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Donor-Stabilized Silyl Cations 4: *N*-Isopropylidene Hydrazides, Novel Bidentate Ligands for Penta- and Hexacoordinate Silicon Chelates[1]

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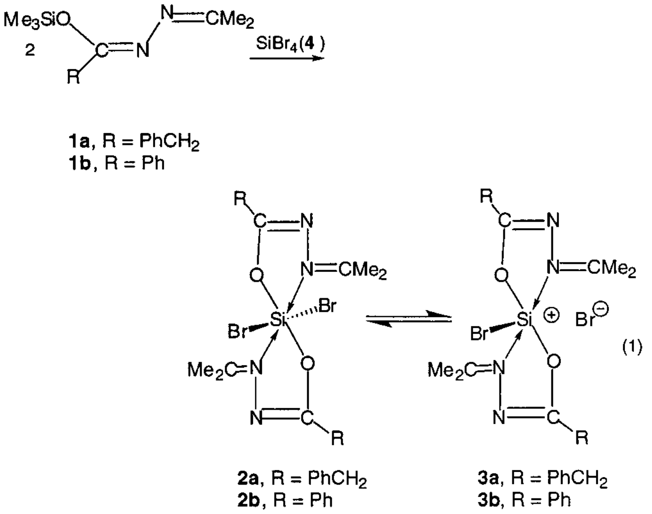
*Summary: Novel chelating agents derived from N-isopropylidene hydrazides, N-isopropylideneimino-O-(trimethylsilyl)acylimidates (**1**), have been utilized to prepare hexacoordinate dihalosilicon complexes (**2**) unique in their trans geometry and in their facile ionization to pentacoordinate siliconium halide salts (**3**).*

Numerous crystal structures of neutral hexacoordinate silicon bis-chelates have been described in the literature to date.[3,4] All of these complexes featured a *cis* orientation of the two monodentate ligands.[5] In this note we report on the use of novel chelating agents [*N*-isopropylideneimino-*O*-(trimethylsilyl)acylimidates] for the preparation of neutral hexacoordinate dihalosilicon chelates. The new chelates are unique in that the halogeno ligands possess a *trans* orientation, in contrast to previous observations. In addition, these complexes undergo spontaneous ionization in solution to pentacoordinate siliconium halide salts, in contrast to previously studied hexacoordinate dihalosilicon chelates.[1,6]

The reaction of *N*-isopropylideneimino-*O*-(trimethylsilyl)acylimidates (**1a**,**b**) with tetrabromosilane (**4**) produces bis-chelates with the novel *N*-(isopropylideneimino)acylimidato-*N*,*O* bidentate ligands (**2a**,**b**, eq 1).



1a, R = PhCH$_2$
1b, R = Ph

2a, R = PhCH$_2$
2b, R = Ph

3a, R = PhCH$_2$
3b, R = Ph

Surprisingly, the ^{1}H NMR spectra of **2a** suggest that the bromo ligands are oriented *trans* to each other: the benzyl methylene protons feature a singlet in a number of different solvents; that is, the compound is achiral (Table 1). This result is confirmed by a single-crystal analysis of **2b** (Figure 1, Table 2), with C_{2h} molecular symmetry.

Table 1. Selected NMR Chemical Shifts (ppm) for Complexes 2a,b, 3a,b, 8, and 9 in CDCl$_3$ Solutions at Different Temperatures

			^{1}H	^{13}C	
compound	*T*, K	^{29}Si	C*H*$_2$	Me$_2$*C*=N	O*C*=N
2a ⇄ **3a-Br**	330	−165.5	3.77	177.9	165.6
	300	−159.2	3.81	180.4	165.6
	260	−133.7	3.81	184.0	165.6
	230	−120.2	3.81	186.4	165.5
	200	−118.2	3.81	186.6	165.4
3a-AlBr$_4$	262	−108.0	3.80, 3.82[a]	186.6	166.0
8	300	−167.1[b]	3.40; 3.46[c]	173.0	169.5
9	300	−163.7	3.72	174.4	166.0
2b ⇄ **3b-Br**	330	−153.9		179.9	161.7
	300	−140.2		182.3	161.4
	268	−127.5		184.4	161.0
	223	−120.5		185.5	160.5
3b-AlBr$_4$	300	−107.3		185.6	161.6

[a] AB quartet ($^2J_{AB}$ = 15.3 Hz). [b] Triplet ($^1J_{SiF}$ = 193 Hz). [c] AB quartet ($^2J_{AB}$ = 14.6 Hz).

