R = PhCH$_2$

Fig. 6. Molecular structre of **20** in the crystal.

The fact that in **17** the monodentate ligands are *cis* to each other, as has generally been observed in other hexacoordinate bis-acylimidato-*N*,*O* chelates **1** [7], as well as in the dihalo-dimethylamino chelates **20–22**, suggests that in the absence of special constraints the *cis* orientation is preferred. It follows that the uncommon *trans* geometry, found in **18** and **19**, is the result of steric repulsion [6]. Examination of molecular models shows that in the *cis* geometry of **18** and **19** one of the isopropylidene methyl groups is very close to the adjacent halogen ligand, while in the *trans* geometry this repulsive interaction is replaced by a methyl–oxygen interaction. It follows that the *trans* geometry is preferred as long as the halogen is bulkier than oxygen, i.e., in the case of Cl or Br (**18**, **19**) while for the fluoro ligands the *cis* geometry prevails.

20, X = F, R = Ph
21, X = Cl, R = CF₃
22, X = Br, R = Ph

**24a**, R = Ph
24b, R = PhCH₂

25
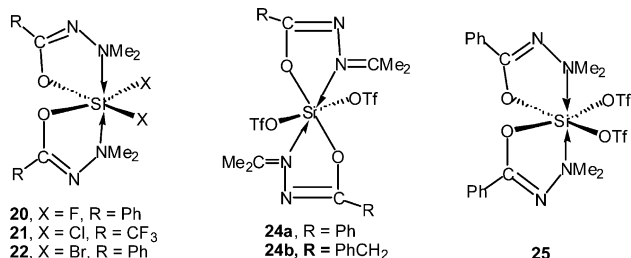
In addition to the obvious different geometries for the dihalo complexes **17–19**, their crystal structures can help in the comparison of the isopropylideneimino and dimethylamino donor groups: Table 3 lists selected bond lengths and ^{29}Si chemical shifts for **17–19**, in comparison with the corresponding data for the dimethylamino analogs **20–22**. For **17a** and **20** also the one-bond ^{29}Si–^{19}F coupling constants are listed. The data in Table 3 agree well with the results of Table 2: in all of the comparisons, the N–Si distances for the isopropylideneimino complexes are shorter than the corresponding bond lengths in the dimethylamino analogs. This strongly supports the conclusion that the isopropylideneimino ligand acts as a stronger donor,

regardless of the coordination number, the charge, or the monodentate ligands in the chelate.

It is interesting to compare also the Si–halogen bond distances of the two complex series in Table 3: while the Si–N distances are shorter in the isopropylideneimino series relative to the dimethylamino analogs, the opposite is found for the Si–halogen bonds: they are consistently longer in the isopropylideneimino compounds relative to their dimethylamino analogs. This result is in line with the stronger donor assignment to the isopropylideneimino ligand group: the stronger (and shorter) the coordination bond, the longer is the Si–halogen bond. This is also in agreement with the reported ease of ionization of **19a** and **19b** [6], relative to the resistance of the dimethylamino analog **22** [4b]. The opposite trends in N–Si and Si–Cl distances may be viewed as different points along a hypothetical S$_{N2}$ reaction coordinate, in which the stronger donor, the isopropylideneimino group, is associated with a more advanced reaction: the nucleophile–silicon bond is shorter, while the silicon-leaving group distance is longer.

2.2.1. Equilibrium ionization of dibromo complexes

In all of the complexes discussed so far, the ^{29}Si-NMR resonances of the isopropylideneimino complexes were shifted significantly upfield relative to their dimethylamino analogs (Tables 2 and 3), in accord with stronger coordination. This trend is reversed in the dibromo complexes **19** relative to **22** (Table 3). The unexpected downfield shifts in **19a** and **19b**, in connection with strong temperature and solvent effects on the ^{29}Si chemical shift (Table 4), indicate that the dibromo complexes **19**, unlike the difluoro- (**17**) and dichloro- (**18**) analogs, undergo reversible ionization to the bromosiliconium salt **23** already at room temperature (Eq. (6)) [6].

19a,b   **23a,b**

a, R = Ph; b, R = PhCH₂

$$(6)$$
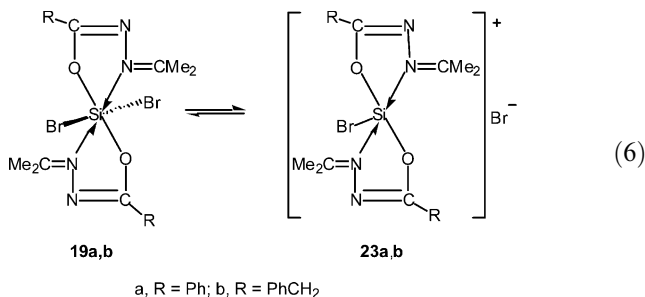
Ionization of **19** is unexpected not only because it is the only dihalo-complex in this series which ionizes, but because the previously reported dihalo-dimethylamino-coordinated complexes, **20–22**, were completely resistant to ionization. Ionization of **19** thus constitutes additional evidence for the stronger donor property of the isopropylideneimino ligand group.

