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# Octahedral and Bicapped-Tetrahedral Silicon Configurations in the Solid State and Their Dynamic Coexistence in Solution

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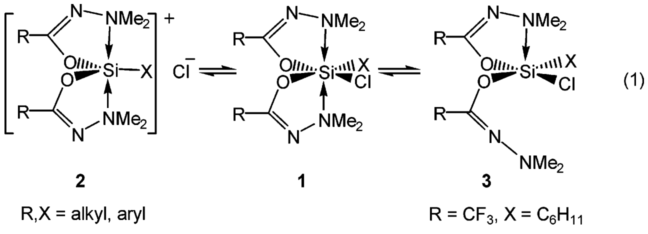
Hexacoordinate silicon bis chelates with the $SiC_2O_2N_2$ ligand framework have been prepared, with different nitrogen-donor ligands, $NMe_2$ and $N{=}CMe_2$. Crystal diffraction analyses revealed that the former type had a bicapped-tetrahedral geometry and the latter an octahedral molecular geometry in the solid state. The two N→Si dative bonds in the isopropylideneimino-coordinated compound are sufficiently strong to change silicon from its tetrahedral ground-state configuration to the higher energy octahedral configuration. In contrast, the weaker $NMe_2$ donor groups do not form strong enough bonds to cause this change, and as a result silicon remains tetrahedral and forms only substantially longer and weaker N→Si dative bonds (2.7−2.8 Å). Remote electron-releasing $NMe_2$ substituents on the chelate rings render the ligand $NMe_2$ groups stronger donors, resulting in reversal of the solid-state geometry back to octahedral. $^{29}Si$, $^{1}H$, and $^{13}C$ NMR spectra at various temperatures provide evidence for the coexistence in equilibrium of the bicapped-tetrahedral and octahedral geometries in solution, with the octahedral to tetrahedral population ratio increasing as the temperature is decreased.

In this work[1] subtle changes in the ligands coordinated to silicon in hexacoordinate complexes cause rather dramatic geometrical changes, associated with promotion of central silicon from tetrahedral to octahedral configurations. The different hypercoordinate silicon configurations (bicapped tetrahedral, trigonal bipyramidal, and octahedral) are found to coexist in dynamic equilibrium in solution.

Neutral hexacoordinate silicon complexes[2] with halogeno ligands (**1**) undergo ionic dissociation (**2**, eq 1) in hydrogen-bond donor solvents ($CDCl_3$, $CD_2Cl_2$ and $CHFCl_2$), under given conditions.[3] A single case of a different, *nonionic* dissociation of the N→Si dative bond has recently been reported,[4] in which strong electron withdrawal by trifluoromethyl substituents weakens the dative bond and enables N→Si dissociation (**3**, eq 1). To study the generality of dative-bond dissociation, other complexes, with relatively weak coordination, were sought: complexes with two monodentate carbon ligands, rather than the commonly studied complexes **1** with one or two halogeno ligands.



(1)

**2** R,X = alkyl, aryl

**1**

**3** R = $CF_3$, X = $C_6H_{11}$

## Results

A series of silicon bis-chelates lacking halogen ligands have been prepared, **4**−**8**, with two monodentate carbon ligands. The

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(1) Preliminary report: Gostevskii, B.; Kalikhman, I.; Tessier, C. A.; Panzner, M. J.; Youngs, W. J.; Kost, D. Proceedings of the 14th International Symposium on Organosilicon Chemistry ISOSXIV, Würzburg, Germany, August 2005; p 49.

(2) For reviews on hypercoordinate silicon complexes see: (a) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99−189. (b) Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 2, pp 1339−1445. (c) Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Vol. 1, pp 839−892. (d) Bassindale, A. R.; Glynn, S. J.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 1, pp 495−511. (e) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17−31; **1996**, *96*, 927−950. (f) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Vol. 1, pp 1241−1288. (g) Chuit, C.; Corriu, R. J. P.; Reyé, C.; Young, J. C. *Chem. Rev.* **1993**, *93,* 1371. (h) Chuit, C.; Corriu, R. J. P.; Reyé, C. In *The Chemistry of Hypervalent Compounds*; Akiba, K., Ed.; Wiley-VCH: Weinheim, Germany, 1999; pp 81−146. (i) Kira, M.; Zhang, L. C. In *The Chemistry of Hypervalent Compounds*; Akiba, K., Ed.; Wiley-VCH: Weinheim, Germany, 1999; pp 147−169. (j) Brook, M. A. *Silicon in Organic, Organometallic and Polymer Chemistry*; Wiley: New York, 2000; pp 97−115. (k) Tacke, R.; Pülm, M.; Wagner, B. *Adv. Organomet. Chem.* **1999**, *44*, 221−273. (l) Tacke, R.; Seiler, O. In *Silicon Chemistry: From the Atom to Extended Systems*; Jutzi, P., Schubert, U., Eds.; Wiley-VCH: Weinheim, Germany, 2003; pp 324−337. (m) Lukevics, E.; Pudova, O. A. *Chem. Heterocycl. Compd. (Engl. Transl.)* **1996,** *32*, 1381−1418. (n) Voronkov, M. G.; Pestunovich, V. A.; Baukov, Yu. I. *Organomet. Chem. USSR* **1991,** *4*, 593. *Chem. Abstr.* **1992**, *116*, 41503y. (o) Verkade, J. G. *Coord. Chem. Rev.* **1994**, *137*, 233−295. (p) Kost, D.; Kalikhman, I. *Adv. Organomet. Chem.* **2004**, *50*, 1−106.

(3) Kost, D.; Kingston, V.; Gostevskii, B.; Ellern, A.; Stalke, D.; Walfort, B.; Kalikhman, I. *Organometallics* **2002**, *21*, 2293.

(4) Gostevskii, B.; Silbert, G.; Adear, K.; Sivaramakrishna, A.; Stalke, D.; Deuerlein, S.; Kocher, N.; Voronkov, M. G.; Kalikhman, I.; Kost, D. *Organometallics* **2005**, *24*, 2913.

