Hydride Migration from Silicon to an Adjacent Unsaturated Imino Carbon: Intramolecular Hydrosilylation

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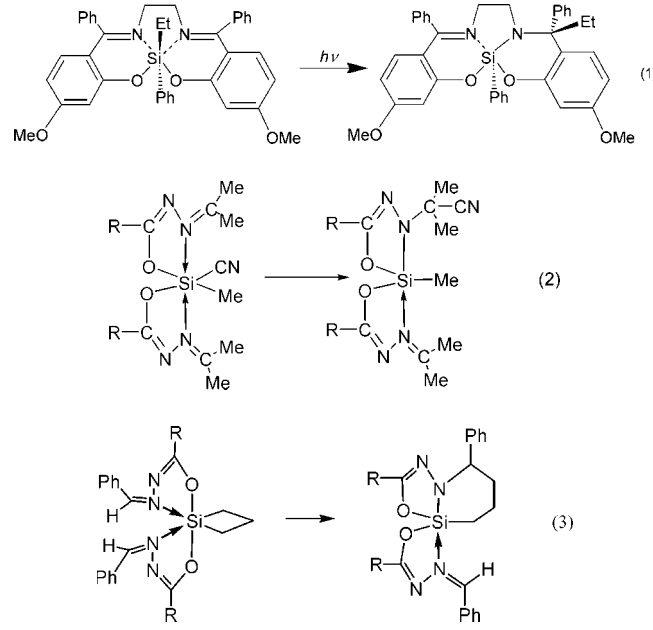
Received May 11, 2008

1,3-Hydride shift from silicon to an adjacent imino carbon ("intramolecular hydrosilylation") is observed in the reaction of $MeSiHCl_2$ with *O*-trimethylsilyl-*N*-(alkylidenimino)imidates [$RC(OSiMe_3)=NN=CR^1R^2$; R = Me, Ph, CH_2Ph, *t*-Bu; R^1, R^2 = Me (**1**), $(CH_2)_n$ (**9**), Ph, H (**14**)], leading to pentacoordinate silicon complexes. The reaction proceeds further to rearrange to the tricyclic pentacoordinate complexes, observed previously as products of intramolecular aldol condensation of imine moieties residing on two chelate rings in the reactions of $XSiCl_3$ (X = alkyl, aryl) and **1**.

Introduction

Hydrido-silicon hypercoordinate[1] complexes have previously been shown to reduce carbonyl[2,3a] and related (isocyanate)[3b] compounds by hydride transfer in the absence of a metal catalyst. Recently *intra*molecular 1,3-hydride shift to a trans-azobenzene moiety has been reported, catalyzed by a fluoride anion, leading to its reduction to the corresponding hydrazobenzene.[4] Reduction presumably was facilitated by the initial conversion of tetracoordinated to higher coordination silicon by reaction with fluoride. Intramolecular 1,3-shifts of *carbon* ligands in hexacoordinate silicon complexes have also been reported: photochemical rearrangement of an alkyl group to a C=N carbon (eq 1)[5] and thermal rearrangements of a cyano ligand (eq 2)[6] and a silacyclobutane-ring residue (eq 3).[7] A similar thermal 1,3-migration of a silicon moiety from a hypercoordinate disilane was reported by Roewer and Wagler.[8]



The present paper describes the facile and spontaneous uncatalyzed intramolecular 1,3-hydride transfer from a formally hexacoordinate silicon to an adjacent imino carbon atom, saturating the double bond and constituting an intramolecular hydrosilylation.

Results and Discussion

O-(Trimethylsilyl)hydrazide derivatives **1** with equimolar amounts of dichloromethylsilane (**2**) undergo a transsilylation reaction, producing Me_3SiCl and the cyclic pentacoordinate complex **3** (eq 4). Addition of a second molar equivalent of **1**, or reaction of a 2:1 reactant ratio of **1** and **2**, respectively, does

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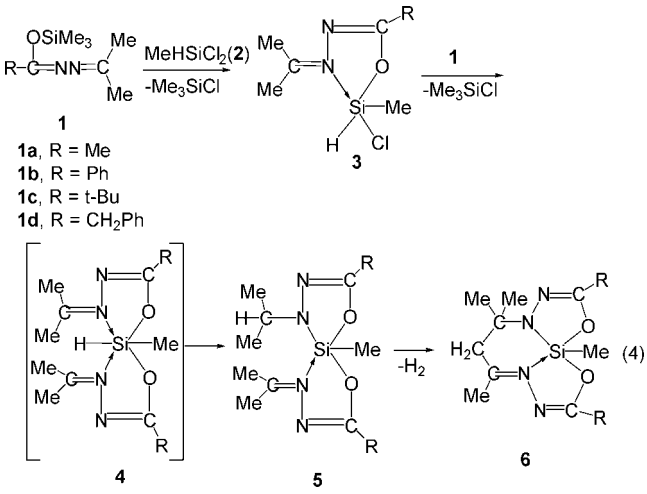
10.1021/om800427x CCC: $40.75
Publication on Web 09/23/2008

not result in the expected hexacoordinate hydrido complex **4**. Instead, a high yield of the dichelate **5** was obtained, as a result of a 1,3-hydride shift and addition to the imino double bond, evident by the disappearance of the $^{1}J_{(H,Si)}$ doublet in the ^{29}Si NMR spectrum and appearance of the typical isopropyl resonances in the ^{1}H spectrum. The rearrangement closely resembles an uncatalyzed intramolecular hydrosilylation, involving Si−H bond cleavage and addition to the imino double bond; conversion of the dative to a fully covalent N−Si bond constitutes silicon addition to the imino nitrogen. **5** might have been formed directly from **1** and **3**, or it could have been formed through **4** as an intermediate, by a rapid rearrangement. However, **4** could not be observed or isolated.



Interestingly, in the initial step of the reaction, in **3**, the hydrogen atom is still attached directly to silicon, as apparent by the doublet due to the $^{1}H-^{29}Si$ coupling of the silicon resonance ($^{1}J_{Si-H}$ = 317−322 Hz). It is only later, during the attachment of a second bidentate ligand and chelate ring formation (producing **5**), that hydride shift takes place.

The structures of **5a** and **5d** were confirmed and characterized by crystallographic analyses, depicted in Figures 1 and 2, respectively. Selected bond lengths and angles are listed in Table 1. Examination of the data in Table 1 shows that both products have very similar molecular structures in the solid state, namely, slightly distorted trigonal bipyramids (TBP). In each of the structures there are two N−Si bonds, one short (1.729(3), 1.736(6) Å) occupying equatorial positions, and the other one long (2.044(3), 2.020(6) Å, respectively) in axial positions.[9] In both of the crystals the sum of equatorial bond angles amounts to 360° (±0.5°), meaning that silicon sits precisely in the equatorial plane.

The tricyclic rearrangement products **6a**,[10a] **6b**,[10b] and **6d**[10b] were characterized by comparison with authentic compounds, obtained previously from the rearrangement of the corresponding chloride complexes **7**, synthesized from the corresponding hydrazide precursors **1** and $MeSiCl_3$ (eq 5).[10] Additional support comes from the crystal structure analysis of **6c**, obtained directly in the present reaction (eq 4, Figure 3) from **1c** and **2** (as opposed to **1c** and $MeSiCl_3$, eq 5). Selected bond lengths and angles are listed in Table 1.

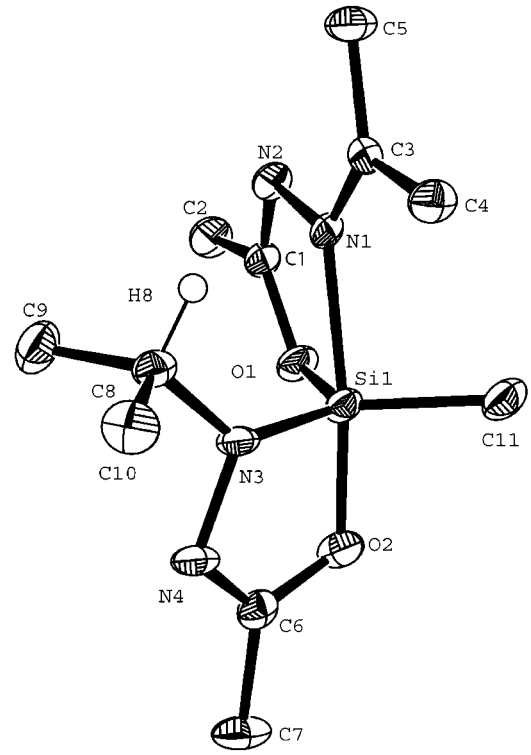


Figure 1. Crystallographic molecular structure of **5a**, depicted at the 50% probability level. Hydrogen atoms have been omitted, except for the shifted hydrogen.

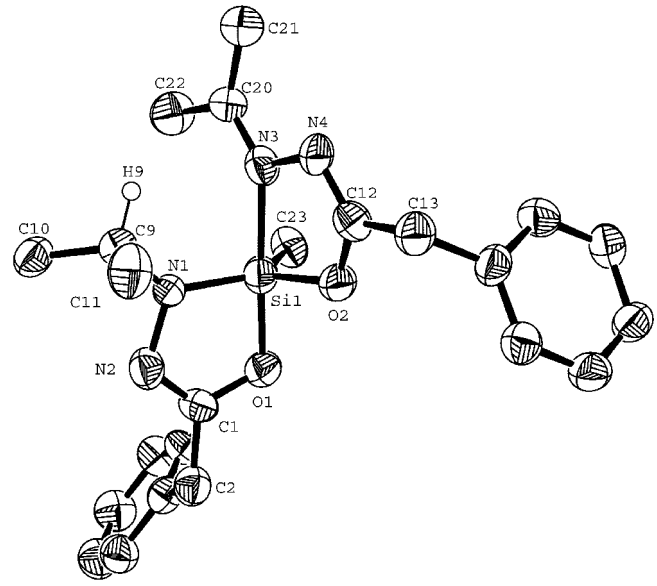


Figure 2. Crystallographic molecular structure of **5d**, depicted at the 50% probability level. Hydrogen atoms have been omitted, except for the shifted hydrogen.