Table 3
Comparison of ^{29}Si-NMR chemical shifts (CDCl$_3$, 300 K) and selected bond lengths for isopropylideneimino- vs. dimethylamino- dihalo (or ditriflato-) complexes

Compound (ligand X)	Si–N (Å)	Si–O (Å)	Si–ligand (Å)	δ(^{29}Si) (ppm) (m, $^1J_{Si-F}$, Hz)
Isopropylideneimino donor				
17a (F)	1.9418(10)	1.7867(8)	1.6543(7)	− 166.9 (t, 194)
18b (Cl)	1.9205(9)	1.7381(8)	2.2088(7)	− 163.7
19a [a] (Br)	1.933(3)	1.716(2)	2.4050(6)	− 140.2
19b (Br)	1.9280(14)	1.7199(13)	2.3990(2)	− 153.2
24b (OTf)	1.8991(10)	1.7055(9)	1.8222(9)	− 172.3
Dimethylamino donor				
20 (F)	1.9591(10)	1.7764(9)	1.6353(7)	− 160.2 (t, 201)
21 [b] (Cl)	2.013(2)	1.6844 (15)	2.141(1)	− 146.2
	2.011(2)	1.6964(14)	2.147(1)	
22 [a] (Br)	2.067(4)	1.789(3)	2.327(14)	− 170.0
	1.985(4)	1.728(3)	2.3498(14)	
25 [c] (OTf)	1.967(3)	1.731(3)	1.793(3)	− 161.5
	1.989(3)	1.724(3)	1.796(3)	

[a] From Ref. [6].
[b] From Ref. [7b].
[c] From Ref. [4a].

The solvent dependence of the ^{29}Si-NMR chemical shift, observed for **19b** (Table 4), shows that the better hydrogen-bond donor solvents cause increased ionization [6], manifest in lower field ^{29}Si chemical shifts. The δ(^{29}Si) values measured in the apolar toluene-d$_8$ and CCl$_4$ solutions represent the fully covalent, non-ionized **19b**. However, the slow-exchange limit temperature and corresponding individual ^{29}Si-NMR signals for the ionic and neutral forms could not be reached, presumably due to rapid bromide exchange. This is in contrast to previous observations in the dimethylamino-coordinated series **1**, in which the ^{29}Si signal in H-bond donor solvents shifted initially downfield upon cooling and, eventually, split in two individual resonances, assigned to **1** and **2** [4b].

Additional support for the ionization of **19b** at low temperature is found in the linear correlation of the ^{29}Si with the (N=CMe$_2$)–^{13}C chemical shifts shown in Fig. 7. The linear relationship is evidence that both changes result from the same phenomenon, as expected from ionization: reduced electron-density on silicon (resulting from ionization) is accompanied by partial compensation from the imino group, i.e., a parallel but smaller reduction in electron density at the imino carbon. The

point labeled * in Fig. 7 represents the fully covalent form (**19b** in CCl$_4$ solution), and it fits well in the line.

2.2.2. Exchange of halogen ligand by triflate

The halogeno ligands in **17–19** were readily exchanged by triflate groups using TfOTMS (Eq. (7)) [3e,3f,3g,4a,4b,12].

| 17a, R = Ph | 24a,b |
| 17b, R = PhCH$_2$ | |

| 18a,b X = Cl | |
| 19a,b X = Br | |

(7)
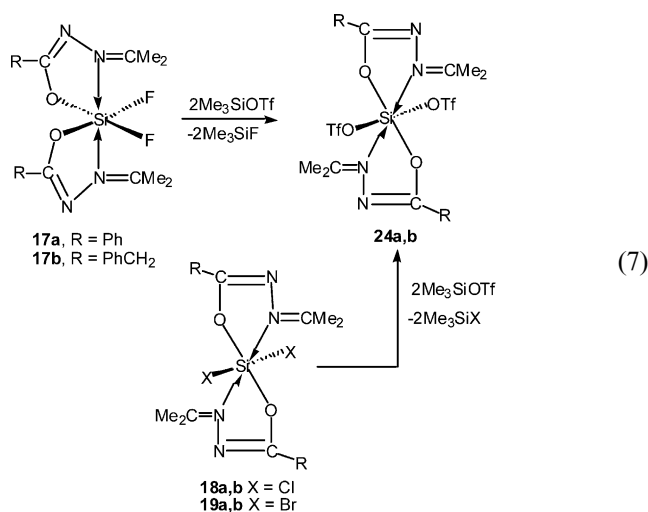
Table 4
^{29}Si chemical shifts (ppm) and corresponding temperatures T (K) for **19a** and **19b** in various solvents

19a in CDCl$_3$	19b				
	CCl$_4$	C$_6$D$_5$CD$_3$	CDCl$_3$	CD$_2$Cl$_2$	CHFCl$_2$
− 153.9 (330)	− 183.4 (300)	− 182.0 (340)	− 165.5 (330)	− 163.9 (300)	− 124.1 (273)
− 140.2 (300)	− 183.6 (340)		− 159.2 (300)	− 152.3 (263)	− 122.0 (263)
− 123.9 (253)			− 133.7 (260)	− 131.3 (213)	− 119.5 (243)
− 120.5 (223)			− 118.2 (200)	− 120.2 (170)	− 118.4 (170)

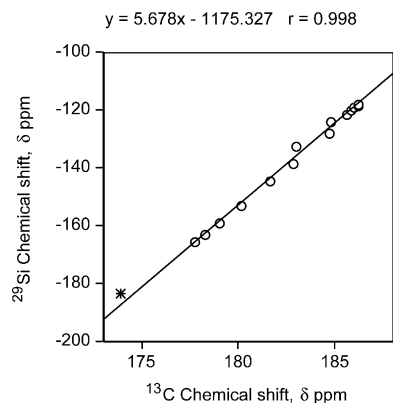y = 5.678x - 1175.327 r = 0.998

Fig. 7. Correlation of ^{29}Si- and ^{13}C-NMR (of the isopropylidene imino-carbon) chemical shifts for **19b** with temperature variation. The point labeled * was taken in CCl_4 solution and represents the fully covalent hexacoordinate complex.