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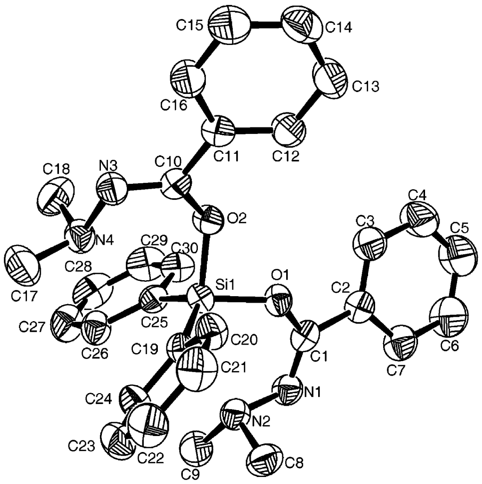
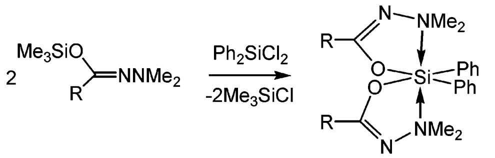


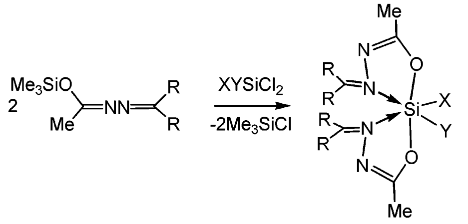
**Figure 1.** Molecular structure of **4** in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, and hydrogen atoms are omitted for clarity.

synthesis utilized the trans-silylation reaction,[2p] as outlined in eqs 2 and 3.[5] Because of the reduced electron-withdrawing



(2)

**4**, R = Ph
**5**, R = NMe$_2$



(3)

**6**, R = Me, X = Y = Ph
**7**, R,R = (CH$_2$)$_4$ , X = Y = Ph
**8**, R,R = (CH$_2$)$_4$ , X = Y = Me

power of the monodentate carbon ligands, relative to halogeno complexes, **4**−**8** were expected to have relatively weak N→Si coordination.

Single crystals of **4**−**6** and **8** were grown, and their crystal structures were determined by X-ray diffraction analysis. The resulting molecular structures are depicted in Figures 1−4, respectively, and selected bond lengths and angles are listed in Table 1.

$^1$H, $^{13}$C, and $^{29}$Si NMR spectra were measured for **4**−**8**, and their temperature dependencies were monitored. Selected NMR data at various temperatures are depicted in Figures 5−10.

## Discussion

**Solid-State Geometries.** Most of the hexacoordinate silicon compounds reported to date possess octahedral or near-octahedral geometries,[2] with the exception of one group of

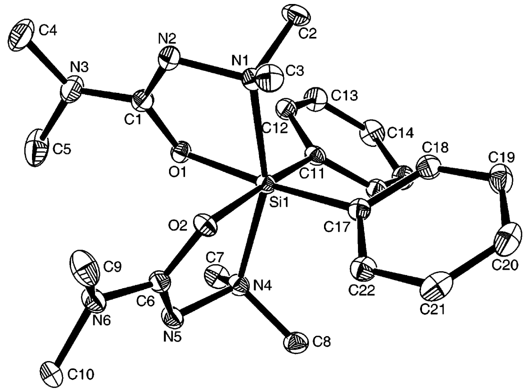


**Figure 2.** Molecular structure of **5** in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, and hydrogen atoms are omitted for clarity.

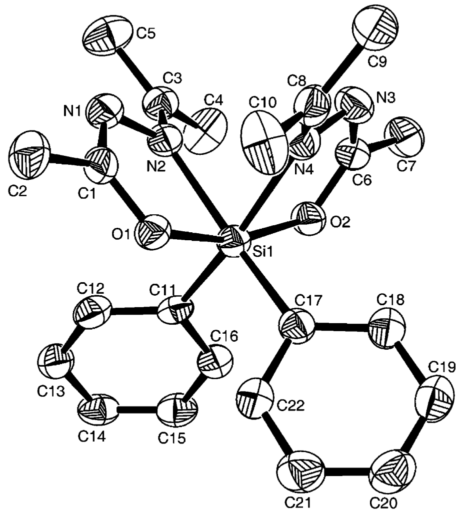


**Figure 3.** Molecular structure of **6** in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, and hydrogen atoms are omitted for clarity.

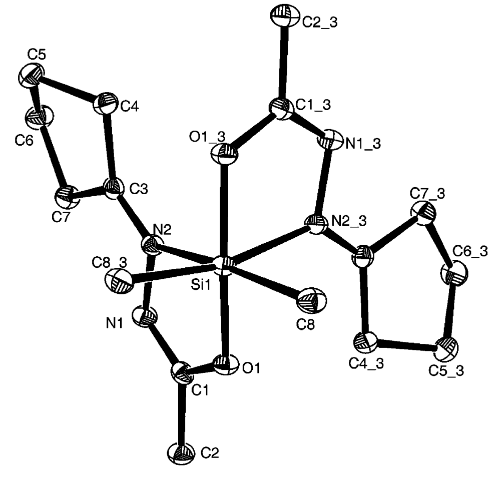


**Figure 4.** Molecular structure of **8** in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, and hydrogen atoms are omitted for clarity.

weakly coordinated complexes, referred to as "bicapped tetrahedral", reported by Corriu and co-workers.[6] Compounds **4** and **6** are neutral hexacoordinate silicon complexes, sharing the same ligand framework, SiC$_2$N$_2$O$_2$, and differing only in the slightly modified nitrogen donor groups: NMe$_2$ in **4** and the acetone imino group N=CMe$_2$ in **6**. Despite this constitutional similarity,

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(5) When 1:1 molar ratios of the reactants in eqs 2 and 3 are used, pentacoordinate monochelate compounds can be isolated: (a) Kalikhman, I. D.; Gostevskii, B. A.; Bannikova, O. B.; Voronkov, M. G.; Pestunovich, V. A. *Metalloorg. Khim.* **1989**, *2*, 205. *Chem. Abstr.* **1990**, *112*, 77291j. (b) Kalikhman, I.; Krivonos, S.; Ellern, A.; Kost, D. *Organometallics* **1996**, *15*, 5073.