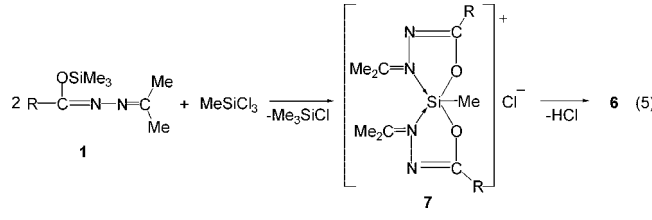


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Table 1. Selected Crystallographic Bond Lengths and Angles for 5a, 5d, 6c, 12a, 12c, 13, and 15a

5a		5d		6c		12a		12c		13		15a	
Bond Lengths (Å)													
Si−O(1)	1.715(3)	Si−O(1)	1.737(5)	Si−O(1)	1.7328(17)	Si−O(1)	1.7506(13)	Si−O(1)	1.7417(13)	Si−O(1)	1.7303(16)	Si−O(1)	1.7543(15)
Si−O(2)	1.748(3)	Si−O(2)	1.712(5)	Si−O(2)	1.7205(17)	Si−O(2)	1.7299(13)	Si−O(2)	1.7357(14)	Si−O(2)	1.7431(15)	Si−O(2)	1.7946(16)
Si−N(1)	2.044(3)	Si−N(3)	2.020(6)	Si−N(2)	1.981(2)	Si−N(3)	1.9485(16)	Si−N(1)	1.9768(16)	Si−N(2)	2.0756(18)	Si−N(3)	1.9238(18)
Si−N(3)	1.729(3)	Si−N(1)	1.736(6)	Si−N(3)	1.7288(16)	Si−N(2)	1.7533(15)	Si−N(3)	1.7360(16)	Si−N(4)	1.7401(18)	Si−N(1)	1.7236(17)
Si−C(11)	1.857(4)	Si−C(23)	1.843(7)	Si−C(7)	1.861(2)	Si−C(25)	1.858(2)	Si−C(31)	1.864(2)	Si−C(25)	1.855(2)	Si−C(19)	1.858(2)
C(8)−N(3)	1.473(5)	C(9)−N(1)	1.473(8)	C(5)−N(3)	1.459(3)	C(20)−N(2)	1.489(2)	C(16)−N(3)	1.475(2)	C(20)−N(2)	1.515(3)	C(10)−N(4)	1.311(3)
C(1)−N(2)	1.287(5)	C(12)−N(4)	1.288(8)	C(4)−N(2)	1.270(3)	C(15)−N(3)	1.286(2)	C(9)−N(1)	1.289(2)	C(16)−N(4)	1.463(3)	C(1)−N(2)	1.275(3)
Bond Angles (deg)													
O(2)SiN(1)	171.76(13)	O(1)SiN(3)	172.8(2)	O(2)SiN(2)	163.01(9)	O(2)SiN(3)	160.36(7)	O(2)SiN(1)	163.77(7)	O(2)SiN(2)	164.92(8)	O(1)SiN(3)	89.71(7)
O(1)SiN(3)	118.13(15)	O(2)SiN(1)	117.7(3)	O(1)SiN(3)	132.22(9)	O(1)SiN(2)	136.28(7)	O(1)SiN(3)	131.27(8)	O(1)SiN(4)	128.75(9)	O(1)SiN(1)	86.00(7)
O(2)SiN(3)	86.91(4)	O(1)SiN(1)	87.2(3)	O(2)SiN(3)	86.78(8)	O(2)SiN(2)	86.96(7)	O(2)SiN(3)	87.09(7)	O(2)SiN(4)	86.90(7)	O(1)SiO(2)	166.71(7)
O(1)SiN(1)	80.76(13)	O(2)SiN(3)	81.0(2)	O(1)SiN(2)	80.01(8)	O(1)SiN(3)	80.38(6)	O(1)SiN(1)	80.47(6)	O(1)SiN(2)	80.62(7)	O(2)SiN(3)	80.87(7)
O(2)SiO(1)	92.39(14)	O(2)SiO(1)	93.0(2)	O(2)SiO(1)	90.80(8)	O(2)SiO(1)	88.64(6)	O(2)SiO(1)	90.21(7)	O(2)SiO(1)	89.13(7)	O(2)SiN(1)	91.28(8)
N(3)SiN(1)	92.27(14)	N(1)SiN(3)	92.1(3)	N(3)SiN(2)	88.90(8)	N(3)SiN(2)	89.79(7)	N(3)SiN(1)	89.14(7)	N(4)SiN(2)	90.90(8)	N(1)SiN(3)	123.09(8)
C(11)SiN(1)	92.25(16)	C(23)SiN(3)	93.2(3)	C(7)SiN(3)	121.13(11)	C(25)SiN(2)	118.17(10)	C(31)SiN(3)	123.74(9)	C(25)SiN(4)	121.61(11)	C(19)SiN(1)	126.26(10)
C(11)SiN(3)	128.83(18)	C(23)SiN(1)	130.0(3)	C(7)SiN(2)	94.13(10)	C(25)SiN(3)	95.71(10)	C(31)SiN(1)	95.07(9)	C(25)SiN(2)	94.41(9)	C(19)SiN(3)	110.56(9)
C(11)SiO(1)	112.90(17)	C(23)SiO(2)	112.1(3)	C(7)SiO(1)	106.03(9)	C(25)SiO(1)	105.21(9)	C(31)SiO(1)	104.63(9)	C(25)SiO(1)	109.44(10)	C(19)SiO(1)	97.71(10)
C(11)SiO(2)	94.65(16)	C(23)SiO(1)	92.7(3)	C(7)SiO(2)	102.17(10)	C(25)SiO(2)	102.89(9)	C(31)SiO(2)	100.15(9)	C(25)SiO(2)	99.45(9)	C(19)SiO(2)	94.40(10)

Figure 3. Crystallographic molecular structure of **6c**, depicted at the 50% probability level. Hydrogen atoms have been omitted.

Formation of **6** in this reaction (eq 4) is rather peculiar. **6** and similar tricyclic compounds were reported previously as products of a facile intramolecular rearrangement of pentacoordinate siliconium chlorides (**7**) and their analogues, constituting an internal aldol condensation of the two imine groups of **7**.[10] This is clearly *not* the case in the present reaction, since there is only one imine function left in **5**. Conversion of **5** to **6** might take place via an equilibrium reaction through **4** as an unstable intermediate, leading eventually to the thermodynamic product **6** through intramolecular aldol condensation. Alternatively, **5** may rearrange directly with formation of H−H and C−C bonds and simultaneous cleavage of two C−H bonds, possibly through a four-membered cyclic transition state (**8**). The latter step may be assisted by preliminary imine−enamine tautomerism, as suggested in **8′**, followed by H_2 elimination and C−C formation through a six-membered cyclic transition state. This mechanism is further discussed below.

8

8'

The progress of the reaction of **1a** and **2** was monitored by ^{29}Si NMR spectroscopy using a toluene-d_8 solution. The reaction proceeded at ambient temperature, and its progress is depicted in Figure 4. Examination of Figure 4 shows that initially **3a** is formed as an intermediate followed by formation of **5a** (Figure 4A). This is accompanied by a trace of another product, identified as the tricyclic rearrangement product **6a**. After 1 h **3a** has completely reacted to form the hydride-shift product **5a**, along with a growing amount of **6a** (Figure 4B). This process was accompanied by evolution of gas bubbles, suggesting that **5a** might have been converted to **6a** with evolution of hydrogen, as shown in eq 4. The mixture was then heated in an oil bath

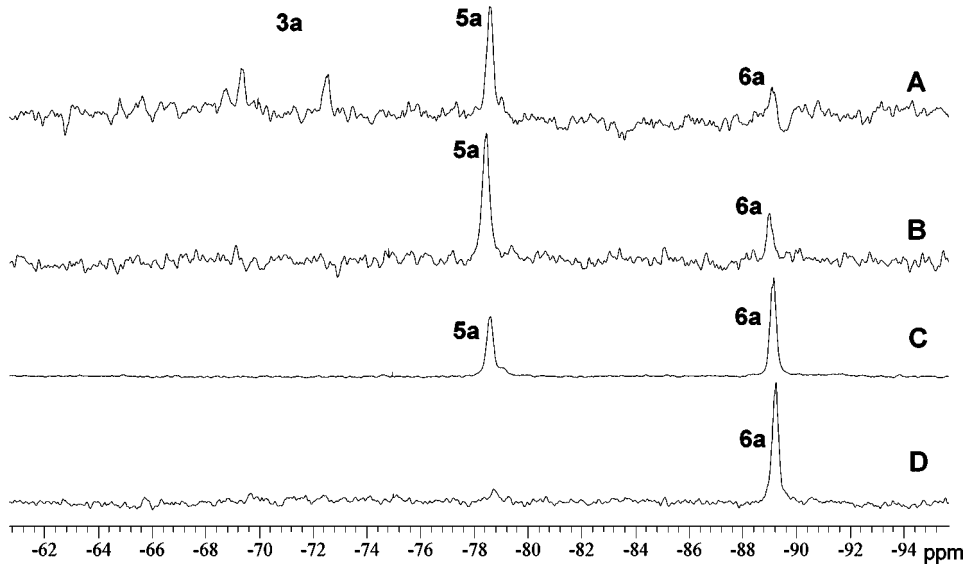
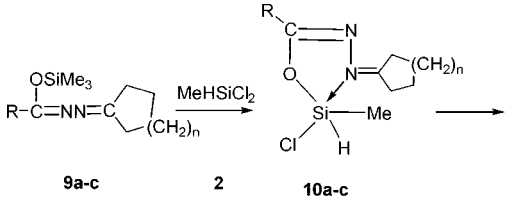