Interestingly, all three complexes, regardless of the initial monodentate geometry, gave the same hexacoordinate *trans* ditriflates, **24a** and **24b**. The [29]Si chemical shifts of **24a** and **24b** were essentially temperature independent at the hexacoordinate-silicon range, indicating that with the powerful electron-withdrawing triflate substituents no NMR-detectable ionization took place. This result is in agreement with previous observations in series **1**, in which no ionization took place when X was Cl, Br, or triflate [4b]. A crystal of the *trans* ditriflate **24b** was analyzed by X-ray crystallography, and the resulting molecular structure is depicted in Fig. 8. The molecule features an inversion center and is achiral.

The data for **24b** are also listed in Table 3, and indeed in this compound, like in the comparison of all other compound pairs in the table, the N–Si distance is shorter and the Si–OTf distance longer than in the corresponding NMe$_2$-coordinated **25**.
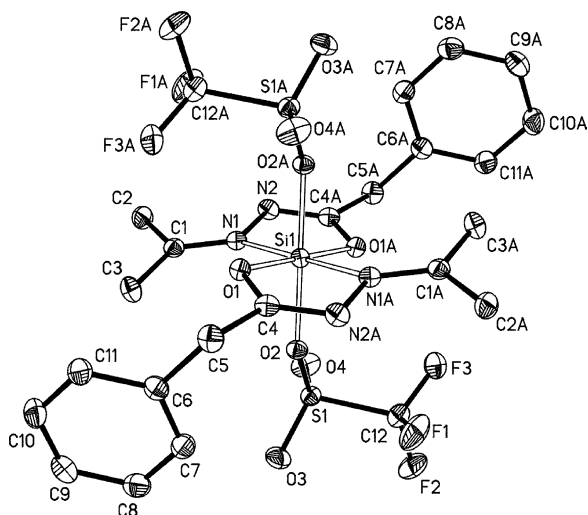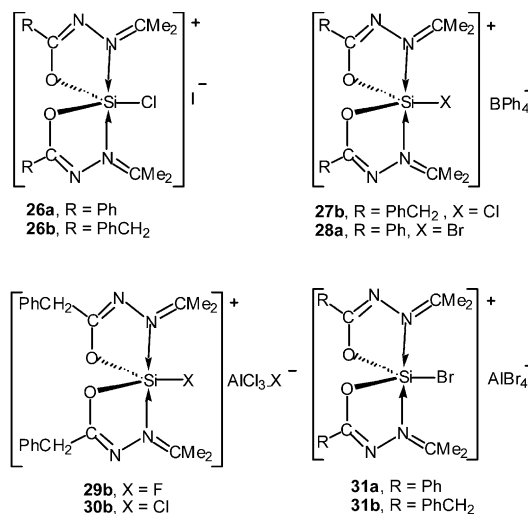

Fig. 8. Molecular structre of **24b** in the crystal.

2.2.3. Stable ionic complexes from hexacoordinate dihalo-precursors

Like in the dihalo complexes **20**–**22** [4b], full ionization of **17**–**19** at room temperature could finally be achieved by exchange of one of the halogen ligands by a better leaving group: BPh_4^- or iodide, or by reaction with powerful ionizing agents ($AlCl_3$, $AlBr_3$). Thus, the iodide salts **26a** and **26b** were obtained by the reaction of **18a** and **18b**, respectively, with access Me_3SiI; likewise, **27b** and **28a** were obtained, respectively, from **18b** and **19a** by reaction with $NaBPh_4$. From **17b** and **18b** the ionic complexes **29b** and **30b** were formed by reaction with $AlCl_3$, and **19a** and **19b** afforded with $AlBr_3$ the tetrabromoaluminates **31a** and **31b** [6].

26a, R = Ph
26b, R = PhCH$_2$

27b, R = PhCH$_2$, X = Cl
28a, R = Ph, X = Br

29b, X = F
30b, X = Cl

31a, R = Ph
31b, R = PhCH$_2$

A crystal structure was obtained for **26a** and is depicted in Fig. 9, and selected bond lengths are given in Table 2. The [29]Si chemical shifts for both series of siliconium tetrahaloaluminate salts and the iodide salts (Table 5), confirm the ionic nature of the compounds, on one hand, and demonstrate again the stronger coordination in the isopropylideneimino complexes, manifest by the higher-field [29]Si chemical shifts, on the other.

It should be noted that while the dimethylamino-coordinated siliconium salt **14**, as well as numerous similar complexes with other counterions [4b], had substantially distorted TBP geometries with N–Si–N angles near 155° and O–Si–O angles near 135°, the present siliconium salts, **13a** and **26a**, have structures much closer to a true TBP (Table 2).

3. Experimental

3.1. General

The reactions were carried out under dry argon using Schlenck techniques. The solvents were dried and
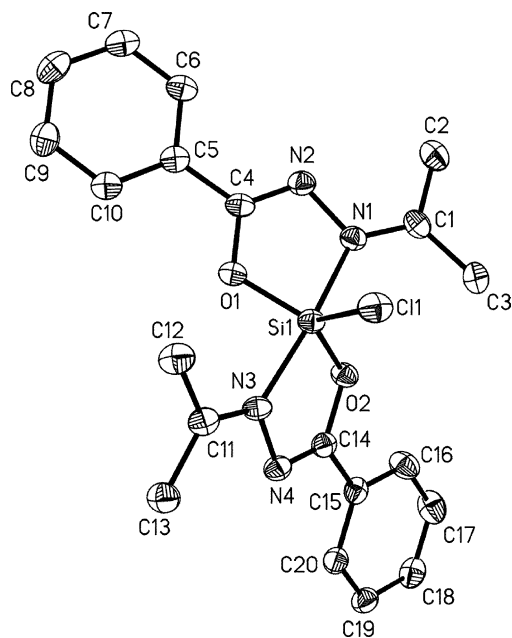
Fig. 9. Molecular structure of **26a** in the crystal. The iodide anion has been omitted because of the substantial distance from other atoms (I–Si distances in the unit cell range between 6 and 8 Å).