The crystal structure stands in sharp contrast to the analogous chelate **5** with the *N*-(dimethylamino)acylimidato-*N′*,*O* ligand, in which the bromo ligands are *cis* to each other (Figure 2, Table 2).[7] The *cis* structure is characteristic of this class of compounds, and numerous similar structures have been reported.[8] This appears to

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(1) For number 3 in the series see: Kost, D.; Kingston, V.; Gostevskii, B.; Ellern, A.; Stalke, D.; Walfort, B.; Kalikhman, I. *Organometallics* **2002**, *21*, 2293.

(2) On leave of absence from the Institute of Chemistry, Russian Academy of Sciences, Siberian Branch, Irkutsk, Russia.

(3) For reviews on crystal structures of organosilicon compounds see: (a) Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*; Apeloig, Y., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, p 181. (b) Lukevics, E.; Pudova, O. A. *Khim. Geterotsiklicheskikh Soedin*. **1966**, 1605; *Chem. Abstr.* **1997**, *126*, 157528w.

(4) For recent reviews on hypervalent silicon complexes see: (a) Brook, M. A. *Silicon in Organometallic and Polymer Chemistry*; Wiley: New York, 2000; p 97. (b) Chuit, C.; Corriu, R. J. P.; Reyé, C. In *The Chemistry of Hypervalent Compounds*; Kin-ya Akiba, Ed.; Wiley-VCH: Weinheim, Germany, 1999; p 81. (c) Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds*; Apeloig, Y., Rappoport, Z., Eds.; Wiely, Chichester, U.K., 1998; Vol. 2, p 1339. (d) Chuit, C.; Corriu, R. J. P.; Reyé, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371.

(5) A single case has been reported of an *inter*molecular silicon bis-chelate [Si(catecholato)$_2$]·2THF possessing *trans*-geometry: Hahn, F. E.; Keck, M.; Raymond, K. N. *Inorg. Chem.* **1995**, *34*, 1402.

(6) Kingston, V.; Gostevskii, B.; Kalikhman, I.; Kost, D. *Chem. Commun.* **2001**, 1272.

(7) The preparation and spectra of **5** have been reported.[1]

(8) (a) Kalikhman, I.; Krivonos, S.; Stalke, D.; Kottke, T.; Kost, D.; *Organometallics* **1997**, *16*, 3255. (b) Kost, D.; Kalikhman, I.; Krivonos, S.; Stalke, D.; Kottke, T. *J. Am. Chem. Soc.* **1998**, *120*, 4209. (c) Kalikhman, I.; Girshberg, O.; Lameyer, L.; Stalke, D.; Kost, D. *Organometallics* **2000**, *19*, 1927.

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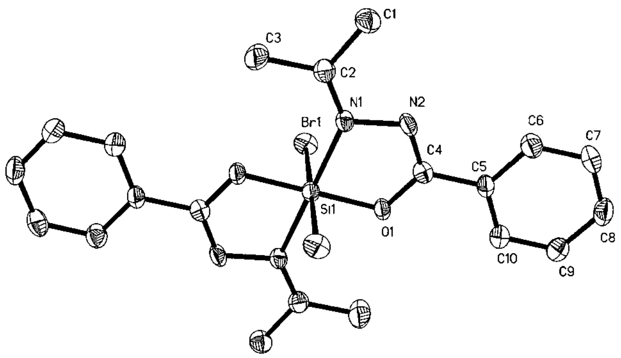