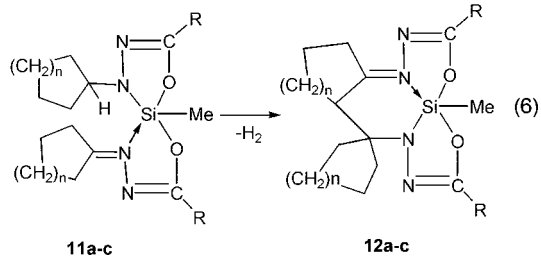
Figure 4. ^{1}H-coupled ^{29}Si NMR monitoring of the progress of the reaction of **1a** with **2** in toluene-d_8 solution (only the high-field portion shown). (A) Minutes after admixture, the monochelate product **3a** has formed (d, $^{1}J_{(Si-H)} = 317$ Hz) and reacted further, yielding dichelate **5a**. Traces of rearranged **6a** are also apparent. (B) After 1 h, all of **3a** has reacted to form **5a** and **6a**. (C) Progress of the reaction after heating for 1 h in an oil bath at 80 °C. (D) After 7 h at 80 °C, a single product **6a** is found.

at 80 °C for 7 h, after which **6a** was obtained almost quantitatively (Figure 4D).

Hydride shift is also observed in the reactions of cycloalkanone-imine analogues of **1** (**9**) with **2** (eq 6). The reactions proceed in a similar manner to that of the acyclic imine precursors; that is, the initial hydride shift product **11** eventually continues to rearrange to form the tricyclic **12**. **11c** appears to be less stable than **11a** and **11b** and rearranges spontaneously to **12c** within hours in solution. When synthesized, it is accompanied by about 10% of **12c** and as a result has only been characterized by NMR spectral analogy with **11a** and **11b**.

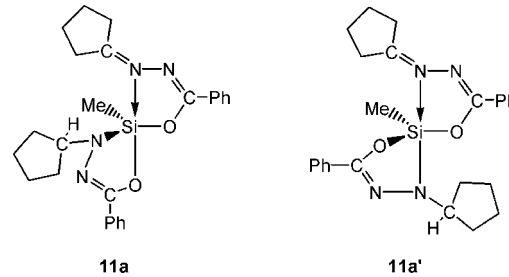


a, R = Ph, n = 1
b, R = Ph, n = 2
c, R = CH_2Ph, n = 3



11a is formed as two distinct diastereomers in equal concentrations, which interchange in $CDCl_3$ solution at a rate compatible with the NMR time scale. At temperatures below 270 K all of the NMR signals double as a result of slowing of the exchange. The temperature-dependent ^{29}Si and ^{13}C NMR spectra reflecting this exchange are shown in Figure 5.

Since neither of the diastereomers of **11a** could be isolated and crystallized for a structural analysis, their exact geometries are unknown. However, it seems likely that the isomers differ in the ligand arrangement about the pentacoordinate silicon center: the relatively long dative N→Si bond generally occupies the axial position, as is found, for example, in the analogous **5a** (Figure 1). Opposite of this bond in **5a** is an oxygen atom, but it is quite reasonable to assume that also the covalently bound nitrogen could occupy the opposing axial position, as was observed previously in numerous SiN_2O_2C dichelates.[11−13] Thus, it is likely that the two diastereomers observed in the NMR spectra of **11a** have the geometries shown schematically in **11a** and **11a′**. However, a structure with both N−Si bonds in equatorial positions cannot be ruled out, in view of the structure found for **15a**, discussed below.



A trace of this behavior is also found in the cyclohexylidene-imino complex **11b**, in which the relative diastereomer population ratio is ∼10:1. A single isomer was observed in the NMR spectra of the cycloheptanone derivative **11c**, i.e., no separation of diastereomers.

12a and **12c** were characterized by single-crystal X-ray analyses, obtained after recrystallization from *n*-hexane solutions. The molecular structures in the solid are depicted in Figures 6 and 7, respectively, and selected bond lengths and angles are listed in Table 1.

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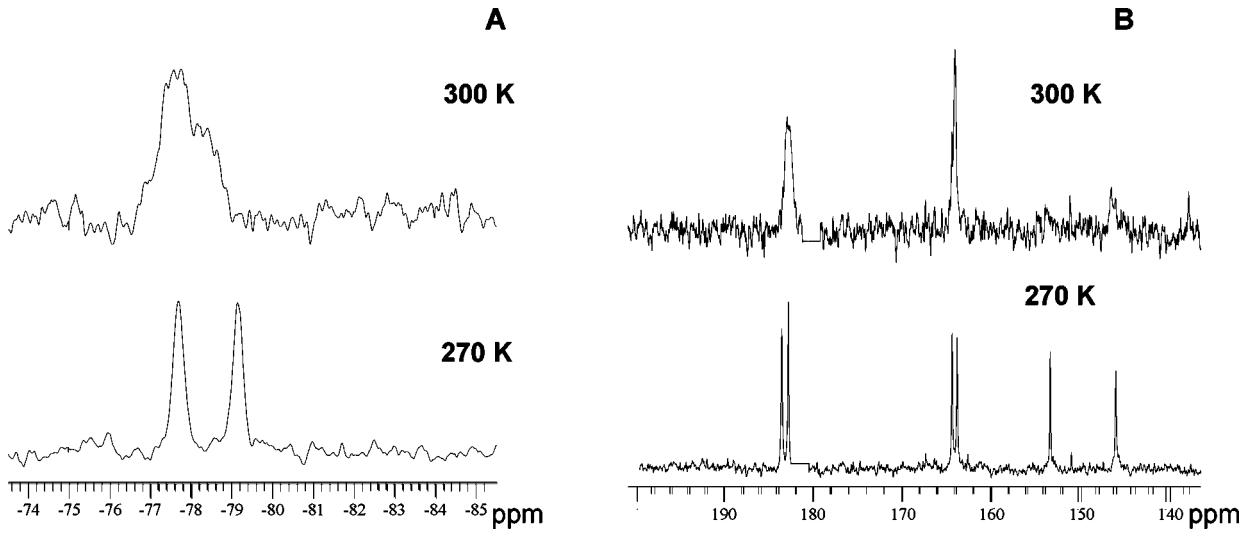


Figure 5. ^{29}Si (A) and ^{13}C (B) NMR spectra of **11a** in $CDCl_3$ solution at 270 and 300 K, reflecting the exchange of two isomers (low-field portion shown in B).

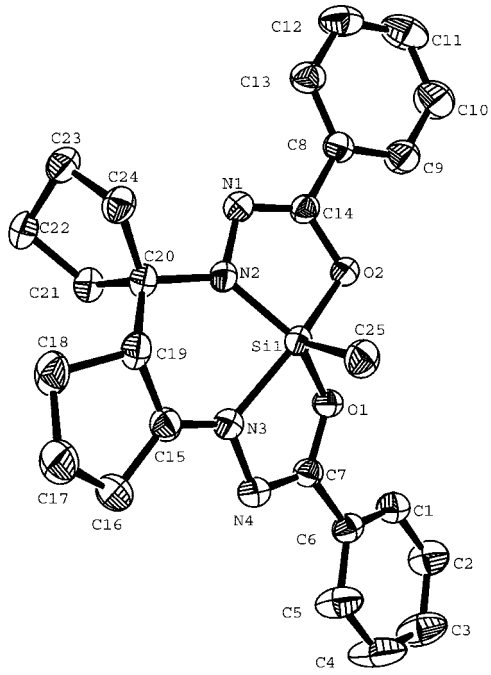
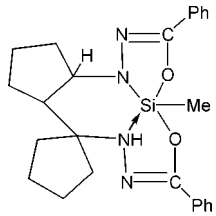


Figure 6. Crystallographic molecular structure of **12a**, depicted at the 50% probability level. Hydrogen atoms have been omitted.

Within the orange crystals of **12a** a few different yellow crystals were found and manually separated (**13**). A single crystal of **13** was isolated and subjected to crystallographic analysis, revealing a *hydrogenated* **12a** (Figure 8, Table 1). Formation of **13** supports the mechanism mentioned above through an enamine (**8′**), which is detailed below (eq 7).



13

A reaction pathway that accounts for the formation of **13** is shown in eq 7.[14] The imine-α hydrogen in **11a** (**H**) is sufficiently acidic and may be abstracted by the nitrogen of the opposing chelate ring to form the enamine intermediate (**I**), through a six-membered cyclic transition state.[15] This is followed (in the second step) by addition to the enamine double bond with migration of the α-hydrogen (*H*) and formation of the C−C bond to form **13**. **13** then undergoes (third step) 1,4-hydrogen elimination by association of a positively polarized hydrogen (**H**) with a negatively polarized (*H*) hydrogen atom, forming **12a**, again through a six-membered cyclic transtion state, involving exchange of nitrogen coordination to silicon. The dehydrogenation step is supported by reported spontaneous dehydrogenations in similar amine-imine systems, although in the presence of a transition metal.[16] A possible alternative is simultaneous formation of the C−C bond and hydrogen elimination from **I** to form **12a** and formation of **13** by hydrogenation of the imino double bond in **12a** (since hydrogen is present in the system).