purified by standard methods. NMR spectra were recorded on a Bruker Avance DMX-500 spectrometer operating at 500.130, 125.758, and 99.362 MHz, respectively, for ^1H, ^{13}C and ^{29}Si spectra, and are reported in δ (ppm) relative to tetramethylsilane (TMS) in CDCl$_3$ solution at 300 K. Melting points were measured in sealed capillaries using a Buchi melting point instrument and are uncorrected. Elemental analyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, Germany.

3.2. X-ray measurements

The data sets for all compounds were collected from oil-coated shock-cooled crystals on a BRUKER SMART-APEX diffractometer with D8 goniometer (graphite-monochromated Mo–Kα radiation, $\lambda = 0.71073$ Å) equipped with a low temperature device in omega-scan mode at 173(2) K (**13a**), 153(2) K (**19b**) and 100(2) K (**15**, **17a**, **18b**, **20**, **14b**, **26a**) [13–15]. The data were integrated with SAINT [16] and an empirical absorption correction was applied [17]. The structures were solved by direct methods (SHELXS-97) [18] and refined by full-matrix least-squares methods against F^2 (SHELXL-97) [19]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms bonded to sp^2 (sp^3) carbon atoms were assigned ideal positions and refined using a riding model with U_{iso} constrained to 1.2 (1.5) times the U_{equiv} value of the parent atom. Disordered moieties were refined using bond lengths and similarity restraints.

In the molecular structures shown in Figs. 1–6, 8 and 9, the anisotropic displacement parameters are depicted at the 50% probability level, and hydrogen atoms are omitted for clarity.

3.3. Bis[N(isopropylideneimino)benzimidato-N,O]methylsiliconium chloride (9a)

To a solution of 0.250 g (1.01 mmol) of **4a** [6] in 4 ml of chloroform was added 0.165 g (1.11 mmol) of **5**. After 10 min at ambient temperature the volatile components were removed under reduced pressure and the remaining solid was washed three times with 4 ml portions of hexane and dried under vacuum. The yield was 0.177 g, 82%. m.p.: 119−121 °C. ^1H-NMR: δ 1.08 (s, 3H, SiCH$_3$), 2.74 (s, 6H, N=CCH$_3$), 2.80 (s, 6H, N=CCH$_3$), 7.24–7.90 (m, 10H, Ph). ^{13}C–NMR: δ 4.2 (SiCH$_3$), 23.8 (N=CCH$_3$), 25.1 (N=CCH$_3$), 126.1, 127.6, 128.6, 133.3 (Ph), 162.0 (O–C=N), 181.9 (N=CCH$_3$). ^{29}Si-NMR: δ − 81.0. Anal. Calc. for C$_{21}$H$_{25}$ClN$_4$O$_2$Si: C, 58.80; H, 5.87; N,13.06; Found: C, 58.32; H, 5.98; N, 12.87%.

Table 5
Selected ^1H-, ^{13}C- and ^{29}Si-NMR chemical shifts for the stable siliconium-ion salts **26–31** in CDCl$_3$ solution

Compound	^{29}Si	^{13}C			^1H		
		C=NN	C=NCO	CH$_2$	C(CH$_3$)$_2$	CH$_3$	CH$_2$
26a	− 113.6	184.6	161.7		25.6, 26.3	2.84, 2.97	
26b [a]	− 108.5	186.2	166.1	37.2	25.1, 25.3	2.17, 2.63	3.82, 3.85; ^2J = 15.2 Hz
27b	− 110.7	186.5	165.8	37.0	24.2, 24.4	1.80, 2.17	3.56 br
28a	− 117.3	186.3	161.3		24.6, 25.3	2.31, 2.33	
29b [a]	− 120.0 [b]	186.5	166.7	37.1	24.2, 24.3	2.13, 2.59	3.77, 3.84; ^2J = 15.2 Hz
30b [a]	− 108.3	186.1	166.3	37.1	24.6, 24.9	2.10, 2.60	3.81, 3.87; ^2J = 15.3 Hz
31a [c]	− 107.3	186.5	162.0		25.4, 25.6	2.78, 2.80	
31b [c]	− 108.0	186.2	166.1	37.1	24.8, 25.0	2.60, 3.10	4.32, 4.38; ^2J = 15.5 Hz

[a] Compound identified by NMR spectral analogy, but not isolated.
[b] Doublet, $^1J_{Si-F}$ = 255 Hz.
[c] From Ref. [6].