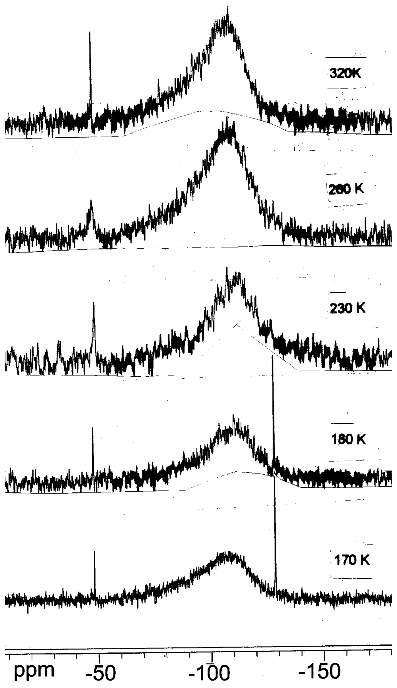
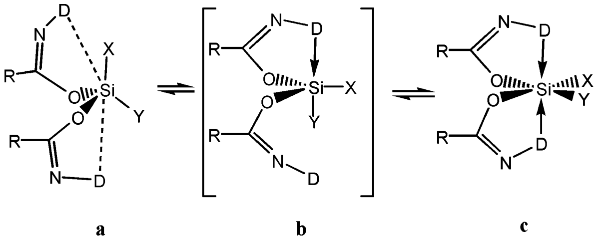


**Figure 5.** Temperature dependence of the $^{29}$Si NMR spectrum of **4** in $CD_2Cl_2$ solution.

examination of the crystal structures in Figures 1 and 3 reveals a dramatic geometrical difference: **4** is essentially a tetrahedral compound (**a**; eq 4), with the two $NMe_2$ ligands pointing their electron lone pairs toward silicon from a substantial distance (2.72 and 2.86 Å), in a bicapped-tetrahedral geometry.[6] In contrast, **6** has a nearly perfect octahedral ligand arrangement about the silicon (**c**; eq 4).



(4)

(D = NMe$_2$, N=CMe$_2$; X, Y = Ph, Me)

It is known from previous experimental reports that the imino group acts as a stronger donor than the dimethylamino group, despite the fact that the lone pair in the former is sp$^2$ and in the latter is sp$^3$.[7] This may be attributed to the fact that in $Me_2N$ the lone pair is conjugated to the adjacent double bond and must break this conjugation in order to bind to silicon. In contrast, in $NN{=}CMe_2$ the lone pair is orthogonal to the double bonds and ready for interaction with Si. It is hence concluded that the difference in molecular geometry between **4** and **6** results from the different coordination strengths: the bonding energy gained from the two dative N→Si bonds in **4** is so weak that it is insufficient to provide the energy required to promote silicon from its tetrahedral ground-state configuration to the octahedral