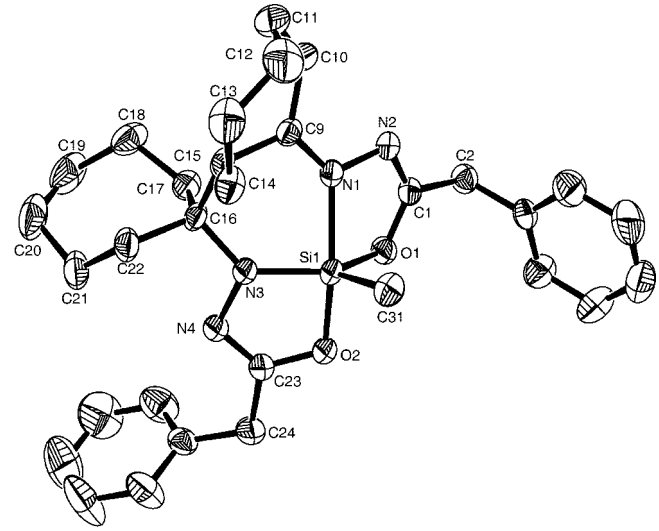


Figure 7. Crystallographic molecular structure of **12c**, depicted at the 50% probability level. Hydrogen atoms have been omitted.

(14) We thank a referee for suggesting this pathway.
(15) For similar enamine formation see: ref 9 and citations therein.
(16) Taylor, M. K.; Reglinski, J.; Berlouis, L. E. A.; Kennedy, A. R. *Inorg. Chim. Acta* **2006**, *359*, 2455–2464.

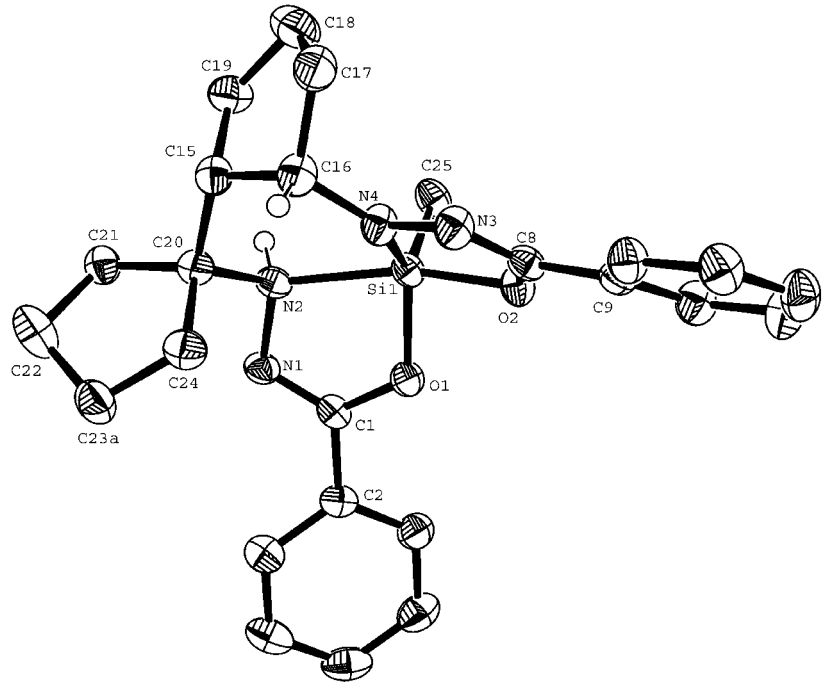
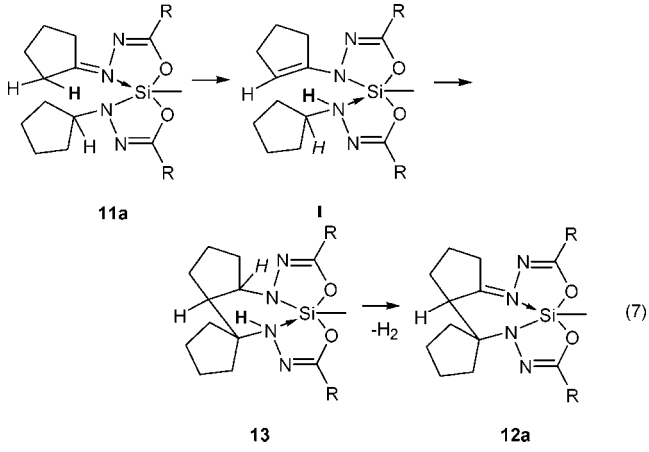


Figure 8. Crystallographic molecular structure of **13**, depicted at the 50% probability level. Hydrogen atoms, except those on N2 and C16, have been omitted.



In order to avoid the complication of the hydride-shift reaction by additional conversion to **6** (eq 4) or **12** (eq 6), the isopropylidene-imino groups in the starting material **1** were replaced by an imine group lacking α-hydrogen atoms: the benzylidene-imino donor group in **14** (eq 8). Indeed, reaction of **14** with **2** led smoothly to the hydrogen-shifted dichelate complexes **15**, in accord with the reactions leading to **5** and to **11** (above), but with no further molecular rearrangement. **15a**−**d** were identified by their NMR spectra, in particular the appearance of a typical AB quartet due to the prochiral CH_2Ph group at 4.5 ppm (J_{AB} = 15−17 Hz) in the ^1H spectrum, the corresponding ^{13}C NMR signal at 52−53 ppm, and the observation of three unique imino-carbon signals within the range 140−180 ppm.

15a was further characterized by a single-crystal X-ray diffraction analysis (Figure 9). Selected bond lengths and angles are listed in Table 1. Interestingly, *both* of the nitrogen atoms bound to silicon occupy equatorial positions, despite the fact that one of these bonds is dative [1.924(2) Å] and the other covalent [1.724(2) Å]. We are aware of only one previous example of a dative nitrogen atom attached to pentacoordinate silicon in an equatorial position.[13] In that example the nitrogen donor atom was part of a dimethylamino group, whereas in **15a** it is an imino-nitrogen.

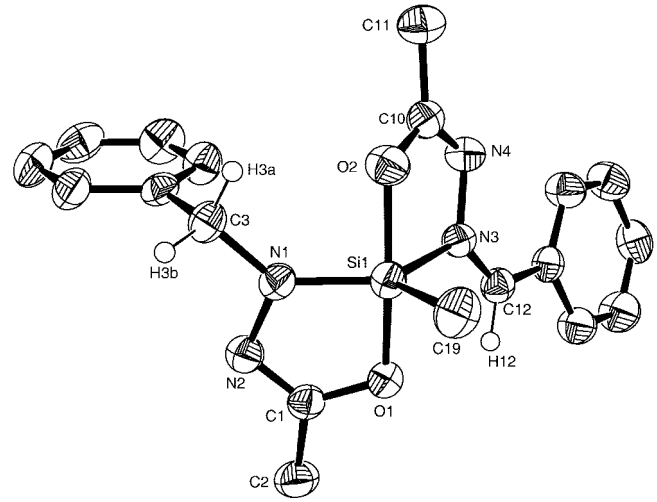
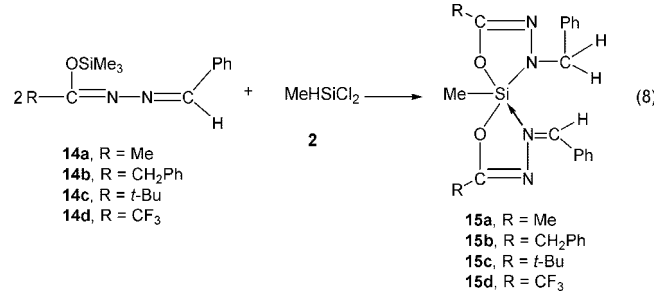


Figure 9. Crystallographic molecular structure of **15a**, depicted at the 50% probability level. Hydrogen atoms have been omitted, except for the imino and benzylic hydrogens.



Also in the series **15a**−**d**, like in **11a**−**c**, diastereomers are found in solution in the various NMR spectra. While in **11** the diastereomer ratio decreases from **11a** to **11c**, following the cycloalkanone-imine ring size, in **15** the population ratio depends

Table 2. Crystallographic Data and Experimental Parameters for the Structure Analyses of 5a, 5d, 6c, 12a, 12c, 13, and 15a

	5a	5d	6c	12a	12c	13	15a
CCDC no.	684647	684648	684649	684650	696871	684651	696872
empirical formula	$C_{11}H_{22}N_4O_2Si$	$C_{23}H_{30}N_4O_2Si$	$C_{17}H_{32}N_4O_2Si$	$C_{25}H_{28}N_4O_2Si$	$C_{31}H_{40}N_4O_2Si$	$C_{25}H_{30}N_4O_2Si$	$C_{19}H_{22}N_4O_2Si$
form mass, g mol^{-1}	270.42	422.60	352.55	444.60	528.76	446.62	366.50
collection *T*, K	140(2)	140(1)	200(2)	273(2)	240(1)	273(2)	240(2)
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic
space group	*P*2(1)/*n*	*P*2(1)/*c*	$P\bar{1}$	*P*2(1)/*n*	$P\bar{1}$	*P*2(1)/*n*	$P\bar{1}$
a, Å	8.437(3)	10.359(2)	9.683(2)	9.0893(18)	9.691(2)	14.293(2)	8.320(2)
b, Å	12.084(9)	20.350(4)	11.351(2)	20.272(4)	11.134(2)	10.3528(16)	9.969(2)
c, Å	14.081(5)	11.092(2)	11.490(2)	12.872(3)	14.777(3)	15.528(3)	11.555(2)
α, deg	90	90	115.096(3)	90	80.57(2)	90	91.54(2)
β, deg	90.94(2)	95.56(2)	110.270(3)	103.255(3)	89.28(2)	99.007(3)	99.44(3)
γ, deg	90	90	95.533(4)	90	68.48(2)	90	90.17(2)
V, Å^3	1435.4(13)	2327.3(8)	1027.9(3)	2308.6(8)	1461.3(5)	2269.5(6)	945.0(3)
Z	4	4	2	4	2	4	2
ρ_{calcd}, Mg/m^3	1.251	1.207	1.139	1.279	1.202	1.307	1.288
F(000)	584	904	192	944	568	952	388
θ range, deg	2.22−25.99	1.98−25.24	2.07−26.55	1.91−28.39	2.23−25.01	1.80−28.36	2.04−25.89
no. of coll. reflns	10 987	15 752	6012	14 805	16 164	13 700	11 506
no. of indep reflns	2698	4026	4112	5404	5077	5261	3531
R_{int}	0.0980	0.0990	0.0302	0.0385	0.0432	0.0483	0.0350
no. of reflns used	2698	4045	4112	5404	5077	5261	3531
no. of params	163	275	318	401	343	418	235
Goof	1.029	0.895	1.062	1.043	0.859	1.040	1.128
R1, wR2 [$I > 2\sigma I$)]	0.0677, 0.1764	0.0974, 0.2268	0.0576, 0.1698	0.0479, 0.1163	0.0456, 0.1301	0.0521, 0.1243	0.0431, 0.1208
R1, wR2 (all data)	0.1209, 0.1932	0.2190, 0.2624	0.0631, 0.1768	0.0830, 0.1317	0.0602, 1395	0.0923, 0.1433	0.0615, 0.1278
max./min. res electron dens, e Å^{-3}	0.535 −0.505	0.497 −0.394	0.510 −0.518	0.284 −0.248	0.351 −0.314	0.380 −0.343	0.378 −0.324