Table 6
Crystal data and experimental parameters for the crystal structure analyses of **13a**, **15**, **17a**, **18b**, **19b**, **20**, **14b** and **26a**

	13a	15	17a	18b	19b	20	14b	26a
CCDC number	206982	206983	206984	206985	206986	206987	206988	206989
Empirical formula	$C_{22}H_{27}F_3N_4O_5SSi$	$C_{17}H_{19}ClN_2OSi$	$C_{20}H_{22}F_2N_4O_2Si$	$C_{22}H_{26}Cl_2N_4O_2Si$	$C_{22}H_{26}Br_2N_4O_2Si$	$C_{18}H_{22}F_2N_4O_2Si$	$C_{24}H_{26}F_6N_4O_8S_2Si$	$C_{22}H_{24}Cl_7IN_4O_2Si$
Form mass (g mol^{-1})	544.63	330.88	416.51	477.46	566.38	392.49	704.70	779.59
Collection T (K)	173	100(2)	100(2)	100(2)	153(2)	100(2)	100(2)	100(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$P2_1/n$	$P2_1/c$	$C2/c$	$P2_1/c$	$P2_1/c$
a (Å)	8.8163(8)	7.1498(4)	21.6385(16)	7.5883(4)	10.1476(7)	19.8155(14)	9.4864(6)	11.9887(7)
b (Å)	10.3707(10)	15.5011(8)	7.9091(6)	10.7876(6)	14.7279(11)	8.5259(6)	8.9519(5)	26.6243(15)
c (Å)	14.4321(14)	15.65776(8)	12.1261(9)	13.5892(7)	7.8884(6)	12.0502(9)	18.0293(10)	19.6477(11)
α (°)	95.129(2)	90	90	90	90	90	90	90
β (°)	97.651(2)	97.2230(10)	90.0100(10)	99.6920(10)	97.3970(10)	113.7300(10)	105.1230(10)	94.6230(10)
γ (°)	107.264(2)	90	90	90	90	90	90	90
V (Å^3)	1237.2(2)	1721.57(16)	2075.3(3)	1096.53(10)	1169.13(15)	1863.7(2)	1479.05(15)	6251.0(6)
Z	2	4	4	2	2	4	2	8
ρ_{calc} (mg m^{-3})	1.462	1.277	1.333	1.446	1.609	1.399	1.583	1.657
$F(0\,0\,0)$	568	696	872	500	572	824	724	3088
θ Range (°)	2.36–28.30	1.86–26.39	1.88–26.38	2.42–27.10	2.45–28.24	2.25–26.37	2.22–26.39	1.29–25.48
Reflections collected	14051	13917	8199	9078	13290	7528	15753	62293
Independent reflections	6127	3511	2102	2392	2704	1904	3034	11603
R_{int}	0.0354	0.0254	0.0203	0.0149	0.0318	0.0217	0.0153	0.0288
No. of parameters	326	202	134	144	144	125	207	795
Goodness-of-fit	1.015	1.038	1.031	1.063	1.055	1.055	1.038	1.037
R_1 [a], wR_2 [b] [$I>2\sigma(I)$]	0.0544, 0.1516	0.0362, 0.0917	0.0334, 0.0913	0.0261, 0.0709	0.0270, 0.0690	0.0315, 0.0828	0.0283, 0.0790	0.0275, 0.0652
R_1 [a], wR_2 [b] (all data)	0.0692, 0.1631	0.0424, 0.0965	0.0347, 0.0923	0.0269, 0.0714	0.0294, 0.0701	0.0339, 0.0843	0.0292, 0.0798	0.0317, 0.0670
Max/min res. electron density (eÅ^3)	0.745/ −0.719	+0.491/ −0.298	+0.345/ −0.294	+0.323/ −0.208	0.454/ −0.724	+0.343/ −0.296	+0.470/ −0.360	+0.895/ −0.399

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$.

3.4. Bis[N(isopropylideneimino)phenylacetimidato-N,O]methylsiliconium chloride (9b)

9b was prepared like **9a** using 0.245 g (0.94 mmol) of **4b** and 0.175 g (1.17 mmol) of **5**. The yield was 0.192 g (89%). m.p.: 80–83 °C. ^{1}H-NMR: δ 0.61 (s, 3H, SiCH$_3$), 2.04 (s, 6H, N=CCH$_3$), 2.40 (s, 6H, N=CCH$_3$), 3.57, 3.65 (ABq, ^2J = 15.2 Hz, 4H, CH$_2$), 7.10–7.21 (m, 10H, Ph). ^{13}C-NMR: δ 3.6 (SiCH$_3$), 23.6 (N=CCH$_3$), 24.2 (N=CCH$_3$), 37.1 (CH$_2$), 127.4, 128.6, 128.7, 132.6 (Ph), 166.5 (O–C=N), 182.2 (N=CCH$_3$). ^{29}Si-NMR: δ −82.0.

3.5. Bis[N(isopropylideneimino)benzimidato-N,O]phenylsiliconium chloride (10a)

To a solution of 0.252 g (1.02 mmol) of **4a** in 4 ml of chloroform was added 0.218 g (1.03 mmol) of **6**. After 1 h at ambient temperature the volatile components were evaporated and 10 ml of hexane were added to the remaining yellow oil. A white solid precipitated after 20 h of stirring, and was separated by decantation and dried under vacuum. The yield was 0.179 g (72%). m.p.: 130–132 °C. ^{1}H-NMR: δ 2.00 (s, 6H, N=CCH$_3$), 2.53 (s, 6H, N=CCH$_3$), 7.01–7.76 (m, 20H, Ph). ^{13}C-NMR: δ 23.7 (N=CCH$_3$), 24.5 (N=CCH$_3$), 125.3–133.1 (Ph), 162.3 (O–C=N), 183.5 (N=CCH$_3$). ^{29}Si-NMR: δ −93.7.

