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Competing reactions of hypercoordinate silicon dichelates

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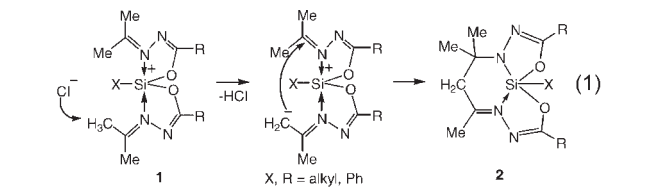
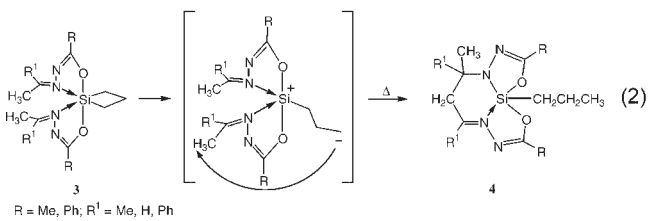
Neutral hexacoordinate silicon complexes derived from hydrazide chelating ligands with imino-donor groups, and their pentacoordinate ionic dissociation products, undergo facile intramolecular aldol-type condensation catalyzed by their chloride counterion leading to formation of a third chelate ring. In analogous silacyclobutane dichelates, in the absence of halide counterion, a similar *uncatalyzed* rearrangement takes place, accompanied by opening of the four-membered ring. In the absence of α-protons necessary for the condensation, the four-membered ring residue adds directly to one of the imino-carbon atoms forming a new C—C bond and closing a different chelate ring. This latter addition to the imino carbon is the preferred reaction pathway, even in the presence of 12 α-protons, when cyanide ion replaces the chloride counterion and acts as nucleophile. The cyanide reactivity is rationalized in terms of the HSAB concept. An unusual intramolecular rearrangement involving the migration of a *t*-butyl group from silicon to carbon, while enabling the unprecedented attachment of a *third* hydrazide chelating agent, leading to a hexacoordinate trichelate complex, is presented. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: hypercoordinate silicon; molecular rearrangement; silacyclobutane complex; aldol condensation of imines; silicon trichelate

INTRAMOLECULAR ALDOL CONDENSATION OF IMINES

Pentacoordinate hydrazide-based siliconium chloride complexes were recently shown to undergo a facile base-catalyzed molecular rearrangement Eqn (1), forming a new carbon–carbon bond and closing a third chelate ring.[1] A closer examination reveals that the rearrangement is equivalent to an intramolecular aldol-type condensation between two adjacent imine groups,[2,3,4,5] catalyzed by its own counterion, chloride, acting as a base to abstract an allylic proton. The catalysis by the counterion was recognized from the observation that chloride reacted faster than bromide, which in turn reacted faster than iodide in this reaction, under otherwise similar conditions (boiling chloroform solution).





It was therefore quite surprising to find later that even in the absence of any counterions in the silacyclobutane complexes **3**, which are purely *hexa*coordinate in solution (judging from the high field ^{29}Si NMR chemical shift: −134.7 ppm for R = Me, R^1 = H, and from the lack of easily ionizable halide ligands), a very similar molecular rearrangement took place Eqn (2).[6] There are two distinct differences between these rearrangements: the absence of apparent catalysis, and the accompanying opening of the four-membered ring in the latter reaction. Clearly, the fact that the silacyclobutane ring opens and forms an *n*-propyl ligand requires that a proton be abstracted by the terminal carbon atom of the opening ring. It follows that the ring very likely opens spontaneously due to ring strain resulting in a positively charged pentacoordinate silicon center and a primary carbanion. The latter rapidly abstracts one of the allylic protons, initiating the interchelate aldol condensation. Because of the high energy generally attributed to primary carbanions,[7] it seems more likely that ring opening and proton abstraction take place simultaneously, during collision of a methyl group with the four-membered ring carbon, such that no free carbanion actually exists at any point in time.