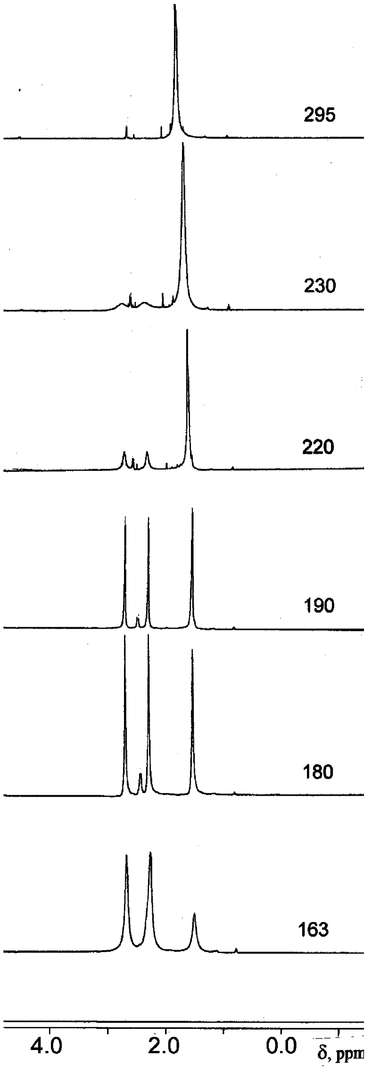


**Figure 6.** Temperature dependence of the *N*-methyl region of the $^1$H NMR spectrum of **4** in $CD_2Cl_2$ solution.

**Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4−6 and 8**

| 4 | | 5 | | 6 | | 8 | |
|---|---|---|---|---|---|---|---|
| Si−O1 | 1.680(2) | Si−O1 | 1.800(1) | Si−O1 | 1.765(3) | Si−O1 | 1.7768(9) |
| Si−O2 | 1.684(2) | Si−O2 | 1.803(1) | Si−O2 | 1.768(3) | Si−O1_3 | 1.7768(9) |
| Si−C19 | 1.854(2) | Si−C11 | 1.952(2) | Si−C17 | 1.906(4) | Si−C8 | 1.8986(1) |
| Si−C25 | 1.854(2) | Si−C17 | 1.952(2) | Si−C11 | 1.917(4) | Si−C8_3 | 1.899(1) |
| Si−N2 | 2.724(3) | Si−N1 | 2.075(1) | Si−N4 | 2.123(3) | Si−N2 | 2.130(1) |
| Si−N4 | 2.868(3) | Si−N4 | 2.098 (1) | Si−N2 | 2.138(3) | Si−N2_3 | 2.130(1) |
| O1−Si−O2 | 90.95(7) | O1−Si−O2 | 86.05(5) | O1−Si−O2 | 163.14(1) | O1−Si−O_3 | 164.95(7) |
| O1−Si−C25 | 107.82(9) | O2−Si−C11 | 169.43(6) | O1−Si−C17 | 94.24(2) | O1−Si−C8_3 | 98.17(5) |
| O2−Si−C25 | 108.84(9) | O1−Si−C17 | 170.42(6) | O2−Si−C17 | 96.72(2) | O1A-Si−C8_3 | 91.37(5) |
| O1−Si−C19 | 113.51(9) | O1−Si−C11 | 88.96(6) | O1−Si−C11 | 96.74(2) | O1−Si−C8 | 91.37(5) |
| O2−Si−C19 | 105.59(8) | O2−Si−C17 | 89.30(6) | O2−Si−C11 | 94.21(2) | O1A-Si−C8 | 98.17(5) |
| C25−Si−C19 | 124.70(9) | O2−Si−N1 | 84.66(5) | C17−Si−C11 | 98.78(2) | C8A-Si−C8 | 101.36(9) |
| | | N1−Si−N4 | 159.06(5) | N2−Si−N4 | 80.78(1) | N2−Si−N2_3 | 81.01(6) |
| | | C11−Si−N1 | 103.65(6) | C11−Si−N4 | 167.76(1) | N2−Si−C8 | 166.03(5) |
| | | C17−Si−N1 | 91.22(6) | C17−Si−N2 | 169.19(1) | N2A-Si−C8_3 | 166.03(5) |

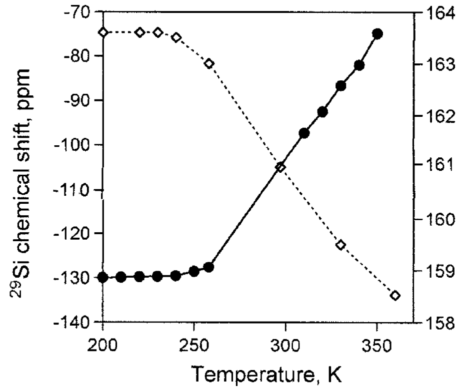


**Figure 7.** Plot of $^{29}$Si (●) and $^{13}$C (◇, imino carbon) chemical shifts of **5** in toluene-$d_8$ solution as a function of temperature.

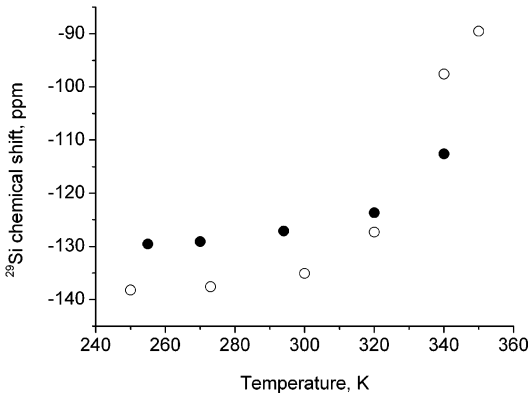


**Figure 8.** Temperature dependence of the $^{29}$Si chemical shifts of **6** (●) and **7** (○) in toluene-$d_8$ solution.

configuration. As a result, silicon retains its tetrahedral geometry and gains only the relatively weak stabilization from the distant "capping" nitrogen donors. In contrast, the slightly stronger coordination in **6** provides just enough energy to promote silicon to its octahedral geometry (**c**), thus enabling the formation of substantially stronger and shorter dative bonds (Table 1).

It appears that the energy required to change the silicon configuration from tetrahedral to octahedral has been delimited between the coordination energies of **4** and **6**, which differ only in the donor groups. This narrow energy gap may be decreased even further, when the structures of **4** and **5** are compared: the immediate environments surrounding silicon in **4** and **5** are equal, including the donor groups, and the only difference is in the remote substituent R. Thus, when R = phenyl (in **4**) is replaced by R = $NMe_2$ (in **5**), the molecular geometry in the solid state changes back to the octahedral geometry characteristic of hexacoordination (Figure 2). The dimethylamino substituents in **5** effectively release electrons, through the carbon−nitrogen double bonds, to make the donor groups just sufficiently stronger so as to make the coordination energy of the two dative bonds large enough to overcome the silicon promotion energy, resulting in an essentially octahedral molecule.