on the size of the ring substituent R. **15a** features two equally populated isomers, evident by doubling of all of the NMR signals. When R = benzyl, in **15b**, this ratio becomes 5:95, while no diastereomer separation is observed in **15c** and **15d**.

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.

Compounds **1a**,[10] **1b**,[17] **1d**,[17] **6a**,[10] **6b**,[17] **6c**,[17] **14a**,[7] and **14d**[7] were described previously. Analogues of **14a** were prepared similarly and are reported below.

Single-crystal X-ray diffraction measurements were performed on a Bruker Smart Apex on D8-goniometer. Crystallographic details are listed in Table 2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers are listed in Table 2.

***O*-(Trimethylsilyl)-*N*-(isopropylidenimino)pivaloimidate (1c).** A solution of 42.0 g (0.41 mol) of pivalic acid with 35 mL (0.81 mol) of MeOH and 1 mL of H_2SO_4 was boiled under reflux for 48 h. After cooling to room temperature the upper organic phase was separated and dissolved in 50 mL of Et_2O. The solution was washed with 3 × 50 mL of saturated NaCl solution and dried with $MgSO_4$. A neat mixture of the crude methyl pivaloate (27 g, 0.23 mol) and $H_2NNH_2 \cdot H_2O$ (11.5 g, 0.23 mol) was heated in an oil bath at 100 °C for 2 weeks. The volatiles were removed under reduced pressure (0.5 mmHg), and an azeotropic distillation of toluene and water was carried out to dryness. The resultant solid was dissolved in 100 mL of dry acetone and boiled for 2 h. The solvent was evaporated to dryness and the residue dissolved in 150 mL of ether. To the solution was added 9.1 g (0.09 mol) of Et_3N, and 9.8 g (0.09 mol) of Me_3SiCl was added dropwise over 1 h, followed by 5 h of reflux. After cooling the Et_3NHCl was filtered under argon and the solid washed twice with ether (2 × 20 mL). The solvent was removed from the combined solution under reduced pressure, followed by distillation. The fraction boiling at 80 °C at 10 mmHg was collected as **1c**, 15 g (71% yield). ^{1}H NMR ($CDCl_3$, 295 K): *δ* 0.23 (s, 9H, $SiCH_3$), 1.16 (s, 9H, $C(CH_3)_3$), 1.95, 1.98 (2s, 6H, $N{=}C(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 295 K): *δ* 1.8 ($SiCH_3$), 17.9, 24.5 ($N{=}C\underline{Me}_2$), 27.6 ($C(\underline{C}H_3)_3$), 37.0 ($\underline{C}(CH_3)_3$), 162.9, 164.2 (C═N).^{29}Si NMR ($CDCl_3$, 295 K): *δ* 16.2. Anal. Calcd for $C_{11}H_{24}N_2OSi$: C, 57.84; H, 10.59; N, 12.26. Found: C, 57.69; H, 10.60; N, 12.12.

Chloro[*N*-(isopropylidenimino)acetimidato-*N′*,*O*]methylsilicon(IV) (3a). A mixture of 0.68 g (3.6 mmol) of **1a**[10] and 0.42 g (3.6 mmol) of $MeHSiCl_2$ in 5 mL of chloroform was stirred at room temperature for 30 min. The volatiles were removed under reduced pressure (0.1 mmHg), and the solid residue was washed with 10 mL of *n*-hexane and dried; 0.63 g was obtained (91%), mp 83−85 °C. ^{1}H NMR ($CDCl_3$, 295 K): *δ* 0.72 (s, 3H, $SiCH_3$), 2.11 (s, 3H, CCH_3), 2.24, 2.28 (2s, 6H, $N{=}C(CH_3)_2$), 6.02 (s, 1H, SiH). ^{13}C NMR ($CDCl_3$, 295 K): *δ* 8.7 ($SiCH_3$), 17.3 ($O{-}C\underline{Me}$), 21.1, 21.9 ($N{=}C\underline{Me}_2$), 166.9, 168.5 (C═N). ^{29}Si NMR ($CDCl_3$, 295 K): *δ* −73.2 (d, $^1J_{Si-H}$ = 319 Hz). **3a** could not be isolated in analytical purity, due to it being an intermediate and further reaction to **5a**. This is also the case for **3b**−**d** below. **5c** was prepared directly from 2 molar equiv of **1c**, without observation of **3c**.

Chloro[*N*-(isopropylidenimino)benzimidato-*N′*,*O*]methylsilicon(IV) (3b). 3b was prepared directly in the NMR sample tube by dissolving equimolar quantities of **1b**[17] and $MeHSiCl_2$ in $CDCl_3$. It was characterized by spectral analogy with other compounds in the series. ^{1}H NMR ($CDCl_3$, 295 K): *δ* 0.88 (s, 3H, $SiCH_3$), 2.38, 2.48 (2s, 6H, $N{=}C(CH_3)_2$), 6.25 (s, 1H, SiH), 7.50−8.19 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 295K): *δ* 9.2 ($SiCH_3$), 21.6, 22.3 ($N{=}C\underline{C}H_3$), 127.9, 128.2, 128.8, 132.3 (Ph), 163.7, 169.7 (C═N). ^{29}Si NMR ($CDCl_3$, 295 K): *δ* −71.2 (d, $^1J_{Si-H}$ = 317 Hz).

Chloro[*N*-(isopropylidenimino)phenylacetimidato-*N′*,*O*]methylsilicon(IV) (3d). 3d was prepared directly in the NMR sample tube by dissolving equimolar quantities of **1d**[17] and $MeHSiCl_2$ in $CDCl_3$ and characterized by analogy of the NMR spectra with other

(17) Kalikhman, I.; Gostevskii, B.; Girshberg, O.; Krivonos, S.; Kost, D. *Organometallics* **2002**, *21*, 2551–2554.

compounds in the series. ^{1}H NMR ($CDCl_3$, 295 K): δ 0.76 (s, 3H, $SiCH_3$), 2.24, 2.30 (2s, 6H, N=C(CH_3)$_2$), 3.74 (s, 2H, CH_2Ph), 6.10 (s, 1H, SiH), 7.25−7.41 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 295 K): δ 8.8 ($SiCH_3$), 21.4, 22.0 (N=CMe_2), 37.7 (CH_2−Ph), 126.8, 128.2, 128.7, 133.9 (Ph), 168.1, 169.4 (C=N). ^{29}Si NMR ($CDCl_3$, 295 K): δ −71.9 (d, $^1J_{Si\text{-}H}$ = 317 Hz).

[*N*-(Isopropylidenemino)acetimidato-*N′*,*O*][*N*-(isopropylamino)acetimidato-*N′*,*O*]methylsilicon(IV) (5a). A mixture of 2.40 g (13.0 mmol) of **1a**[10] and 0.75 g (6.5 mmol) of $MeHSiCl_2$ in 5 mL of chloroform was stirred at room temperature for 6 h followed by removal of volatiles under reduced pressure (0.1 mmHg). The solution color turned yellow. A single crystal for X-ray analysis was grown from Et_2O, and 1.7 g was obtained (97%). Mp: 101−104 °C. ^{1}H NMR ($CDCl_3$, 295 K): δ 0.36 (s, 3H, $SiCH_3$), 0.92, 1.19 (2d, $^3J_{H\text{-}CH3}$ = 6.4 Hz, 6H, N-CH(CH_3)$_2$), 1.89, 2.02 (2s, 6H, N=C(CH_3)$_2$), 2.24 (s, 6H, OCCH_3), 3.03 (sept, $^3J_{H\text{-}CH3}$ = 6.4 Hz, 1H, CHMe$_2$). ^{13}C NMR ($CDCl_3$, 295 K): δ 6.0 ($SiCH_3$), 16.6, 17.8 (O−CMe), 21.2, 23.9 (N-CHMe), 22.5, 24.3 (N=CMe_2), 46.4 (CHMe$_2$), 153.7, 167.3, 169.5 (C=N). ^{29}Si NMR ($CDCl_3$, 295 K): δ −78.9. Anal. Calcd for $C_{11}H_{22}N_4O_2Si$: C, 48.86; H, 8.20; N, 20.72. Found: C, 48.45; H, 8.28; N, 20.29.