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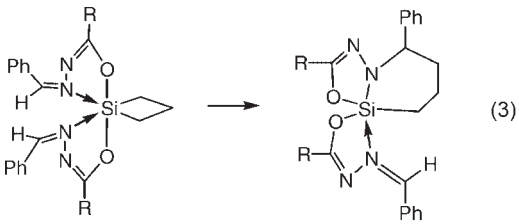
It is obvious that both of the reactions described in Eqs. 1 and 2 require the presence of activated (allylic) α-protons, to initiate the condensation. In the absence of α-protons, the reaction takes a different course: the transient carbanion intermediate, unable to abstract a proton, acts as a nucleophile and attacks the most electrophilic carbon atom in the system, the imino carbon Eqn (3).[6] As a result a different third chelate ring is closed, with the formation of a new C—C bond, and the conversion of one of the N → Si dative bonds to a substantially shorter covalent bond (1.758(1) vs. 2.044(2) Å, respectively, in **6a**). In this case the alternative reaction pathways are dictated by the presence or absence of α-protons; the aldol condensation Eqn (2) takes place preferentially over addition to the imino double bond Eqn (3), and the latter is only observed when the first pathway is unavailable.



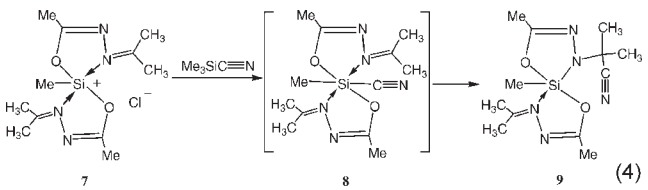
(3)

5a, R = Me
5b, R = CF_3
5c, R = t-Bu

6a, R = Me
6b, R = CF_3
6c, R = t-Bu

REARRANGEMENTS INVOLVING THE CYANIDE GROUP

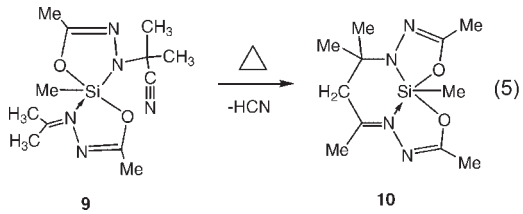
The selectivity order described above (preference for aldol condensation over addition to imino carbon) is completely reversed in the following reactions involving the cyanide group. Attempts to replace chloride by cyanide in a silicon complex via transsilylation, using Me_3SiCN Eqn (4), did not result in the expected hexacoordinate cyano-complex **8**, but in spontaneous addition of the cyano group to the imino carbon of one of the chelate rings (**9**), despite the availability of no less than 12 α-protons![8] Thus, when instead of the presumed alkyl carbanion in Eqn (2) a cyanide ion (also a carbon base) is present in the reaction, addition to the imino carbon becomes the overwhelmingly preferred reaction.[8]



(4)

The preference of the cyanide ion to add to the imino carbon, in contrast to the condensations of Eqs. 1 and 2, may be rationalized by reference to the Hard Soft Acid Base (HSAB) concept:[9,10,11] the cyanide is a soft base, and therefore prefers to react with the soft imino-carbon acid, rather than to abstract a hard proton acid.

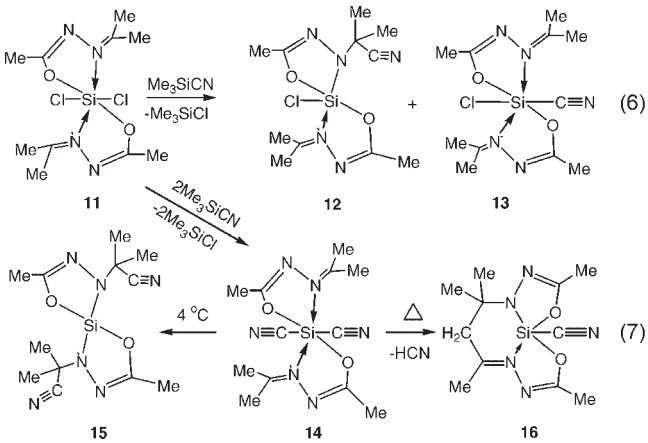
Traces of the intramolecular condensation product **10** are always found as a by-product along with **9** in the reaction shown in Eqn (4). **10** could, in principle, be either the result of chloride reacting with the reactant **7**, as in Eqn (1), or could result from cyanide acting as a base, abstracting a proton and initiating the condensation, or could be formed by rearrangement of **9**. When carefully purified **9** was heated for several hours in boiling chloroform, it eventually produced the rearrangement product **10** Eqn (5).[8] **10** was identified by its ^1H, ^{13}C and ^{29}Si NMR spectral analogy with the corresponding spectra of an authentic sample,[1] prepared and isolated from the rearrangement of **7**, and by the appearance of a distinct HCN signal at 108.8 ppm in the ^{13}C NMR spectrum of the reaction mixture.