3.6. Bis[N(isopropylideneimino)phenylacetimidato-N,O]phenylsiliconium chloride (10b)

10b was prepared like **10a** using 0.247 g (0.94 mmol) of **4b** and 0.205 g (1.0 mmol) of **5**. The solid was washed twice with dry ether. The yield was 0.192 g (83%). m.p.: 155–158 °C. ^{1}H-NMR: δ 1.59 (s, 6H, N=CCH$_3$), 2.51 (s, 6H, N=CCH$_3$), 3.82, 3.88 (ABq, ^2J = 15.1 Hz, 4H, CH$_2$), 6.97–7.45 (m, 15H, Ph). ^{13}C-NMR: δ 24.0 (N=CCH$_3$), 24.2 (N=CCH$_3$), 37.2 (CH$_2$), 127.6–132.8 (Ph), 167.6 (O–C=N), 184.2 (N=CCH$_3$). ^{29}Si-NMR: δ −94.3. Anal. Calc. for C$_{28}$H$_{31}$ClN$_4$O$_2$Si: C, 64.78; H, 6.02; N, 10.79. Found: C, 64.68; H, 5.95; N, 10.68%.

3.7. Bis[N(isopropylideneimino)benzimidato-N,O]cyclohexylsiliconium chloride (11a)

To a solution of 0.640 g (2.58 mmol) of **4a** in 5 ml of chloroform, was added 0.303 g (1.39 mmol) of **7**. The reaction mixture was stirred for 1 h at ambient temperature, followed by removal of the volatiles under reduced pressure. The remaining pale yellow oil was crystallized by stirring with 15 ml of hexane for 36 h. The yield was 0.52 g, (59%). m.p.: 74–76 °C. ^{1}H-NMR: δ 1.00–1.90 (m, 11H, C$_6$H$_{11}$), 2.93 (s, 6H, N=CCH$_3$), 3.06 (s, 6H, N=CCH$_3$), 7.52–8.05 (m, 10H, Ph). ^{13}C-NMR: δ 23.2 (N=CCH$_3$), 25.3 (N=CCH$_3$), 23.2–31.8

(C$_6$H$_{11}$), 124.9, 126.7, 127.7, 131.9 (Ph), 160.9 (O–C=N), 182.5 (N=CCH$_3$). ^{29}Si-NMR: δ −80.2. Anal. Calc. for C$_{26}$H$_{33}$ClN$_4$O$_2$Si: C, 62.82; H, 6.69; N, 11.27. Found: C, 62.14; H, 6.50; N, 11.23%.

3.8. Bis[N(isopropylideneimino)benzimidato-N,O]isobutylsiliconium chloride (12a)

0.317 g (1.66 mmol) of **8** was added to a solution of 0.825 g (3.32 mmol) of **4a** in 5 ml of chloroform. The mixture was allowed to stir at room temperature for 1 h after which the volatiles were removed under reduced pressure, leaving an oily residue. A white solid precipitated after 24 h stirring with 10 ml of hexane. The solution was decanted and dried under reduced pressure for 2 h. The yield was 0.61 g (78%). m.p.: 110–112 °C. ^{1}H-NMR: δ 0.75, 0.89 (2d, ^3J = 7.0 Hz, 6H, (CH$_3$)$_2$CH) 1.12 (m, (CH$_3$)$_2$CH), 1.49 (m, 2H, CHCH$_2$), 2.76 (s, 6H, N=CCH$_3$), 2.82 (s, 6H, N=CCH$_3$), 7.36–8.05 (m, 10H, Ph). ^{13}C-NMR: δ 23.2 (CH), 24.1, 25.4 ((CH$_3$)$_2$CH), 27.8 (CH$_2$) 24.4 (N=CCH$_3$), 25.4 (N=CCH$_3$), 125.2, 126.9, 127.9, 132.5 (Ph), 161.2 (O–C=N), 182.0 (N=CCH$_3$). ^{29}Si-NMR: δ −80.4.

3.9. Bis[N(isopropylideneimino)benzimidato-N,O]methylsiliconium triflate (13a)

To a solution of 0.286 g (1.15 mmol) of **4a** in 4 ml of chloroform was added 0.250 g (1.67 mmol) of **5**. The solution was stirred for 5 min and 0.283 g (1.27 mmol) of trimethylsilyl friflate was added. About a quarter of the solvent was removed under reduced pressure. The product crystallized after 1 week at 4 °C. The yield was 0.257 g (0.82%). m.p.: > 260 °C. ^{1}H-NMR: δ 1.03 (s, 3H, SiCH$_3$), 2.74 (s, 6H, N=CCH$_3$), 2.76 (s, 6H, N=CCH$_3$), 7.48–8.00 (m, 10H, Ph). ^{13}C-NMR: δ 3.8 (SiCH$_3$), 23.7 (N=CCH$_3$), 24.8 (N=CCH$_3$), 126.5, 128.0, 128.9, 133.5 (Ph), 162.4 (O–C=N), 182.0 (N=CCH$_3$). ^{29}Si-NMR: δ −81.1. Anal. Calc. for C$_{22}$H$_{25}$F$_3$N$_4$O$_5$SSi: C, 48.70; H, 4.64; N, 10.33. Found: C, 48.53; H, 4.60; N, 10.04%.

3.10. Chloro[N(isopropylideneimino)benzimidato-N,O]methylphenylsilane (15)

To a solution of 0.759 g (3.97 mmol) of PhMeSiCl$_2$ in 15 ml of chloroform was added 0.841 g (3.38 mmol) of **4a**. The mixture was kept for 1 h at room temperature under reduced pressure. After removal of one-third of the solvent the solid product precipitated and was washed twice with hexane. The yield was 0.967 g (86%). m.p.: 125–127 °C. ^{1}H-NMR: δ 1.10 (s, 3H, SiCH$_3$), 1.62 (s, 3H, N=CCH$_3$), 2.27 (s, 3H, N=CCH$_3$), 7.26–8.24 (m, 10H, Ph). ^{13}C-NMR: δ 10.2 (SiCH$_3$), 21.7 (N=CCH$_3$), 23.1 (N=CCH$_3$), 162.9 (O–C=N), 170.0 (N=CCH$_3$). ^{29}Si-NMR: δ −52.9. Anal.