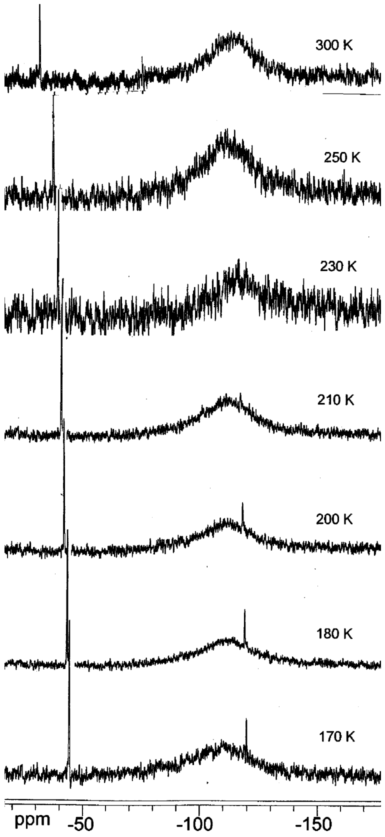


**Figure 9.** Temperature dependence of the $^{29}$Si NMR spectrum of **8** in $CD_2Cl_2$ solution.

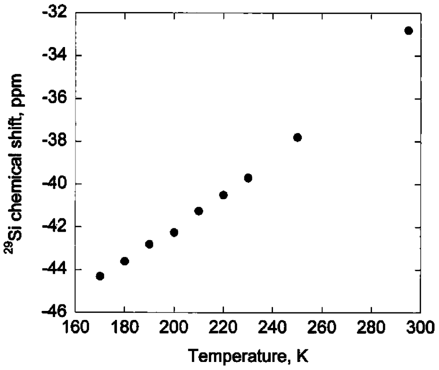


**Figure 10.** Plot of the $^{29}$Si chemical shift of **8** in $CD_2Cl_2$ solution as a function of temperature.

Compound **8** represents two opposing constitutional changes, relative to **6**: on one hand, the donor groups have been made slightly stronger by replacement of the acetone imine by cyclopentanone imine; on the other hand, the electron-withdrawing phenyl ligands have been replaced by electron-releasing methyl groups, which tend to reduce the coordination strength. The molecular structure obtained from X-ray diffraction analysis of **8** reveals a distorted octahedral geometry (Figure 4); i.e., it seems that the donor-strength enhancement has been more effective than the decrease in ligand electron-withdrawing power, resulting in sufficiently strong coordination to form an octahedral molecule. The solid-state $^{29}$Si NMR chemical shift of **8** (−115.8 ppm) confirms its hexacoordinate structure in the solid at room temperature. However, solution NMR results,

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(6) (a) Breliere, C.; Carré, F.; Corriu, R. J. P.; Poirier, M.; Royo, G.; Zwecker, J., *Organometallics* **1989**, *8*, 1831. (b) Carré, F.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reyé, C. *New J. Chem*, **1992**, *16*, 63. (c) Boyer-Elma, K.; Carré, F.; Corriu, R. J. P.; Douglas, W. E. *J. Chem. Soc., Chem. Commun.* **1995**, 725. (d) Carré, F.; Chuit, C.; Corriu, R. J. P.; Mehdi, A.; Reyé, C. *Organometallics* **1995**, *14*, 2754. (e) Belzner, J.; Schär, D.; Herbst-Irmer, R.; Kneisel, B. O,; Noltemeyer, M. *Tetrahedron* **1998**, *54*, 8481. (f) Ahdab, A. A.-E.; Rima, G.; Gornitzka, H.; Barrau, J. *J. Organomet. Chem.* **2001**, *636*, 96. (g) Karsch, H. H.; Deubelly, B.; Keller, U.; Bienlein, F.; Richter, R.; Bissinger, P.; Heckel, M.; Mueller, G. *Chem. Ber.* **1996**, *129*, 759. (h) Wagler, J.; Schley, M.; Gerlach, D.; Böhme, U.; Brendler, E.; Roewer, G. *Z. Naturforsch.* **2005**, *60b*, 1054.

(7) (a) Kalikhman, I.; Gostevskii, B.; Girshberg, O.; Krivonos, S.; Kost, D. *Organometallics* **2002**, *21*, 2551. (b) Kalikhman, I.; Gostevskii, B.; Girshberg, O.; Sivaramakrishna, A.; Kocher, N.; Stalke, D.; Kost, D. *J. Organomet. Chem*. **2003**, *686*, 202.

reported in the next section, suggest that only at relatively low temperatures does **8** prefer the octahedral geometry in solution.

A further geometrical aspect of interest in these compounds is their ordering of ligands: in the octahedral **5** the nitrogen ligands are in trans positions relative to each other, as commonly found in previously reported hydrazide-based hexacoordinate complexes with one or two halogeno ligands.[2p,7b,8] In contrast, **6** and **8** have their nitrogen ligands in cis positions, as observed in only few previous cases.[9,10] The exact reasons for the ligand-order preferences in octahedral molecules are not fully understood. However, it may be concluded that in the presence of two phenyl ligands the free-energy differences between the possible diastereomers diminish, so that several geometries can be realized, as opposed to the single diastereomer observed previously.

**Geometry Equilibration in Solution.** In view of the discrete geometries found for **4**−**6** and **8** in the solid state, the question arises whether the octahedral and bicapped-tetrahedral geometries can be found in solution and whether they coexist simultaneously. The data in Figures 5 and 6 clearly demonstrate the coexistence in dynamic equilibrium of these two geometries for **4**: at 320 K (Figure 5), a single $^{29}$Si resonance ($\delta$ −48.5 ppm) is found for **4**, corresponding to geometry **a**. As the temperature is decreased, the signal first broadens, evidence that an exchange process takes place, and at lower temperature sharpens again while a *second* signal appears at the hexacoordinate $^{29}$Si chemical shift range, $\delta$ −128.9 ppm, corresponding to geometry **c**. This equilibrium situation is completely reversible and represents the first *direct* and apparently *nondissociative* equilibrium between hexacoordinate octahedral and bicapped-tetrahedral configurations in silicon complexes.

The data in Figure 5 are supported by the temperature-dependent $^1$H NMR spectra of **4**, presented in Figure 6 for the *N*-methyl region. At high temperatures a single resonance is found for all four equivalent *N*-methyl groups, corresponding to the $C_{2v}$-symmetric **4.** When the temperature is lowered, this resonance eventually broadens and splits and two new signals appear at lower field, which are assigned to the *N*-methyl groups of the $C_2$-symmetric structure **c**. The **c**:**a** population ratio increases gradually as the temperature decreases, from 0.14 at 230 K to 4.6 at 163 K, as might be expected for the more tightly bound and compact (and hence of lower entropy) structure **c**. Similar spectral changes are also observed in the temperature-dependent $^{13}$C NMR spectra of **4** (see Experimental Section), corresponding to the same geometrical equilibrium.