(5)

9 **10**

The reaction takes a slightly different course when the dichloro complex **11** reacts with one molar equivalent of Me_3SiCN Eqn (6);[8] in addition to the major product (**12**) in which the cyanide group has added to the imino carbon, also the hexacoordinate complex (**13**) is found as a minor product in contrast to the total absence of **8** in the analogous reaction of the monochloro complex **7**, Eqn (4). The formation of **13** as a by-product in Eqn (6), and the lack of a similar product in Eqn (4), probably reflect the additional electron-withdrawal from silicon by the additional chloro ligand in **11**, resulting in a greater tendency of the silicon to attract donor ligands and, hence, a relatively more stable hexacoordinate complex **13**.



(6)

11 **12** **13**

(7)

15 **14** **16**

This greater tendency of silicon to form hexacoordinate complexes in the presence of electron-withdrawing ligands becomes even more evident when **11** is treated with two molar equivalents Me_3SiCN Eqn (7). The hexacoordinate dicyano complex (**14**) is now the major product.[8] Only upon prolonged heating (20 h) in boiling chloroform it eventually rearranges to the tricyclic cyano complex **16**. However, upon attempts to

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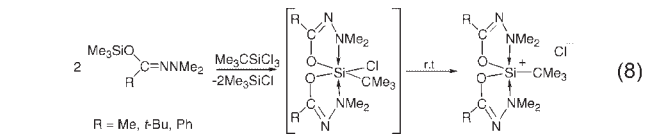
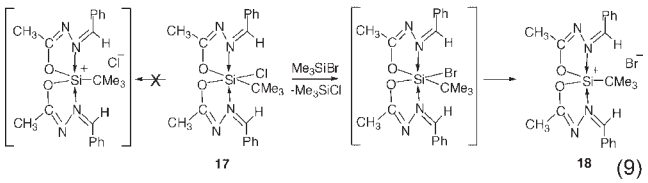
crystallize **14**, by keeping its chloroform solution at 4 °C for several days, the doubly rearranged **15** was obtained, with no trace of the pentacoordinate, singly rearranged, presumed intermediate.

Formation of **14** in the presence of excess Me_3SiCN provides indirect evidence that **12** does not form directly from **11**, but probably via initial formation of **13**: the latter is required for the formation of **14**, and thus the reactions leading from **13** to either **12** or **14** are competitive, and the outcome is dictated by the concentration of the reactant Me_3SiCN. If **13** were not the intermediate during formation of **12**, **14** would probably not form.

REACTIONS INVOLVING A *t*-BUTYL LIGAND AT HEXACOORDINATE SILICON

It has been shown previously that the bulky *t*-butyl ligand, when attached to silicon, causes an adjacent chloro ligand to dissociate already at room temperature Eqn (8), in contrast to less sterically-demanding ligands which cause significant dissociation only at lower temperatures (in CD_2Cl_2 solutions).[12] However, depending on the nature of the chelating ligand, a *t*-butyl ligand attached to silicon can act in a variety of different ways, described below. When the chelating ligand is substituted with relatively strong electron-withdrawing groups, such as in the benzylideneimino complex **17** (having phenyl and H groups pulling electrons from the donor-nitrogen through the imino double bond), silicon becomes sufficiently electron poor to resist ionic dissociation Eqn (9). **17** is the first undissociated hexacoordinate chlorosilicon complex with a *t*-butyl ligand. The solution ($CDCl_3$) ^{29}Si NMR spectrum of **17** showed two stereoisomers (−132.1 and −135.4 ppm) both of which were well within the hexacoordinate silicon resonance range. The hexacoordinate nature of one of the isomers was confirmed by an X-ray crystal analysis.[8]