Figure 1. Molecular structure in the crystal of **2b**: formula $C_{22}H_{26}Br_2Cl_6N_4O_2Si$; monoclinic, space group $P2(1)/n$: unit cell $a = 11.991(3)$ Å; $b = 7.389(2)$ Å; $c = 17.162(5)$ Å; $\alpha = 90°$; $\beta = 100.271(7)°$; $\gamma = 90°$; $Z = 2$, temperature 173(2) K, $R(wR2) = 0.0861$ (0.0912 for all data). The complete data can be found in the Supporting Information. Hydrogen atoms have been omitted for clarity.

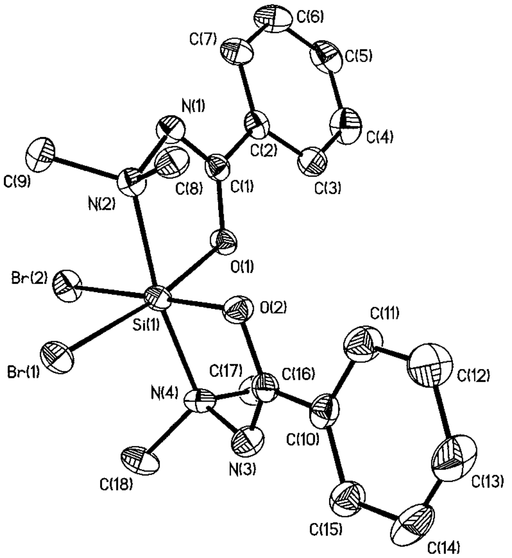
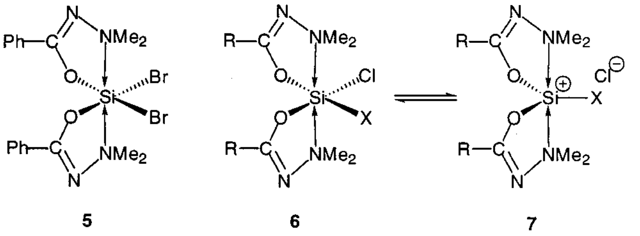


Figure 2. Molecular structure in the crystal of **5**: formula $C_{19}H_{24}Br_3Cl_3N_4O_2Si$; monoclinic, space group $P2(1)/n$: unit cell $a = 13.1350(17)$ Å; $b = 11.9524(16)$ Å; $c = 17.130(2)$ Å; $\alpha = 90°$; $\beta = 101.560(3)°$; $\gamma = 90°$; $Z = 4$, temperature 173(2) K, $R(wR2) = 0.1098$ (0.1163 for all data). The complete data can be found in the Supporting Information. Hydrogen atoms have been omitted for clarity.

be the first report of a *trans* geometry in a neutral intramolecular hexacoordinate silicon bis-chelate.



5 **6** **7**

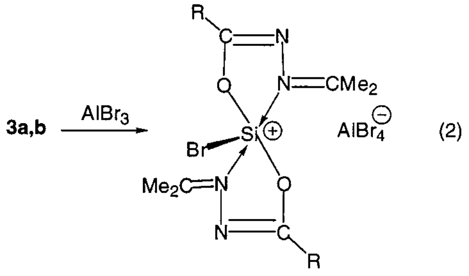
R = Me, Ph, PhCH2, t-Bu; X = Me, Ph, PhCH2, t-Bu

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Dibromo Complexes 5 and 2b

bond	5	2b	angle	5	2b
Si−O1	1.789(3)	1.716(2)	O2−Si−O1	89.87(16)	180.000(1)
Si−O2	1.728(3)	1.716(2)	O2−Si−N4	82.99(17)	84.82(11)
Si−N2	2.067(4)	1.933(3)	O1−Si−N4	92.98 (17)	95.18(11)
Si−N4	1.985(4)	1.933(3)	O2−Si−N2	89.52 (16)	84.82(11)
Si−Br1	2.3271(14)	2.4050(6)	O1−Si−N2	81.88 (16)	95.18(11)
Si−Br2	2.3498(14)	2.4050(6)	N4−Si−N2	170.95(17)	180.000(1)