The evidence for the assignment of **a**, and not **b**, to the low-field signal in Figure 5 and the corresponding signal in Figure 6, is as follows. (a) The $^{29}$Si chemical shift of **4** in solution is equal to that found in the solid state ($\delta$ −49.0 ppm), proving that the structures in the crystal state and in solution are essentially the same. (b) This $^{29}$Si chemical shift corresponds closely to that reported for $[\mathrm{Ph_2Si(O)_2}]_n$ ($\delta$ −46.1 ppm[11]). (c) The $^{29}$Si chemical shift is essentially independent of temperature (Figure 5), as required by tetracoordinate silanes, in contrast to the well-documented temperature dependence of $^{29}$Si chemical shifts in pentacoordinate compounds.[2a,n,p] (d) In the temperature-dependent $^1$H NMR spectra (Figure 6), as well as in the $^{13}$C spectra, the single high-field *N*-methyl signal remains sharp down to 163 K, without splitting into the two *N*-methyl resonances expected for **b**, indicating that no rapid "flip-flop" type exchange takes place and, hence, excluding geometry **b**.

Even in **5**, which has the octahedral geometry **c** in the solid state, the solution $^{29}$Si NMR spectra (Figure 7) are temperature-dependent: at low temperature the $^{29}$Si chemical shift corresponds to the octahedral **c**, while at temperatures above 250 K the geometry gradually changes to the lower coordination compounds **a** and/or **b**, in equilibrium with **c**. Rapid exchange at these relatively high temperatures prevents resolution of individual species in the NMR spectra and, hence, no definite assignment can be made. The observation that in **4** the two species (**c** and **a**) are resolved at low temperatures (Figures 5 and 6), and in **5** they are not (Figure 7), results from the complete predominance of geometry **c** in **5**: at low enough temperatures (<230 K) at which exchange would have been sufficiently slow to permit resolution of individual species, the equilibrium is shifted completely to **c** and, hence, no exchange can be observed.

The $^{13}$C NMR spectrum of **5** is also temperature-dependent (Figure 7), in the imino-carbon range, in a manner which clearly follows the same geometrical changes causing the temperature dependence of the $^{29}$Si chemical shift, although the magnitude of the change is much smaller.

Complexes **6** and **7** differ from **4** only at the donor groups: they have the slightly stronger alkylideneimino donors coordinated to silicon, rather than the dimethylamino group in **4**. The resulting stronger coordination in **6** caused the geometrical changes in the crystal, discussed above, as well as different NMR spectral behavior in solution: Figure 8 shows the temperature dependence of the $^{29}$Si NMR chemical shifts for **6** and **7**. It is evident from the figure that compounds **6** and **7** undergo a dynamic equilibrium reaction between species of different coordination numbers (**c** $\rightleftarrows$ **a**, **b**), in analogy to **4** and **5**, such that at higher temperature the coordination number decreases. However, the shift to lower coordination occurs at significantly higher temperatures than in **4**, and in **6** it remains substantially hexacoordinate even at 340 K (average $\delta$ −112.5 ppm), as a result of the stronger N→Si coordination and corresponding increased stability of the octahedral geometry **c**.

Perhaps the most striking equilibrium situation is found in **8**. The presence of the two methyl ligands suggests that coordination should be relatively weak. It was therefore surprising to find that in the single crystal obtained from an *n*-hexane solution, **8** had the octahedral **c** molecular geometry. Indeed, examination of the $^{29}$Si NMR spectra of **8** (Figure 9) suggests that at room temperature the compound is predominantly either tetra- or pentacoordinate, as judged from the relatively low-field resonance (−32.8 ppm at 295 K in $\mathrm{CD_2Cl_2}$). The significant temperature dependence of this signal (Figure 10) indicates that it arises from a *penta*coordinate silicon species, possibly **b**, and that the temperature dependence probably results from a dynamic equilibrium between the tetra- and pentacoordinate complexes, **a** and **b**. Upon cooling, a second resonance appears at much higher field (−119.8 ppm, Figure 9), assigned to the octahedral complex (geometry **c**), in good agreement with the solid-state $^{29}$Si chemical shift (−115.8 ppm). Thus, equilibrium is demonstrated possibly among *three* different geometries of the same constitutional complex, **8**, in which the relative populations of the bicapped-tetrahedral, trigonal-bipyramidal, and octahedral components vary as a function of temperature.[12]

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[8] Kalikhman, I.; Krivonos, S.; Stalke, D.; Kottke, T.; Kost, D. *Organometallics,* **1997**, *16*, 3255.

[9] Klebe, G.; Tran Qui, D. *Acta Crystallogr.* **1984**, *C40*, 476.

[10] Gostevskii,B.; Kalikhman, I.; Tessier, C. A.; Panzner, M. J.; Youngs, W. J.; Kost, D. *Organometallics* **2005**, *24*, 5786.

[11] Engelhardt, G.; Mägi, M.; Lippmaa, E. *J. Organomet. Chem*. **1973**, *54*, 115. Kintzinger, J.-P.; Marsmann, H. *Nucl. Magn. Reson.* **1981**, *17,* 65.

[12] For the only previously reported similar situation see ref 6h and: Wagler, J.; Böhme, U.; Brendler, E.; Roewer, G. *Organometallics* **2005**, *24*, 1348.