This situation can easily be reversed by substitution of the chloro by the bulkier and better leaving group bromo ligand. Transsilylation of **17** with Me_3SiBr results in the dissociated *penta*coordinate *t*-butylsiliconium bromide (**18**). **18** was characterized by its single crystal X-ray analysis (Fig. 1, Table 1), that features a distorted trigonal bipyramid (TBP) geometry about the pentacoordinate silicon, and a well separated bromide counterion. The solid state structure agrees well with the solution ^{29}Si NMR chemical shift ($CDCl_3$ solution 300 K) of −79.6 ppm, characteristic of pentacoordination. Clearly, the tendency of silicon to keep the halogeno ligand attached, due to weak coordination by the relatively weak nitrogen donors, is counterbalanced by the steric bulk of the halogen, which in **18** is dominant and causes dissociation.

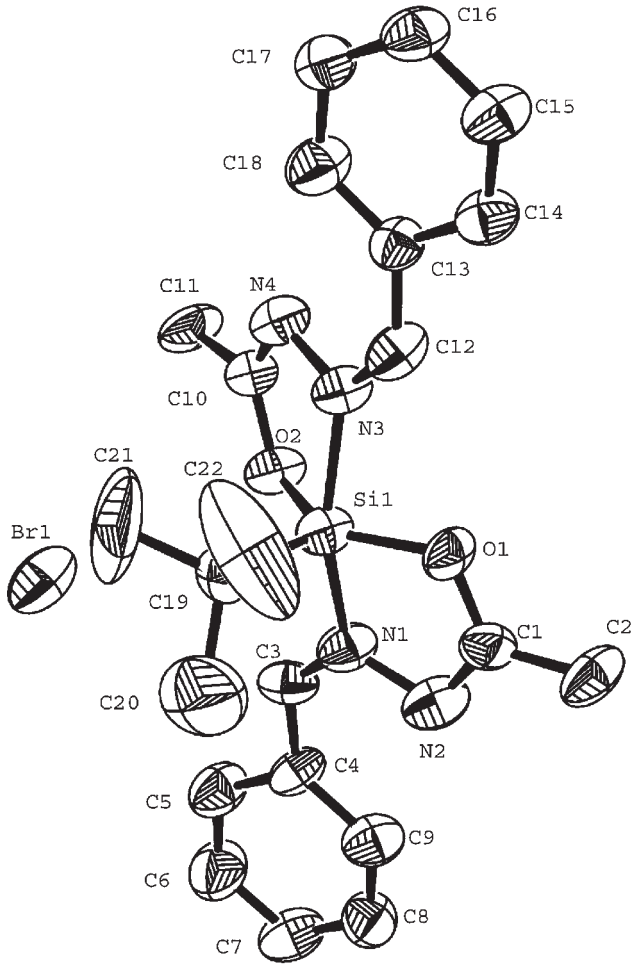
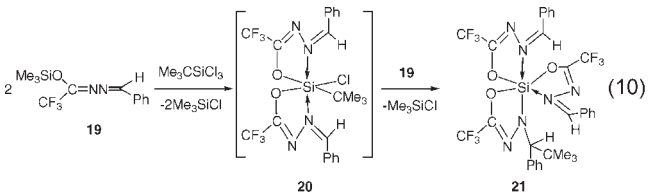


Figure 1. Molecular structure of **18** in the crystal, depicted at the 50% probability level. Hydrogen atoms omitted for clarity

Perhaps the most striking case of intramolecular rearrangement, involving the *t*-butyl ligand, is the following: synthesis of the dichelate **20** was attempted by transsilylation[13] of **19** with *t*-$BuSiCl_3$ as shown in Eqn (10). However, instead of the expected **20** a red crystalline *tri*chelate **21** was obtained. The latter was subjected to single crystal X-ray analysis, which confirmed its structure (Figure 2). Selected bond lengths and angles are presented in Table 1. **21** is the first of the hydrazide-derived silicon complexes[13] in which all three chlorine atoms of the $XSiCl_3$ precursor (X = *t*-Bu in the present case, and alkyl, aryl or halogens in others) have been replaced by the chelate-forming bidentate O—Si ligands.