Calc. for $C_{17}H_{19}ClN_2OSi$: C, 61.71; H, 5.79; N, 8.47. Found: C, 61.47; H, 5.89; N, 8.29%.

The syntheses of **17b**, **18b**, **19a**, **19b**, **31a**, and **31b** have been reported in a preliminary account [6].

3.11. Difluorobis[N-(isopropylideneimino)benzimidato-N,O]silicon(IV) (17a)

SiF_4 (0.2536 g, 2.44 mmol) was condensed in a vacuum line into a solution of 0.694 g (2.79 mmol) of **4a** in 10 ml of chloroform. The solution was stirred for 12 h at room temperature, followed by addition of a second portion of **4a** (0.622 g, 2.50 mmol) and heating to 70 °C for 2 h. The volatiles were removed under vacuum leaving a solid residue which was washed twice with hexane and dried under vacuum. The yield was 0.941 g (93%). m.p.: 179–181 °C. ^{1}H-NMR: δ 2.62 (s, 6H, N= CCH_3), 2.64 (s, 6H, N= CCH_3), 7.15–7.25 (m, 10H, Ph). ^{13}C-NMR: δ 23.5 (t, $^4J_{F-C} = 8.2$ Hz, N= CCH_3), 24.1 (N= CCH_3), 127.9, 128.0, 131.4, 131.8 (Ph), 165.4 (O C=N), 173.1 (N= CCH_3). ^{29}Si-NMR: δ -166.9 (t, $^1J_{F-Si} = 194$ Hz). Anal. Calc. for $C_{20}H_{22}F_2N_4O_2Si$: C, 57.68; H, 5.32; N, 13.45. Found: C, 57.39; H, 5.23; N, 13.49%.

3.12. Dichlorobis[N-(isopropylideneimino)benzimidato-N,O]silicon(IV) (18a)

To a solution of 0.597 g (2.40 mmol) of **4a** in 15 ml of THF was added 0.229 g (1.35 mmol) of $SiCl_4$ by vacuum condensation. The product precipitated and was isolated by decantation, and washed twice with hexane. The yield was 0.538 g (99%). m.p.: 184–185 °C. ^{1}H-NMR: δ 2.62 (s, 6H, N= CCH_3), 2.94 (s, 6H, N= CCH_3), 7.40–8.00 (m, 10H, Ph). ^{13}C-NMR: δ 24.8 (N= CCH_3), 25.5 (N= CCH_3), 128.0, 128.5, 129.8, 132.2 (Ph), 162.5 (O C=N), 174.3 (N= CCH_3). ^{29}Si-NMR: δ -162.8. Anal. Calc. for $C_{20}H_{22}Cl_2N_4O_2Si$: C, 53.45; H, 4.93; N, 12.47. Found: C, 53.33; H, 4.97; N, 12.52%.

3.13. Difluorobis[N-(dimethylamino)benzimidato-N,O]silicon(IV) (20)

To a solution of 0.729 g (3.09 mmol) of O-trimethylsilyl-N-(dimethylamino)benzimidate [7a] in 5 ml of chloroform was added by condensation 0.251 g (2.41 mmol) of SiF_4. The solution was stirred for 8 h at room temperature, followed by addition of another portion of 0.251 g (2.41 mmol) of O-trimethylsilyl-N-(dimethylamino)benzimidate. After 24 h the volatiles were evaporated and the solid residue was recrystallized from ether, and dried under vacuum. The yield was 0.577 g (60.9%). m.p.: 139–140 °C. ^{1}H-NMR: δ 3.00 (s, 6H, NCH_3), 3.17 (s, 6H, NCH_3), 7.30–7.85 (m, 10H, Ph). ^{13}C-NMR: δ 50.8 (NCH_3), 50.9 (t, $^3J_{F-C} = 5.4$ Hz, NCH_3), 127.4, 128.1, 130.4, 131.3 (Ph), 165.0 (N=C). ^{29}Si-NMR: δ -160.2 (t, $^1J_{F-Si} = 201$ Hz). Anal. Calc. for

$C_{18}H_{22}F_2N_4O_2Si$: C, 55.09; H, 5.65; N, 14.28. Found: C, 55.21; H, 5.82; N, 14.43%.

3.14. Ditriflatobis[N-(isopropylideneimino)benzimidato-N,O]silicon(IV) (24a)

To a solution containing 0.464 g (1.87 mmol) of **4a**, 0.232 g (1.37 mmol) of $SiCl_4$ and 5 ml of chloroform was added by condensation 5 ml of CH_2Cl_2 and 0.446 g (2.00 mmol) of Me_3SiOTf. The precipitated white solid was dried under reduced pressure. The yield was 0.632 g (100%). m.p. (dec.): 226 °C. ^{1}H-NMR: δ 2.69 (s, 6H, N= CCH_3), 2.89 (s, 6H, N= CCH_3), 7.25–8.00 (m, 10H, Ph). ^{29}Si-NMR: δ -171.9. Anal. Calc. for $C_{22}H_{22}F_6N_4O_8S_2Si$: C, 39.05; H, 3.28; N, 8.28. Found: C, 38.98; H, 3.30; N, 8.35%.