**Table 2. Crystal Data and Experimental Parameters for the Structure Analyses of 4−6 and 8**

| | **4** | **5** | **6** | **8** |
|---|---|---|---|---|
| CCDC no. | 289152 | 289153 | 289154 | 289155 |
| empirical formula | $C_{30}H_{32}N_4O_2Si$ | $C_{22}H_{34}N_6O_2Si$ | $C_{22}H_{28}N_4O_2Si$ | $C_{16}H_{28}N_4O_2Si$ |
| formula mass, g mol$^{-1}$ | 508.69 | 442.64 | 408.57 | 336.51 |
| collection *T*, K | 230(1) | 100(2) | 230(1) | 100(2) |
| cryst syst | monoclinic | monoclinic | monoclinic | orthorhombic |
| space group | $P2_1/c$ | $C2/c$ | $P2_1/c$ | *Pbcn* |
| *a*, Å | 10.367(2) | 34.890(3) | 9.225(2) | 13.5760(9) |
| *b*, Å | 25.806(5) | 9.3494(8) | 10.709(2) | 8.0012(5) |
| *c*, Å | 11.119(2) | 15.879(1) | 22.519(4) | 16.481(1) |
| *β*, deg | 108.74(3) | 114.996(1) | 99.66(3) | 90 |
| *V*, Å$^3$ | 2817.0(9) | 4694.7(7) | 2193.1(8) | 1790.2(2) |
| *Z* | 4 | 8 | 4 | 4 |
| $\rho_{calcd,}$ Mg m$^{-3}$ | 1.199 | 1.253 | 1.237 | 1.249 |
| *F*(000) | 1080 | 1904 | 872 | 728 |
| *θ* range, deg | 1.58−25.35 | 1.29−28.30 | 1.83−25.40 | 2.47−28.28 |
| no. of coll rflns | 19 149 | 20 503 | 12 999 | 14 847 |
| no. of indep rflns | 4981 | 5637 | 3900 | 2204 |
| $R_{int}$ | 0.0631 | 0.0389 | 0.1099 | 0.0328 |
| no. of rflns used | 4981 | 5637 | 3900 | 2204 |
| no. of params | 335 | 288 | 263 | 107 |
| GOF | 0.962 | 1.061 | 0.963 | 1.109 |
| R1, wR2 ($I > 2\sigma(I)$) | 0.0472, 0.1096 | 0.0468, 0.1073 | 0.0617, 0.1500 | 0.0402, 0.1028 |
| R1, wR2 (all data) | 0.0958, 0.1254 | 0.0585, 0.1127 | 0.1366, 0.1775 | 0.0420, 0.1039 |
| max/min res electron dens, e Å$^{-3}$ | 0.283/−0.244 | 0.486/−0.347 | 0.391/−0.446 | 0.386/−0.260 |

It is evident from a comparison of Figures 5 and 9 that the population ratios (**a** + **b**):**c** at the low-temperature end are different for **4** and **8**: at 170 K, structure **c** by far predominates for **4** (Figure 5), whereas the opposite ratio is found for **8** in Figure 9. This suggests that the coordination strength in **4**, at 170 K, is greater than in **8**, and it may provide some further insight into these complexes: while the donor is expected to be stronger in **8** relative to **4**, the monodentate ligands are less electron withdrawing in **8** vs **4** and, hence, are less effective in promoting coordination. The end result suggests that in these two systems the electron-withdrawal effect by the monodentate ligands plays a more dominant role than the donor strength.

It is interesting to note that **8** is essentially tetra- and/or pentacoordinate at room temperature in $CD_2Cl_2$ solution, while in the crystal form, which is stable at room temperature, it is octahedral. This seems to result from the entropy effect, which in solution favors looser, lower coordination species at relatively high temperature (room temperature), while in the solid state the enthalpy effect associated with the stronger bonding in the octahedral geometry prevails.

## 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 Büchi 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 (**4** and **6**) and a Bruker Apex CCD diffractometer (**5** and **8**). Experimental details are listed in Table 2, and full data tables are included in the Supporting Information. Crystallographic data for **4**−**6** and **8** have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers are listed in Table 2. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (internat.) + 44(1223)336-033; e-mail, deposit@ccdc.cam.ac.uk). CP-MAS solid-state NMR spectra were measured on a Varian Unityplus-4.7 T (200 MHz) spectrometer using a Doty scientific magic-angle spinning probe, at ambient temperature.

**Bis[*N*-(dimethylamino)benzimidato-*N*,*O*]diphenylsilicon(IV) (4).** A solution of 0.891 g (3.77 mmol) of *N*-(dimethylamino)-*O*-(trimethylsilyl)benzimidate[13] and 0.417 g (1.65 mmol) of $Ph_2SiCl_2$ in 5 mL of trichloromethane was kept at room temperature for 24 h, followed by removal of volatiles under reduced pressure. A 0.839 g amount of a white crystalline residue was obtained (100% crude yield). Recrystallization from 10 mL of *n*-hexane gave colorless crystals: 0.608 g (73% yield) of **4**; mp 119 °C. $^1$H NMR ($CD_2Cl_2$, 295 K): *δ* 1.78 (s, 12H, $NMe_2$), 7.34−8.15 (m, 20H, Ph). $^1$H NMR ($CD_2Cl_2$, 170 K): *δ* 1.55, 2.28, 2.69 (3s, 12H, $NMe_2$), 7.16−8.15 (m, 20H, Ph). $^{13}$C NMR ($CD_2Cl_2$, 295 K): *δ* 47.1 ($NMe_2$), 127.3−134.9 (Ph). $^{13}$C NMR ($CD_2Cl_2$, 170 K): *δ* 46.1, 50.2, 50.6 ($NMe_2$), 127.3−134.9 (Ph) 157.1, 163.8 (C═N). $^{29}$Si NMR ($CD_2Cl_2$, 295 K): *δ* −48.5. $^{29}$Si NMR ($CD_2Cl_2$, 170 K): *δ* −48.5, −128.9. CPMAS solid-state $^{29}$Si NMR (300 K): *δ* −49.0. Anal. Calcd for $C_{30}H_{32}N_4O_2Si$: C, 70.93; H, 6.34; N, 11.01. Found: C, 70.90; H, 6.54; N, 11.10.