Why is **21** different from so many previously reported hexacoordinate silicon dichelates of this family? The answer must relate to the exceptionally electron-withdrawing groups attached to the chelating (hydrazide derived) ligands. In each

Table 1. Selected bond lengths (Å) and angles (°) for **18** and **21**

18		21	
$Si–O_1$	1.695(2)	$Si–O_1$	1.7317(16)
$Si–O_2$	1.701(3)	$Si–O_2$	1.8054(15)
$Si–C_{19}$	1.894(2)	$Si–O_3$	1.7781(16)
$Si–N_3$	1.908(3)	$Si–N_2$	1.7873(18)
$Si–N_1$	1.908(2)	$Si–N_4$	1.9424(18)
$C_{12}–N_3$	1.302(3)	$Si–N_6$	1.9495(19)
$C_1–N_3$	1.310(4)	$C_3–N_2$	1.466(3)
$O_1–Si–O_2$	132.73(11)	$C_{16}–N_4$	1.291(3)
$O_1–Si–C_{19}$	113.60(13)	$C_{25}–N_6$	1.280(3)
$O_2–Si–C_{19}$	113.65(13)	$N_4–Si–N_6$	162.59(8)
$O_1–Si–N_3$	87.75(11)	$O_1–Si–O_3$	175.52(8)
$N_3–Si–N_1$	157.94(11)	$N_2–Si–O_2$	175.66(8)
$O_2–Si–N_1$	88.73(10)	$O_1–Si–N_4$	96.74(8)
$O_1–Si–N_2$	82.81(11)	$O_2–Si–N_4$	80.82(7)

chelate ring in the presumed intermediate **20** (and in two of the three in **21**) the donor nitrogen atom is part of a benzylideneimino group, with its relatively strong electron-withdrawing hydrogen and phenyl groups. In addition, the powerful electron-withdrawing CF_3 substituents in each ring make the donor nitrogen a very weak electron donor, even weaker than in **17** and **18** above. These chelating ligands are probably the weakest N-donor ligands of the hydrazide family prepared and reported so far.[13] As a result of this weak donor property, the coordination of nitrogen to silicon is weak, resulting in a relatively electron-poor silicon atom. This, in turn, causes the residual chloro ligand in **20** to resist ionic dissociation (in contrast to Eqn (8)).[12] Rather than dissociate, the chloro ligand of **20** is readily exchanged by the less-electronegative oxygen atom of a third chelating agent **19**, which also forms a substantially stronger bond to silicon.[14] Therefore, **20** quickly forms **21**, in which *three* of the hydrazide residues are ligated. Formation of **21** by attachment of a third hydrazide residue is accompanied by an intramolecular 1,3-*t*-butyl shift from silicon to the adjacent imino-carbon, replacing the relatively weak carbon–silicon bond by the stronger carbon–carbon bond,[14] and releasing the steric congestion caused by the *t*-butyl ligand, while closing a third chelate ring by attachment of the N-donor group to silicon. Thus the unusual **21** is formed, with the (unprecedented) three hydrazide-derived chelate rings, two of which have the benzylideneimino group, while the third imino double bond has been saturated by addition of a *t*-butyl group to the imino carbon.

The results described above demonstrate that in the same basic molecular system all three different species can be observed: the undissociated, hexacoordinate *t*-butylchlorosilicon dichelate **17**, the dissociated ionic (pentacoordinate) *t*-butylsiliconium bromide **18**, and when additional electron-withdrawing CF_3 substituents are introduced in the chelate rings, the *t*-butyl group migrates to the imino-carbon, making room for the attachment of a third chelating ligand and formation of the rearranged trichelate **21**.