A second surprising observation in the isopropylidene complexes (**2**) is the huge dependence of the ^{29}Si chemical shift upon temperature, as well as a substantial dependence of the ^{13}C shift of the isopropylidene carbon atoms (Table 1). Downfield changes in the ^{29}Si signal of compounds **6** in $CDCl_3$ or CD_2Cl_2 solution upon cooling were shown previously to indicate a gradual shift of equilibrium toward ionization to a pentacoordinate siliconium salt (**7**).[1,6] On the basis of this observation it was concluded that also in this case ionization took place at low temperature. However, in previous reports dihalosilicon bis-chelates (**6**, X = Cl, and the dibromo analogue) did not ionize at any temperature, and the present report is the first example for ionization of a neutral dihalosilicon bischelate.[1,6]

Additional evidence for the ionization was obtained by treating the equilibrium mixtures **2a** $\rightleftarrows$ **3a** and **2b** $\rightleftarrows$ **3b** with $AlBr_3$ (eq 2): an immediate downfield change in the ^{29}Si chemical shift at room temperature (Table 1) indicated complete ionization to **3a-AlBr$_4$**, **3b-AlBr$_4$**, as had been reported previously for **6** → **7-AlCl$_4$**.[1] Furthermore, the ^{1}H NMR spectrum of **3a-AlBr$_4$** featured an AB quartet for the geminal methylene protons, proving the loss of the central symmetry plane, in accord with the structure assignment for **3a**. The low-temperature ^{13}C chemical shifts of the isopropylidene carbons in the equilibrium mixtures **2a** $\rightleftarrows$ **3a** and **2b** $\rightleftarrows$ **3b** are nearly equal to those in the corresponding tetrabromoaluminates (Table 1), supporting the assignment.

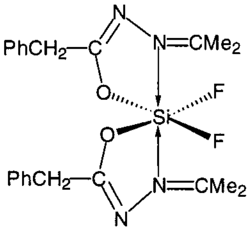


3a-AlBr$_4$, 3b-AlBr$_4$

The observation that **2a**,**b** ionize spontaneously in solution at low temperature is rather surprising, in view of the resistance to ionization found in the *N*-dimethylamino analogue **5**.[1] The resistance to ionization in **5** was attributed to the electron-withdrawing power of the bromo ligands, which caused the silicon to be relatively electron poor and hence to resist the release of an anion. It must therefore be concluded that the isopropylideneimino group in **2a**,**b** acts as a stronger donor than the dimethylamino group in **5**.

This is further supported by the data in Table 2: comparison of bond lengths reveals significantly shorter N−Si dative bonds in **2b** relative to **5**, evidence for stronger coordination, i.e., more powerful donor. The stronger coordination in **2b** is also reflected in the Si−Br distances, which are substantially longer in **2b** than in **5**. This is in agreement with the observation of easier ionization of the Si−Br bond in **2b** relative to **5**.

It remains to be determined whether the unusual *trans* geometry in **2a**,**b** is due to the donor ability of the new ligand or due to a steric effect. This question is readily answered by comparison of the three halogeno complexes: **2a**, **8**, and **9**; while the ^{1}H NMR spectrum of **9** is similar to that of **2a**, with isochronous methylene protons and hence with *trans* geometry, the spectrum of **8** features an AB quartet, evidence that the difluoro complex has the more common *cis* geometry. This suggests that steric requirements of the rigid *N*-isopropylidene-*N′*-acylimidato-*N,O* ligand force the larger halogen ligands, Br and Cl, out of the generally preferred *cis* orientation, while the smaller fluoro ligands remain unaffected. Examination of models provides an explanation for this phenomenon: the rigid isopropylidene double bond forces one of the methyl groups in each chelate ring in the *cis* geometry to point directly toward the monodentate ligands, causing severe steric crowding. This in turn is eliminated by adopting the *trans* geometry. In the case of the relatively small fluorine atoms and the rather short Si−F bonds, the steric congestion is insufficient to impose the *trans* geometry.