[*N*-(Isopropylidenimino)benzimidato-*N′*,*O*][*N*-(isopropylamino)benzimidato-*N′*,*O*]methylsilicon(IV) (5b). A mixture of 3.24 g (13.0 mmol) of **1b**[17] and 0.75 g (6.5 mmol) of $MeHSiCl_2$ in 5 mL of chloroform was left standing at room temperature for 3 weeks, during which the color changed from colorless to orange. The volatiles were removed under reduced pressure (0.1 mmHg) to leave a foamy residue. The foam was broken by freeze−thaw cycles, and the solid residue was dried at reduced pressure to yield 2.34 g (91%) of **5b**. Mp: 115−119 °C. ^{1}H NMR ($CDCl_3$, 260 K): δ 0.63 (s, 3H, $SiCH_3$), 1.21 (d, $^3J_{H\text{-}CH3}$ = 6.4 Hz, 6H, N-CH(CH_3)), 1.45 (d, $^3J_{H\text{-}CH3}$ = 6.4 Hz, 6H, N-CH(CH_3)), 2.48 (s, 6H, N=C(CH_3)$_2$), 3.33 (sept, H, CHMe$_2$), 7.25−8.15 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 270 K): δ 6.6 ($SiCH_3$), 21.6, 22.6 (N=CCH_3), 22.9, 24.5 (N-CH(CH_3)$_2$), 47.1 (CHMe$_2$), 124.9, 127.8, 128.0, 128.2, 128.9, 132.1 (Ph), 153.2, 163.4, 170.3 (C=N). ^{29}Si NMR ($CDCl_3$, 295 K): δ −76.1. Anal. Calcd for $C_{21}H_{26}N_4O_2Si$: C, 63.93; H, 6.64; N, 14.20. Found: C, 63.98; H, 6.52; N, 13.96.

[*N*-(Isopropylidenimino)pivaloimidato-*N′*,*O*][*N*-(isopropylamino)pivaloimidato-*N′*,*O*]methylsilicon(IV) (5c). A mixture of 0.93 g (4.0 mmol) of **1c** and 0.23 g (2.0 mmol) of $MeHSiCl_2$ in 5 mL of chloroform was stirred at room temperature for 5 days. The volatiles were removed under reduced pressure (0.1 mmHg). The solid product was dried to yield 0.5 g (65%). Mp: 50−52 °C. ^{1}H NMR ($CDCl_3$, 295 K): δ 0.41 (s, 3H, $SiCH_3$), 0.96, 1.26 (2d, $^3J_{CH3\text{-}H}$ = 6.2 Hz, 6H, CH(CH_3)), 1.17, 1.21 (2s, 18H, C(CH_3)$_3$), 2.30, 2.31 (2s, 6H, N=C(CH_3)$_2$), 3.15 (sept, $^3J_{CH3\text{-}H}$ = 6.2 Hz, 1H, CHMe$_2$). ^{13}C NMR ($CDCl_3$, 295 K): δ 5.5 ($SiCH_3$), 21.3, 23.5 (CH(CH_3)$_2$), 22.5, 24.1 (N=CH_3), 27.0, 27.5 (C(CH_3)$_3$), 34.1, 35.5 (C(CH_3)$_3$), 47.2 (CHMe$_2$), 161.0, 168.9, 175 (C=N). ^{29}Si NMR ($CDCl_3$, 295 K): δ −76.1.

[*N*-(Isopropylidenimino)phenylacetimidato-*N′*,*O*][*N*-(isopropylamino)phenylacetimidato-*N′*,*O*]methylsilicon(IV) (5d). A mixture of 1.57 g (5.9 mmol) of **1d**[17] and 0.35 g (3.0 mmol) of $MeHSiCl_2$ in 5 mL of chloroform was stirred at room temperature for 4 days. The volatiles were removed under reduced pressure (0.1 mmHg). The solid residue weighed 2.3 g (91%). Mp: 62−67 °C. A single crystal was grown from *n*-hexane. ^{1}H NMR ($CDCl_3$, 295 K): δ 0.36 (s, 3H, $SiCH_3$), 0.87, 1.24 (2d, $^3J_{CH3\text{-}H}$ = 6.5 Hz, 6H, N-CH(CH_3)$_2$), 2.23, 2.27 (2s, 6H, N=C(CH_3)$_2$), 3.11 (sept, $^3J_{H-CH3}$= 6.5 Hz, 1H, CHMe$_2$), 3.57 (ABq, $\Delta\nu$ = 3.5 Hz, J_{AB} = 15.5 Hz, 2H, CH_2), 3.61 (s, 2H, CH_2), 7.25 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, 295 K): δ 5.6 ($SiCH_3$), 21.2, 23.3 (N-CHMe), 22.4, 23.9 (N=CMe_2), 36.8, 37.8 (CH_2), 46.3 (CHMe$_2$), 125.6, 126.6, 127.7, 128.1, 128.2, 128.6, 134.3, 137.5 (Ph), 154.4, 168.4, 170.1 (C=N). ^{29}Si NMR ($CDCl_3$, 295 K): δ −77.1. Anal. Calcd for $C_{23}H_{28}N_4O_2Si$: C, 65.68; H, 6.71; N, 13.32. Found: C, 65.47; H, 6.51; N, 13.43.

6c. A yellow, single crystal of **6c** grew and was manually separated from an *n*-hexane slurry of **5c** after standing at room temperature for 4 months. ^{1}H NMR ($CDCl_3$, 295 K): δ 0.13 (s, 3H, $SiCH_3$), 1.11, 1.42 (2s, 6H, CMe_2), 1.17, 1.25 (2s, 18H, C(CH_3)$_3$), 2.36 (s, 3H, N=CMe), 2.43, 2.46 (ABq, $^2J_{H\text{-}H}$ = 15.9 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 295 K): δ 1.5 ($SiCH_3$), 21.7, 26.2, 30.4 (NCMe), 27.1, 27.8 (C(CH_3)$_3$), 34.1, 35.5 (C(CH_3)$_3$), 46.6 (CH_2), 53.2 (CMe_2), 160.2, 168.3, 178.5 (C=N). ^{29}Si NMR ($CDCl_3$, 295 K): δ −88.3. Anal. Calcd for $C_{17}H_{32}N_4O_2Si$: C, 57.92; H, 9.15; N, 15.89. Found: C, 57.87; H, 9.08; N, 15.75.

***N*-(Cyclopentylidenimino)-*O*-(trimethylsilyl)benzimidate (9a).** A solution of 13.6 g (0.10 mol) of benzhydrazide with 8.8 mL (0.10 mol) of cyclopentanone and 50 mL of MeOH was refluxed for 2 h. The volatiles were removed under reduced pressure (0.5 mmHg), leaving a colorless crystalline residue. The solid was dissolved in 150 mL of dry Et_2O, and 10.1 g (0.10 mol) of Et_3N was added. To this solution 10.8 g (0.10 mol) of Me_3SiCl was added dropwise over 30 min, followed by 4 h of reflux. After cooling to room temperature the solid Et_3NHCl was filtered off under argon and washed twice with ether (2 × 20 mL). The filtrate and washings were combined, and the solvent was removed under reduced pressure, followed by distillation. The fraction boiling at 118−124 °C at 0.02 mmHg was collected, 25.5 g (93% yield). ^{1}H NMR ($CDCl_3$, 295 K): δ 0.52 (s, 9H, Si(CH_3)$_3$), 1.95 (s, 3H, CH_3), 1.94, 2.65, 2.75 (3m, 8H, (CH_2)$_4$), 7.53−8.19 (m, Ph). ^{13}C NMR ($CDCl_3$, 295 K): δ 2.1 (Si(CH_3)$_3$), 24.5, 29.6, 32.7 (CH_2)$_4$, 127.3, 127.8, 130.1, 134.0 (Ph), 155.0, 176.6 (C=N). ^{29}Si NMR ($CDCl_3$, 295 K): δ 17.6. Anal. Calcd for $C_{15}H_{22}N_2OSi$: C, 65.65; H, 8.08; N, 10.21. Found: C, 65.69; H, 8.10; N, 10.09.

***N*-(Cyclohexylidenimino)-*O*-(trimethylsilyl)benzimidate (9b).** **9b** was prepared as described for **9a**, from 7.1 g (0.05 mol) of benzhydrazide and 5.2 mL (0.05 mol) of cyclohexanone. The fraction boiling at 140−141 °C at 0.02 mmHg was collected, 13 g (88% yield). ^{1}H NMR ($CDCl_3$, 295 K): δ 0.51 (s, 9H, Si(CH_3)$_3$), 1.84−2.89 (m, 10H, (CH_2)$_5$), 7.52−8.17 (m, Ph). ^{13}C NMR ($CDCl_3$, 295 K): δ 2.2 (Si(CH_3)$_3$), 26.0−35.3 (CH_2)$_5$, 127.3, 127.9, 130.0, 134.3 (Ph), 155.0, 169.6 (C=N). ^{29}Si NMR ($CDCl_3$, 295 K): δ 18.1. Anal. Calcd for $C_{16}H_{24}N_2OSi$: C, 66.62; H, 8.39; N, 9.71. Found: C, 66.46; H, 8.40; N, 9.65.