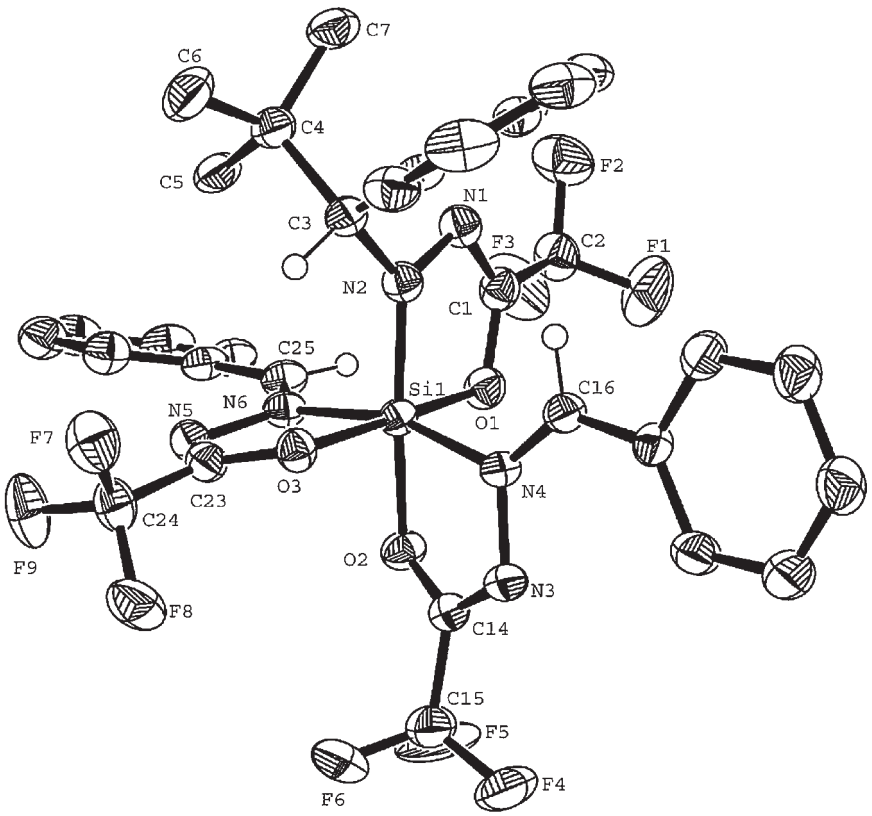


Figure 2. Molecular structure of **21** in the crystal, depicted at the 50% probability level. Hydrogen atoms, except the two imino hydrogens and one saturated imino hydrogen, were omitted for clarity

EXPERIMENTAL SECTION

The reactions were carried out under dry argon using Schlenk techniques. Solvents were dried and purified by standard methods. NMR spectra were recorded on a Bruker Avance DMX-500 spectrometer operating at 500.13, 125.76, and 99.36 MHz, respectively, for ^{1}H, ^{13}C and ^{29}Si spectra. Spectra are reported in δ (ppm) relative to TMS, as determined from standard residual solvent-proton (or carbon) signals for ^{1}H and ^{13}C and directly from TMS for ^{29}Si. 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.

Single crystal X-ray diffraction measurements were performed on a Nonius Kappa-CCD Diffractometer (**18**), and a Bruker Smart Apex on a D8-Goniometer (**21**). Crystallographic details are listed in Table 2. Crystallographic data for **18** and **21** have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers are listed in Table 2.

Bis[*N*-(benzylideneimino)acetimidato-*N′,O*]*tert*-butylsiliconium bromide(18)