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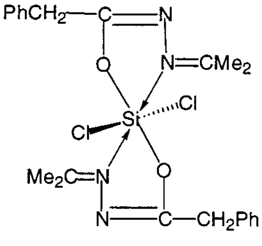

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Remarkably, while in the equilibrium **6** ⇄ **7** at low temperature both species freeze out on the NMR time scale and are observed individually,[1,6] the ^{29}Si signal in **2a**,**b** remains sharp throughout the entire temperature range, and no sign of resolution to two signals for hexa- and pentacoordinate species is detected. It must be concluded that the effective activation barrier for the ionization is substantially lower in **2a**,**b** than in **6**. This may be due to intermolecular exchange of bromo ligands, in an S_N2 type substitution.

Experimental Section

Syntheses were carried out in an inert atmosphere by passing a stream of dry nitrogen or argon through or above the reaction. NMR spectra were recorded on a Bruker DMX-500 NMR spectrometer, operating at 500.13 MHz for ^{1}H, and are reported in ppm (δ) downfield of internal TMS. Melting points (mp) were measured in sealed capillaries on a Büchi melting point instrument and are uncorrected. Single-crystal X-ray diffraction patterns were measured at 173(2) K on a Bruker Smart CCD 1000 diffractometer [λ(Mo Kα) = 0.71073 Å, graphite monochromator, a scan width of 0.3° in ω and exposure time of 10 s frame^{-1}, detector−crystal distance = 4.95 cm]. Detailed data for the crystal structures of **2b** and **5** can be found in the Supporting Information and have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-179135 (**2b**) and CCDC-179136 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) + 44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk].

***N*-Isopropylideneimino-*O*-(trimethylsilyl)phenylacetimidate (1a).** Phenylacethydrazide (15.0 g, 100 mmol) was dissolved in 150 mL of anhydrous acetone, and the solution was stirred for 30 min at ambient temperature. The solvent was removed under vacuum (0.01 mmHg for 1 h), and the resulting white crystalline product was dissolved in 150 mL of dry ether and used directly for silylation. To the ether solution was added 10.1 g (100 mmol) of Et_3N followed by dropwise addition of 10.8 g (100 mmol) of Me_3SiCl with stirring during 10 min. The mixture was refluxed for 4 h and cooled to room temperature, and the solid precipitate was removed by filtration and washed twice with 40 mL portions of ether. The solvent was removed from the combined filtrate and washings under vacuum (1 mmHg), and the residue was distilled to yield 23.5 g (94% yield) of **1a**, collected at 89−93 °C at 0.02 mmHg. The NMR spectra feature a 5:1 mixture of geometrical isomers. ^{1}H NMR ($CDCl_3$) δ major isomer: 0.26 (s, 9H, Me_3Si), 1.91 (s, 3H, CMe), 2.02 (s, 3H, CMe), 3.88 (s, 2H, CH_2), 7.19−7.32 (m, Ar); minor: 0.09 (s, 9H, Me_3Si), 1.99 (s, 3H, CMe), 2.00 (s, 3H, CMe), 3.57 (s, 2H, CH_2), 7.19−7.32 (m, Ar). ^{13}C NMR ($CDCl_3$) δ major: 0.27 (SiMe), 18.38 (C*Me*), 25.10 (C*Me*), 35.81 (CH_2), 126.05, 128.15, 128.99, 129.30, 136.86 (Ph), 162.73 (C=N), 164.20 (C=N); minor: 1.51 (SiMe), 18.12 (C*Me*), 24.69 (C*Me*), 41.95(CH_2), 157.30 (C=N), 162.80 (C=N). ^{29}Si NMR ($CDCl_3$) δ major: 20.6; minor: 18.3. Anal. Calcd for $C_{14}H_{22}N_2OSi$: C, 64.08; H, 8.45; N, 10.67. Found: C, 63.92; H, 8.35; N, 10.41.