***N*-(Cycloheptylidene)-*O*-(trimethylsilyl)phenylacetimidate (9c).** **9c** was prepared as described for **9a**, from 15 g (0.1 mol) of phenylacethydrazide and 8.5 mL (0.07 mol) of cycloheptanone with 5 drops of acetic acid and 60 mL of methanol. The fraction boiling at 133−137 °C at 0.04 mmHg was collected, 12.7 g (60%). ^{1}H NMR ($CDCl_3$): δ 0.42 (s, 9H, Si(CH_3)$_3$), 1.56−1.90, 2.58−2.86 (m, 12H, (CH_2)$_6$), 3.28, 3.44 (s, 4H, CH_2), 4.01 (s, 2H, PhCH_2), 7.30−7.52 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 0.1 (Si(CH_3)$_3$), 25.0, 26.9, 29.8, 30.3, 31.7, 35.8 (CH_2)$_6$), 37.1 (PhCH_2), 125.9, 128.0, 128.8, 136.8 (Ph), 163.3, 170.8 (C=N). ^{29}Si NMR ($CDCl_3$): δ 20.5. Anal. Calcd for $C_{18}H_{28}N_2OSi$: C, 68.30; H, 8.92; N, 8.85. Found: C, 68.29; H, 8.84; N, 8.89.

10b is the only member of the monocyclic complexes **10** fully isolated and characterized. No attempts to isolate **10a** or **10c** were made, because the corresponding **11a** and **11c** were prepared directly from 2 molar equiv of **9a** and **9c**, respectively.

Chloro[*N*-(cyclohexylidenimino)benzimidato-*N′*,*O*]hydridomethylsilicon(IV) (10b). A mixture of 0.59 g (2.1 mmol) of **9b** and 0.27 g (2.4 mmol) of $MeHSiCl_2$ in 5 mL of chloroform was stirred at room temperature for 24 h. The volatiles were removed under reduced pressure (0.1 mmHg), yielding 0.58 g (95%) of **10b**. Mp: 149−151 °C. ^{1}H NMR ($CDCl_3$, 295 K): δ 0.75 (s, 3H, $SiCH_3$), 1.67−2.96 (m, 10H, CH_2), 6.16 (s, 1H, SiH), 7.25−8.07 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 295 K): δ 9.6 ($SiCH_3$), 24.8, 26.5, 26.7, 30.4, 32.3 (CH_2), 127.8, 128.2, 128.6, 132.2 (Ph), 164.0, 175.3 (C=N). ^{29}Si NMR ($CDCl_3$, 295 K): δ −72.0 (d, $^1J_{Si\text{-}H}$ = 318 Hz). Anal. Calcd for $C_{14}H_{19}ClN_2OSi$: C, 57.03; H, 6.50; N, 9.50. Found: C, 57.68; H, 6.91; N, 9.10.

[*N*-(Cyclopentylidenimino)benzimidato-*N′,O*][*N*-(cyclopentylamino)benzimidato-*N′,O*]methylsilicon(IV) (11a). A mixture of 3.78 g (13.8 mmol) of **9a** and 0.79 g (6.9 mmol) of $MeHSiCl_2$ in 5 mL of chloroform was stirred at room temperature for 30 min and then kept in the refrigerator for 2 days. The color of the solution turned yellow. The volatiles were removed under reduced pressure (0.1 mmHg), and the residue was washed with 10 mL of *n*-hexane. Yield: 2.8 g (93%). Mp: 129−132 °C. Two isomers in 1:1 ratio. ^{1}H NMR ($CDCl_3$, 270 K): δ 0.53, 0.68 (2s, 3H, $SiCH_3$), 1.30−3.26 (m, 16H, $(CH_2)_4$), 3.50, 4.08 (2br s, 2H (N-CH)), 7.20−8.17 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, 270 K): δ 3.4, 5.5 ($SiCH_3$), 23.3, 23.5, 23.6, 24.2, 24.4, 24.8, 25.3, 25.5 (β-$CH_2)_4$, 31.6, 31.9, 32.4, 32.6, 32.9, 33.6, 33.9, 34.0 (α-$CH_2)_4$, 57.6, 58.5 (CH), 123.0−132.3 (Ph), 146.1, 153.4, 163.8, 164.4, 182.6, 183.4 (C═N). ^{29}Si NMR ($CDCl_3$, 270 K): δ −77.7, −79.1. Anal. Calcd for $C_{25}H_{30}N_4O_2Si$: C, 67.23; H, 6.77; N, 12.54. Found: C, 67.79; H, 7.00; N, 12.16.

[*N*-(Cyclohexylidenimino)benzimidato-*N′,O*][*N*-(cyclohexylamino)benzimidato-*N′,O*]methylsilicon(IV) (11b). A mixture of 0.66 g (2.30 mmol) of **9b** and 0.14 g (1.20 mmol) of $MeHSiCl_2$ in 5 mL of chloroform was stirred at room temperature for 30 min. The volatiles were removed under reduced pressure (0.1 mmHg). Yield: 0.3 g (60%). Mp: 133−136 °C. Major isomer ^{1}H NMR ($CDCl_3$, 270 K): δ 0.73 (br s, 3H, $SiCH_3$), 1.30−3.18 (m, 20H, $(CH_2)_5$), 3.23 (br s, 1H, N-CH), 7.36−8.23 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, 270 K): δ 7.0 ($SiCH_3$), 24.9, 25.2, 26.3, 26.3, 26.3, 26.8, 30.3, 32.8, 34.1, 34.7 (CH_2), 57.7 (CH), 124.8, 127.7, 128.1, 129.1, 131.9 (Ph), 153.1, 162.9, 175.6 (C═N). ^{29}Si NMR ($CDCl_3$, 270 K): δ −78.1.

[*N*-(Cycloheptylidenimino)phenylacetimidato-*N′,O*][*N*-(cycloheptylamino)phenylacetimidato-*N′,O*]methylsilicon(IV) (11c). A mixture of 0.56 g (1.80 mmol) of **9c** and 0.1 g (0.90 mmol) of $MeHSiCl_2$ in 5 mL of chloroform was kept for 5 days at refrigerator temperature and then 5 days at room temperature. The volatiles were removed under reduced pressure (0.1 mmHg), and the residue was washed with 10 mL of *n*-hexane. The material contained initially ca. 20% of the rearranged **12c**, which continued to accumulate upon standing in solution, and hence no yield or mp is reported. ^{1}H NMR ($CDCl_3$, 295 K): δ 0.51 (s, 3H, $SiCH_3$), 1.19−3.06 (m, 24H, CH_2), 3.06 (m, 1H, N-CH), 3.67, 3.68 (m, 4H, Ph$C\underline{H}_2$), 7.33−7.39 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, 295 K): δ 6.0 ($SiCH_3$), 23.6−38.0 (CH_2), 56.9 (CH), 125.4, 126.4, 127.6, 127.9, 128.1, 128.5, 134.4, 137.5 (Ph), 153.6, 167.5, 177.8 (C═N). ^{29}Si NMR ($CDCl_3$, 295 K): δ −76.84.

12a. A mixture of 1.7 g (6.2 mmol) of **9a** and 0.36 g (3.1 mmol) of $MeHSiCl_2$ in 10 mL of Et_2O was stirred at room temperature for 50 h. The volatiles were removed under reduced pressure (0.1 mmHg), and the yellow residue was washed twice with *n*-hexane and dried to yield 1.04 g (75%) of **12a**. Mp: 178−181 °C. ^{1}H NMR ($CDCl_3$, 295 K): δ 0.41 (s, 3H, $SiCH_3$), 1.56−3.38 (m, 15H, CH_2, CH), 7.36−8.29 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, 295 K): δ 2.5 ($SiCH_3$), 23.3, 27.3, 27.9, 28.3, 37.6, 40.0 (CH_2), 51.3 (CH), 67.3 (quaternary C), 124.8, 127.6, 127.9, 128.3, 129.2, 132.1, 132.3 (Ph), 151.3, 167.7, 181.0 (C═N). ^{29}Si NMR ($CDCl_3$, 295 K): δ −89.3. Anal. Calcd for $C_{25}H_{30}N_4O_2Si$: C, 67.23; H, 6.77; N, 12.54. Found: C, 67.21; H, 6.72; N, 12.49.

12b. 12b has not been fully isolated because it contained **11b**. It is characterized by NMR analogy with **12a** and **12c**. ^{1}H NMR ($CDCl_3$, 295 K): δ 0.26 (s, 3H, $SiCH_3$), 0.66−3.32 (m, 20H, CH_2), 3.90 (m, 1H, CC$\underline{H}CH_2$), 7.24−7.42 (m, 6H, *m*-Ph and *p*-Ph), 7.75−8.16 (m, 4H, *o*-Ph). ^{13}C NMR ($CDCl_3$, 295 K): δ 3.9 ($SiCH_3$), 24.2, 25.5, 26.3, 26.6, 30.3, 32.2, 32.8, 34.0, 35.0, 37.8 (CH_2), 46.4 (CH), 58.5 (quat. C), 124.7, 127.8, 127.9, 128.2, 128.4, 129.2, 132.0, 132.6 (Ph), 151.9, 163.5, 181.9 (C═N). ^{29}Si NMR ($CDCl_3$, 295 K): δ −88.6.

12c. A yellow single crystal of **12c** was obtained from an *n*-hexane slurry of **11c** after standing at room temperature for 6 months. ^{1}H NMR ($CDCl_3$, 295 K): δ 0.20 (s, 3H, $SiCH_3$), 0.88−2.59 (m, 22H, CH_2), 3.02−3.05 (m, 1H, CC$\underline{H}CH_2$), 3.67−3.82 (m, 4H, C$\underline{H}_2$Ph), 7.34−7.42 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, 295 K): δ 2.6 ($SiCH_3$), 24.0, 24.3, 24.7, 25.9, 27.9, 30.0, 30.7, 37.3, 38.2, 38.7, 40.8 (CH_2), 49.0 (CH), 61.2 (quat. C), 125.8, 126.9, 127.9, 128.4, 128.7, 129.1, 134.7, 137.9 (Ph), 153.3, 171.3, 178.9 (C═N). ^{29}Si NMR ($CDCl_3$, 295 K): δ −88.6. Anal. Calcd for $C_{31}H_{40}N_4O_2Si$: C, 70.42; H, 7.62; N, 10.60. Found: C, 70.35; H, 7.48; N, 10.70.