A mixture of 1.013 g (4.32 mmol) of *N*-(benzylideneimino)*O*-(trimethylsilyl)acetimidate[6] and 0.458 (2.39 mmol) of *t*-$BuSiCl_3$ in 5 mL of chloroform was kept at room temperature for 48 h, followed by removal of volatiles under 0.2 mmHg. The white solid was washed in 10 mL of *n*-hexane to yield 0.895 g (94%) of **17**.[8] The product was stirred with 0.319 g (2.09 mmol) of Me_3SiBr in 5 mL of chloroform for 24 h. The white solid was isolated by decantation and vacuum drying to yield 0.926 g (90%), mp 173–174 °C. Crystals for X-ray diffraction analysis were grown from acetonitrile solution. Anal. Calcd for $C_{22}H_{27}BrN_4O_2Si$: C, 54.21; H, 5.58; N, 11.49. Found: C, 54.30; H, 5.73; N, 11.35. ^{1}H NMR ($CDCl_3$, 300 K): δ 1.02 (s, 9H, C_4H_9), 2.53 (s, 6H, Me), 7.56–8.73 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, 300 K): δ 18.3 (Me), 19.8 ($\underline{C}(CH_3)_3$), 27.0 ($C(\underline{C}H_3)_3$), 128.9, 129.2, 135.9, 136.4 (Ph), 161.7, 171.4 (C═N). ^{29}Si NMR ($CDCl_3$, 300 K): δ -79.6.

Bis[*N*-(benzylideneimino)trifluoroacetimidato-*N′,O*][*N*-(1-(*tert*-butyl)benzylamino)trifluoroacetimidato-*N′,O*]silicon(IV) (21)

A mixture of 1.292 g (4.48 mmol) of *N*-(benzylideneimino)*O*-(trimethylsilyl)trifluoroacetimidate (**19**) and 0.423 g (2.21 mmol) of *t*-$BuSiCl_3$ in 5 mL of chloroform was kept at 100 °C for 170 h. The volatiles were removed under reduced pressure leaving a viscous orange residue that formed red crystals after treating with 5 mL *n*-hexane. 0.48 g (41%) of **21** was isolated, mp. 108–110 °C. Anal. Calcd for $C_{31}H_{27}F_9N_6O_3Si$: C, 50.96; H, 3.72; N, 11.50. Found: C, 50.65; H, 3.74; N, 11.38. ^{1}H NMR ($CDCl_3$, 300 K): δ 0.86 (s, 9H, C_4H_9), 3.89 (s, 1H, N–CH) 7.06 - 8.35 (m, 15H, Ph), 7.24, 8.11 (2s, N═CH). ^{13}C NMR ($CDCl_3$, 300 K): δ 28.4 ($\underline{C}(CH_3)_3$), 37.5 ($C(\underline{C}H_3)_3$), 117.5 (q, $^{1}J_{C-F} = 280$ Hz, CF_3), 126.2–142.8, (Ph), 159.2, 160.5 (C═N), 153.0, 158.3 ($CF_3\underline{C}$═N). ^{29}Si NMR ($CDCl_3$, 300 K) δ -149.8.

Table 2. Crystal data and experimental parameters for the structure analyses of **18** and **21**

	18	**21**
CCDC number	681007	681008
Empirical formula	$C_{46}H_{57}Br_2N_9O_4Si_2$	$C_{31}H_{27}F_9N_6O_3Si$
Form mass (g mol^{-1})	1016.01	730.68
Collection T, K	240(1)	133(2)
Cryst. syst.	Triclinic	Orthorhombic
Space group	$P\overline{1}$	Pbca
a (Å)	10.232(2)	18.367(1)
b (Å)	10.486(2)	18.285(1)
c (Å)	26.163(5)	19.431(1)
α (°)	94.97(2)	90
β (°)	92.14(2)	90
γ (°)	118.70(3)	90
V (Å^3)	2442.9(8)	6525.6(6)
Z	2	8
ρcalc, (Mg/m^3)	1.360	1.487
F (000)	1052	2992
θ range (°)	2.27–25.02	1.89–24.85
No. of coll. reflns	16355	73735
No. of indep. reflns	8409	5641
*R*int	0.0406	0.1048
No. of reflns used	8409	5641
No. params.	570	514
Goof	0.968	0.927
R1 w*R*2[$I > 2\sigma(I)$]	0.0423 0.1028	0.0388 0.0773
R1 w*R*2(all data)	0.0774 0.1104	0.0704 0.0846
Max./min. res electron dens (eÅ^{-3})	0.481/0.386	0.373/0.172

Acknowledgements

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