***N*-Isopropylideneimino-*O*-(trimethylsilyl)benzimidate (1b).** **1b** was prepared like **1a**, using benzoyl chloride instead of phenylacetyl chloride. The yield of colorless liquid was 88%, collected at 84−85 °C at 0.5 mmHg. ^{1}H NMR ($CDCl_3$): δ 0.38 (s, 9H, Me_3Si), 2.13 (s, 3H, CMe), 2.14 (s, 3H, CMe), 7.42−8.05 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$): δ 2.08 (SiMe), 18.38 (C*Me*), 24.75 (C*Me*), 127.47, 127.99, 130.15, 134.35 (Ph), 155.60 (C=N), 164.08 (C=N). ^{29}Si NMR ($CDCl_3$): δ 18.41. Anal. Calcd for $C_{13}H_{20}N_2OSi$: C, 62.86; H, 8.12; N, 11.28; Si, 11.31. Found: C, 61.98; H, 7.95; N, 11.56; Si, 11.20.

Dibromobis[*N*-(isopropylideneimino)phenylacetimidato-*N,O*]silicon(IV) (2a). To a solution of 0.590 g (1.68 mmol) of $SiBr_4$ in 5 mL of chloroform was added 0.837 g (3.37 mmol) of **1a** in one portion. The temperature rose initially, and the mixture was allowed to cool for 1 h, after which the volatiles were removed under 0.02 mmHg pressure. The remaining white solid was washed twice with hexane and dried under vacuum for 2 h to yield essentially pure **2a** (0.902 g, 99% yield), mp 184−185 °C. ^{1}H NMR ($CDCl_3$): δ 2.20 (s, 6H, CMe), 2.56 (s, 6H, CMe), 3.81 (s, 4H, CH_2), 7.22−7.40 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$): δ 24.70 (C*Me*), 25.86 (C*Me*), 37.76 (CH_2), 127.41, 128.66, 129.41, 133.28 (Ph), 165.6 (C=N), 180.4 (C=N). ^{29}Si NMR ($CDCl_3$): δ −159.2. Anal. Calcd for $C_{22}H_{26}Br_2N_4O_2Si$: C, 46.66; H, 4.63; N, 9.89. Found: C, 46.33; H, 4.80; N, 9.74.

Dibromobis[*N*-(isopropylideneimino)benzimidato-*N,O*]silicon(IV) (2b). **2b** was prepared like **2a**, using 0.458 g (1.32 mmol) of $SiBr_4$ and 0.693 g (2.64 mmol) of **1b**. The yield was quantitative (0.743 g) of a white solid, mp 153−155 °C. ^{1}H NMR ($CDCl_3$): δ 2.71 (s, 6H, CMe), 2.87 (s, 6H, CMe), 7.37−7.94 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$): δ 25.44 (C*Me*), 25.71 (C*Me*), 126.67, 128.07, 128.89, 133.40 (Ph), 161.40 (C=N), 182.3 (C=N). ^{29}Si NMR ($CDCl_3$): δ −140.2. Anal. Calcd for $C_{20}H_{22}Br_2N_4O_2Si$: C, 44.62; H, 4.12; N, 10.41. Found: C, 44.55; H, 4.17; N, 10.38.