3.15. Ditriflatobis[N-(isopropylideneimino)-phenylacetimidato-N,O]silicon(IV) (24b)

24b was prepared as described for **24a**, using 0.540 g (2.06 mmol) of **4b**, 0.238 g (1.40 mmol) of $SiCl_4$ and 0.545 g (2.45 mmol) of Me_3SiOTf. The yield was 0.712 g (98%). m.p.: 178–180 °C. ^{1}H-NMR: δ 2.03 (s, 6H, N= CCH_3), 2.47 (s, 6H, N= CCH_3), 3.73 (s, 4H, CH_2), 7.30–7.85 (m, 10H, Ph). ^{13}C-NMR: δ 23.9 (N= CCH_3), 26.1 (N= CCH_3), 37.8 (CH_2), 118.8 (q, $^1J_{F-C} = 317$ Hz, CF_3) 127.2, 128.6, 129.4, 133.5 (Ph), 166.9 (O C=N), 182.4 (N= CCH_3). ^{29}Si-NMR: δ -172.3. Anal. Calc. for $C_{24}H_{26}F_6N_4O_8S_2Si$: C, 40.91; H, 3.72; N, 7.95. Found: C, 40.75; H, 3.80; N, 7.81%.

3.16. Chlorobis[N(isopropylideneimino)benzimidato-N,O]siliconium iodide (26a)

0.246 g (1.45 mmol) of $SiCl_4$ was condensed into a solution of 0.716 g (2.88 mmol) of **4a** in 5 ml chloroform. The solution was stirred for 30 min at room temperature followed by evaporation of the volatile components. 5 ml of $CHCl_3$ and 0.316 g (1.58 mmol) of Me_3SiI were condensed to the flask. After 20 min the volatiles were removed again and the remaining yellow powder was washed twice with hexane. The yield was 0.779 g (100%). m.p. (dec.): 153–155 °C. ^{1}H-NMR: δ 2.84 (s, 6H, N= CCH_3), 2.97 (s, 6H, N= CCH_3), 7.36–8.10 (m, 10H, Ph). ^{13}C-NMR: δ 25.6 (N= CCH_3), 26.3 (N= CCH_3), 125.7–133.9 (Ph), 161.7 (O C=N), 184.6 (N= CCH_3). ^{29}Si-NMR: δ -113.6. Anal. Calc. for $C_{20}H_{22}ClIN_4O_2Si$: C, 44.41; H, 4.10. Found: C, 44.32; H, 4.27%.

3.17. Chlorobis[N(isopropylideneimino)phenylacetimidato-N,O]siliconium tetraphenylborate (27b)

To a solution of 0.643 g (2.45 mmol) of **4a** in 5 ml of chloroform 0.235 g (1.38 mmol) of $SiCl_4$ was condensed.

The solution was stirred for 1 h at room temperature. The volatiles were evaporated and 0.984 g (2.87 mmol) of NaBPh$_4$ was added to the remaining white solid. 5 ml of CH$_3$CN was condensed to the flask and the solution was heated and kept for 1 h at 80 °C. CH$_3$CN was replaced by CHCl$_3$ and a solid precipitated, which was filtered out. After removal of the solvents at reduced pressure the remaining yellow foam was crystallized from Et$_2$O to yield 0.887 g (95%) of a yellow powder. m.p.: 69–72 °C. ^{1}H-NMR: δ 1.80 (s, 6H, N=CCH$_3$), 2.17 (s, 6H, N=CCH$_3$), 3.66 (s, 4H, CH$_2$), 6.92–7.50 (m, 30H, Ph). ^{13}C-NMR: δ 24.2 (N=CCH$_3$), 24.4 (N=CCH$_3$), 37.0 (CH$_2$), 121.6–138.5 (Ph), 165.8 (OC=N), 186.5 (N=CCH$_3$). ^{29}Si-NMR: δ − 110.7. Anal. Calc. for C$_{46}$H$_{46}$BClN$_4$O$_2$Si: C, 72.58; H, 6.09; N, 7.36. Found: C, 72.25; H, 6.20; N, 7.19%.

3.18. Bromobis[N(isopropylideneimino)benzimidato-N,O]siliconium tetraphenylborate (28a)

10 ml of CH$_3$CN was condensed to a pre-evacuated flask containing 0.571 g (1.06 mmol) of **19a** and 1.017 g (2.97 mmol) of NaBPh$_4$. The solution was heated for 1 h at 80 °C, followed by evaporation of CH$_3$CN and replacement by CHCl$_3$. The precipitate was filtered and the solvent was removed from the filtrate. The remaining yellow foam was refluxed in 15 ml of Et$_2$O until a yellow powder had precipitated. The liquid was decanted off and the solid product was dried under vacuum. The yield was 0.716 g (87%). m.p.: 113–115 °C. ^{1}H-NMR: δ 2.31 (s, 6H, N=CCH$_3$), 2.33 (s, 6H, N=CCH$_3$), 6.84–7.93 (m, 30H, Ph). ^{13}C-NMR: δ 24.6 (N=CCH$_3$), 25.3 (N=CCH$_3$), 121.6–138.5 (Ph), 161.3 (OC=N), 186.3 (N=CCH$_3$). ^{29}Si-NMR: δ − 117.3. Anal. Calc. for C$_{44}$H$_{42}$BBrN$_4$O$_2$Si: C, 67.96; H, 5.44; N, 7.20. Found: C, 68.02; H, 5.52; N, 7.16%.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 206982, 206983, 206984, 206985, 206986, 206987, 206988 and 206989 for compounds **13a**, **15**, **17a**, **18b**, **19b**, **20**, **14b** and **26a**, respectively. The CCDC numbers are listed in Table 6. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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