***O*-(Trimethylsilyl)-*N*-(benzylidenimino)phenylacetimidate (14b).** A solution of 15 g (0.1 mol) of phenylacethydrazide and 10.6 g (0.1 mol) of benzaldehyde in 20 mL of methanol was refluxed for 1 h. The volatiles were removed under reduced pressure (0.1 mmHg). The solid was dissolved in 150 mL of dry Et_2O, and 15 mL of Et_3N was added. To this solution was added dropwise 15 mL (0.15 mol) of Me_3SiCl over 10 min, followed by 2 h of reflux. After cooling to room temperature the solid Et_3NHCl was filtered off under argon and washed twice with ether. The solvent was removed from the combined solution under reduced pressure, followed by recrystallization from *n*-hexane. Yield: 28 g (90%). Mp: 60−61 °C. ^{1}H NMR ($CDCl_3$, 295 K): δ 0.32 (s, 9H, $Si(CH_3)_3$), 4.10 (s, 2H, C$\underline{H}_2$-Ph), 7.30−7.84 (m, 10H, Ph), 8.40 (s, 1H, $\underline{H}$CPh). ^{13}C NMR ($CDCl_3$, 295 K): δ 0.3 ($Si(CH_3)_3$), 36.3 ($\underline{C}H_2$−Ph), 126.3, 127.8, 128.3, 128.6, 129.1, 130.1, 135.1, 136.6 (Ph), 156.9, 169.3 (C═N). ^{29}Si NMR ($CDCl_3$, 295 K): δ 22.7.

***O*-(Trimethylsilyl)-*N*-(benzylidenimino)pivaloimidate (14c).** **14c** was prepared as described for **14b**, from 21.4 g (0.18 mol) of pivalohydrazide and 19.5 g (0.18 mol) of benzaldehyde in 50 mL of chloroform. The fraction boiling at 103 °C at 0.02 mmHg was collected. Yield: 37 g (86%). ^{1}H NMR ($CDCl_3$, 295 K): δ 0.44 (s, 9H, $Si(CH_3)_3$), 1.36 (s, 9H, $C(C\underline{H}_3)_3$), 7.51−7.85 (m, 5H, Ph), 8.51 (s, 1H, C$\underline{H}$Ph). ^{13}C NMR ($CDCl_3$, 295 K): δ 1.9 ($Si(CH_3)_3$), 28.1 ($C(\underline{C}H_3)_3$), 37.2 ($\underline{C}(CH_3)_3$), 128.2, 128.5, 130.2, 134.7 (Ph), 158.4, 167.6 (C═N). ^{29}Si NMR ($CDCl_3$, 295 K): δ 19.0. Anal. Calcd for $C_{15}H_{24}N_2OSi$: C, 65.17; H, 8.75; N, 10.13. Found: C, 65.08; H, 8.80; N, 10.21.

[*N*-(Benzylidenimino)acetimidato-*N′,O*][*N*-(benzylamino)acetimidato-*N′,O*]methylsilicon(IV) (15a). A mixture of 0.83 g (3.5 mmol) of **14a**[7] and 0.21 g (1.8 mmol) of $MeHSiCl_2$ in 5 mL of chloroform was stirred at room temperature for 1 h. The volatiles were removed under reduced pressure (0.1 mmHg), and the residue was washed with 10 mL of *n*-hexane. Yield: 1.20 g (93%). Mp: 128−130 °C. 1:1 mixture of two isomers. ^{1}H NMR ($CDCl_3$, 295 K): δ 0.38, 0.51 (2s, 3H, $SiCH_3$), 2.08, 2.30 (2s, 6H, N═CCH_3), 4.39, 4.63, 4.64, 4.71 (2ABq, $^2J_{H-H}$ = 15.0 Hz, 2H, C$\underline{H}_2$Ph), 7.25−8.10 (m, 10H, Ph), 8.51 (s, 1H, $\underline{H}$CPh). ^{13}C NMR ($CDCl_3$, 295 K): δ 3.1, 6.1 ($SiCH_3$), 16.4, 18.1 (N═C$\underline{C}H_3$), 52.1 (N$\underline{C}H_2$Ph), 125.7−134.4 (Ph), 143.0, 152.3, 157.5, 171.3, 172.9 (C═N). ^{29}Si NMR ($CDCl_3$, 295 K): δ −78.2, −83.2. Anal. Calcd for $C_{19}H_{22}N_4O_2Si$: C, 62.27; H, 6.05; N, 15.29. Found: C, 61.76; H, 5.67; N, 15.25.

[*N*-(Benzylidenimino)phenylacetimidato-*N′,O*][*N*-(benzylamino)phenylacetimidato-*N′,O*]methylsilicon(IV) (15b). A mixture of 1.36 g (4.4 mmol) of **14b** and 0.26 g (2.3 mmol) of $MeHSiCl_2$ in 5 mL of chloroform was stirred at room temperature for 30 min. The volatiles were removed under reduced pressure (0.1 mmHg), and the residue was washed with 5 mL of *n*-hexane and Et_2O. Yield: 2.0 g (88%). Mp: 210 °C. ^{1}H NMR ($CDCl_3$, 295 K): δ 0.36 (s, 3H, $SiCH_3$), 3.66, 3.76 (ABq, $^2J_{H-H}$ = 15.2 Hz, 4H, N═CCH_2), 4.57, 4.64 (ABq, $^2J_{H-H}$ = 15 Hz, 2H, N$C\underline{H}_2$Ph), 7.30−8.02 (m, 20H, Ph), 7.92 (s, 1H, N═C$\underline{H}$Ph). ^{13}C NMR ($CDCl_3$, 295 K): δ 3.0 ($SiCH_3$), 37.5, 38.5 ($C\underline{C}H_2$Ph), 52.5 (N$\underline{C}H_2$Ph), 125.8−143.2 (Ph), 154.1, 159.0, 173.9 (C═N). ^{29}Si NMR ($CDCl_3$, 295 K): δ −83.0. Anal. Calcd for $C_{31}H_{30}N_4O_2Si$: C, 71.00; H, 5.83; N, 10.80. Found: C, 70.53; H, 5.70; N, 10.21.

[*N*-(Benzylidenimino)pivaloimidato-*N′,O*][*N*-(benzylamino)pivaloimidato-*N′,O*]methylsilicon(IV) (15c). A mixture of 0.90 g (3.2 mmol) of **14c** and 0.19 g (1.7 mmol) of $MeHSiCl_2$ in 5 mL of

chloroform was stirred at room temperature for 12 h, during which the color changed from colorless to red. The volatiles were removed under reduced pressure (0.1 mmHg). Yield: 0.5 g (67%). Oily liquid at room temperature, solidifies in an ice bath. ^{1}H NMR ($CDCl_3$, 295 K): δ 0.35 (s, 3H, $SiCH_3$), 1.00−1.43 (m, 18H, $C(CH_3)_3$), 4.73, 4.77 (ABq, $^{2}J_{H-H}$ = 17.1 Hz, 2H, $NC\underline{H}_2Ph$), 7.23−8.55 (m, 10H, Ph), 8.64 (s, 1H, $N{=}C\underline{H}Ph$). ^{13}C NMR ($CDCl_3$, 295 K): δ 2.4 ($SiCH_3$), 26.8−27.7 ($C(\underline{C}H_3)_3$), 33.9, 35.6 ($\underline{C}(CH_3)_3$), 52.5 ($\underline{C}H_2Ph$), 125.5−134.5 (Ph), 143.7, 157.8, 180.9 (C=N). ^{29}Si NMR ($CDCl_3$, 295 K): δ −82.8. Anal. Calcd for $C_{25}H_{34}N_4O_2Si$: C, 66.63; H, 7.60; N, 12.43. Found: C, 66.34; H, 7.07; N, 12.42.

[*N*-(Benzylidenimino)trifluoroacetimidato-*N′,O*][*N*-(benzylamino)trifluoroacetimidato-*N′,O*]methylsilicon(IV) (15d). A mixture of 0.80 g (2.8 mmol) of **14d**[7] and 0.18 g (1.6 mmol) of $MeHSiCl_2$ in 5 mL of chloroform was stirred at room temperature for 12 h, during which the color changed from colorless to orange. The volatiles were removed under reduced pressure (0.1 mmHg). Yield: 0.5 g (75%). Mp: 78−81 °C. ^{1}H NMR ($CDCl_3$, 295 K): δ 0.53 (s, 3H, $SiCH_3$), 4.75, 4.80 (ABq, $^{2}J_{H-H}$ = 15.6 Hz, 2H, $NC\underline{H}_2Ph$), 7.33−8.53 (m, 10H, Ph), 8.78 (s, 1H, $N{=}C\underline{H}Ph$). ^{13}C NMR ($CDCl_3$, 295 K): δ 2.7 ($Si(CH_3)_3$), 53.2 ($\underline{C}H_2Ph$), 116.9, 118.1 (2q, $^{1}J_{C-F}$ = 270.4, 276.9 Hz, CF_3), 126.6, 127.2, 128.2, 129.5, 136.6, 141.3 (Ph), 142.1, 161.1 (2q, $^{2}J_{C\text{-}CF}$ = 39.6, 38.7 Hz, $CF_3\underline{C}{=}N$), 165.7 (C=N). ^{29}Si NMR ($CDCl_3$, 295 K): δ −78.7. Anal. Calcd for $C_{19}H_{16}F_6N_4O_2Si$: C, 48.10; H, 3.40; N, 11.81. Found: C, 47.66; H, 3.54; N, 11.47.

Acknowledgment. Financial support from the Israel Science Foundation, grant No. ISF-139/05, is gratefully acknowledged.

Supporting Information Available: Crystallographic data in CIF format for all seven new crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800427X