Difluorobis[*N*-(isopropylideneimino)phenylacetimidato-*N,O*]silicon(IV) (8). A solution of 1.156 g (4.40 mmol) of **1a** in 5 mL of $CHCl_3$ was partly evacuated, and SiF_4 was introduced to the flask under reduced pressure. The mixture was allowed to stir at ambient temperature for 12 h. A ^{29}Si NMR spectrum of a sample indicated that a monochelate had predominantly formed, and therefore another 0.243 g (0.93 mmol) of **1a** was added and the mixture was allowed to stir in a 70 °C oil bath for another 3 h. The volatiles were removed under reduced pressure, leaving a viscous oily residue, which did not crystallize after washing twice with hexane. The essentially pure (as determined by the ^{29}Si NMR spectrum) oily product was dried at 0.02 mmHg for 2 h. Yield: 0.924 g (91%). ^{1}H NMR (CDCl$_3$): δ 2.26 (s, 6H, CMe), 2.29 (s, 6H, CMe), 3.40, 3.46 (ABq, $^2J_{AB} = 14.6$ Hz, 4H, CH$_2$), 7.15−7.25 (m, 10H, Ph). ^{13}C NMR (CDCl$_3$): δ 22.97 (t, $^3J_{FC} = 8.0$ Hz, C*Me*), 23.85 (C*Me*), 126.49, 128.17, 129.13, 135.65 (Ph), 169.48 (C═N), 173.01 (C═N). ^{29}Si NMR (CDCl$_3$): δ −167.1 (t, $^1J_{FSi} =$ 193 Hz).

Dichlorobis[*N*-(isopropylideneimino)phenylacetimidato-*N,O*]silicon(IV) (9). To a solution of 0.552 g (2.10 mmol) of **1a** in 5 mL of anhydrous THF under argon atmosphere was added at once 0.226 g (1.33 mmol) of SiCl$_4$. The mixture was kept in a 60 °C oil bath for 30 min, followed by removal of the volatiles under reduced pressure. The crystalline residue was washed by hexane and dried for 2 h at 0.02 mmHg. Yield: 0.500 g (quantitative), mp 161−163 °C. ^{1}H NMR (CDCl$_3$): δ 2.24 (s, 6H, CMe), 2.37 (s, 6H, CMe), 3.72 (s, 4H, CH$_2$), 7.24−7.33 (m, 10H, Ph). ^{13}C NMR (CDCl$_3$): δ 23.77 (C*Me*), 25.47 (C*Me*), 38.16 (CH$_2$), 126.88, 128.35, 129.45, 134.35 (Ph), 165.98 (C═N), 174.40 (C═N). ^{29}Si NMR (CDCl$_3$): δ −163.7. Anal. Calcd for $C_{22}H_{26}Cl_2N_4O_2Si$: C, 55.34; H, 5.49; N, 11.73. Found: C, 55.21; H, 5.43; N, 10.95.

Bromobis[*N*-(isopropylideneimino)phenylacetimidato-*N,O*]siliconium Tetrabromoaluminate (3a-AlBr$_4$). ^{1}H NMR (CDCl$_3$, 262 K): δ 2.10 (s, 6H, CMe), 2.51 (s, 6H, CMe), 3.80, 3.82 (ABq, $^2J_{AB} = 15.3$ Hz, 4H, CH$_2$), 7.24−7.38 (m, 10H, Ph). ^{13}C NMR (CDCl$_3$): δ 24.75 (C*Me*), 25.03 (C*Me*), 37.09 (CH$_2$), 126.88, 128.35, 129.45, 134.35 (Ph), 166.08 (C═N), 186.20 (C═N). ^{29}Si NMR (CDCl$_3$): δ −108.0.

Bromobis[*N*-(isopropylideneimino)benzimidato-*N,O*]-siliconium Tetrabromoaluminate (3b-AlBr$_4$). ^{1}H NMR (CDCl$_3$): δ 2.77 (s, 6H, CMe), 2.80 (s, 6H, CMe), 7.25−8.00 (m, 10H, Ph). ^{13}C NMR (CDCl$_3$): δ 25.38 (C*Me*), 25.59 (C*Me*), 124.99, 128.48, 129.54, 134.99 (Ph), 161.60 (C═N), 185.60 (C═N). ^{29}Si NMR (CDCl$_3$): δ −107.3.

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Supporting Information Available: Crystallographic data for **2b** and **5** are available free of charge via the Internet at http://pubs.acs.org.

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