**Bis[*N*′-(dimethylamino)-*N*″,*N*″-dimethylcarbamoimidato-*N*,*O*]-diphenylsilicon(IV) (5).** **5** was prepared from the precursor *N*-(dimethylamino)-*N*′,*N*′-dimethyl-*O*-(trimethylsilyl)carbamoimidate ($Me_2NC(OSiMe_3){=}NNMe_2$; **9**), the synthesis of which follows: to a solution of 15.0 g (0.115 mol) of 1,1,4,4-tetramethylsemicarbazide ($Me_2NCONHNMe_2$) with mp 69−70 °C (lit.[14] mp 69−71) in 150 mL of diethyl ether was added 11.6 g (0.116 mol) of $Et_3N$ and 17.5 g (0.114 mol) of $Me_3SiBr$. The mixture was refluxed for 4 days and cooled to room temperature, and the precipitate was filtered off. The volatiles were removed from the filtrate under reduced pressure, and the residue was distilled. **9** was collected at 42−43 °C at 2 mmHg: 17.4 g (75% yield). $^1$H NMR ($CDCl_3$, 300 K): *δ* 0.1 (s, 9H, $Me_3Si$), 2.14 (s, 6H, $Me_2NC$), 2.67 (s, 6H, $Me_2NN$). $^{13}$C NMR ($CDCl_3$, 300 K): *δ* 0.85 ($Me_3Si$), 36.9 (*Me*$_2$NC), 47.9 ($Me_2NN$), 56.0 (C═N). $^{29}$Si NMR ($CDCl_3$, 300 K): *δ* 14.96.

A mixture of 0.529 g (2.09 mmol) of $Ph_2SiCl_2$ and 0.851 (4.18 mmol) of **9** in 5 mL of trichloromethane was kept for 12 h at room temperature, followed by removal of volatiles under reduced

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[13] Kost, D.; Kalikhman, I.; Raban, M. *J. Am. Chem. Soc.* **1995**, *117*, 11512.

[14] Jensen, K. A. *Acta Chem. Scand., Ser. B* **1977**, *B31*, 145.

pressure. The oily residue was crystallized by addition of 5 mL of *n*-hexane, yielding colorless crystals: 0.664 g (72% yield) of **5**; mp 94−95 °C. $^1$H NMR (CDCl$_3$, 300 K): *δ* 2.07 (s, 12H, NNMe$_2$), 2.85 (s, 12H, CNMe$_2$), 7.22−7.74 (m, 10H, Ph). $^1$H NMR (toluene-*d*$_8$, 200 K): *δ* 1.98, 2.55 (2s, 12H, NNMe$_2$), 2.63, 2.76 (2s, 12H, CNMe$_2$), 6.96−8.10 (m, 10H, Ph). $^{13}$C NMR (toluene-*d*$_8$, 295 K): *δ* 36.6 (CNMe$_2$), 50.79 (NNMe$_2$), 126.8, 127.6, 137.0, 143.6 (Ph), 161.0 (C═N). $^{13}$C NMR (toluene-*d*$_8$, 200 K): *δ* 36.4, 37.1 (CNMe$_2$), 52.1, 52.6 (NNMe$_2$), 128.6−148.6 (Ph). $^{29}$Si NMR (toluene-*d*$_8$, 340 K): *δ* −82.0. $^{29}$Si NMR (toluene-*d*$_8$, 200 K): *δ* −130.0. Anal. Calcd for $C_{22}H_{34}N_6O_2Si$: C, 59.70; H, 7.74; N, 18.95. Found: C, 59.71; H, 7.45; N, 18.60.

**Bis[*N*-(isopropylideneimino)acetimidato-*N,O*]diphenylsilicon(IV) (6).** A mixture of 0.534 g (2.11 mmol) of $Ph_2SiCl_2$ and 0.803 g (4.31 mmol) of *N*-(isopropylideneimino)-*O*-(trimethylsilyl)acetimidate[15] in 5 mL of trichloromethane was stirred for 12 h at ambient temperature. The volatiles were removed under reduced pressure, leaving a yellowish solid, which after washing with *n*-hexane and drying under vacuum yielded a white powder: 0.768 g (89% yield) of **3**; mp 141−142 °C. $^1$H NMR (CDCl$_3$, 295 K): *δ* 1.88 (s, 6H, CMe), 2.10, 2.29 (2s, 12H, NCMe$_2$), 7.12−7.44 (m, 10H, Ph). $^{13}$C NMR (CDCl$_3$, 295 K): *δ* 19.0 (OC*Me*), 22.5, 23.1 (NC*Me*$_2$), 126.2, 126.5, 134.1, 150.0 (Ph), 165.3, 166.9 (C═N). $^{29}$Si NMR (CDCl$_3$, 295 K): *δ* −127.1. Anal. Calcd for $C_{22}H_{28}N_4O_2Si$: C, 64.67; H, 6.91; N, 13.71. Found: C, 64.49; H, 7.05; N, 13.58.

**Bis[*N*-(cyclopentylideneimino)acetimidato-*N,O*]diphenylsilicon(IV) (7). 7** was prepared from *N*-(cyclopentylideneimino)-*O*-(trimethylsilyl)acetimidate (**10**),[15] obtained from MeCONHN═C(CH$_2$)$_4$ (mp 117−119 °C, lit.[16] mp 121−123 °C) and $Me_3SiCl$ in the usual manner[13] (bp 65 °C at 0.6 mmHg). $^1$H NMR for **10**: *δ* (CDCl$_3$, 295 K) 0.22 (s, 9H, SiMe), 1.69, 2.35 (2m, 8H, (CH$_2$)$_4$), 1.99 (s, 3H, CMe). $^{13}$C NMR for **10** (CDCl$_3$, 295 K): *δ* 0.0 (SiMe), 15.6 (C*Me*), 24.6, 24.7, 29.8, 33.0 ((CH$_2$)$_4$), 164.2, 175.5 (C═N). $^{29}$Si NMR for **10** (CDCl$_3$, 295 K): 19.7.

A solution of 0.470 g (1.86 mmol) of $Ph_2SiCl_2$ and 0.814 (3.83 mmol) of **10** in 5 mL of trichloromethane was stirred for 24 h at ambient temperature. The volatiles were removed under reduced pressure, and the remaining pale green precipitate was washed with *n*-hexane and dried under vacuum, yielding a powder: 0.774 g (90% yield) of **7**; mp 173−174 °C. $^1$H NMR (CDCl$_3$, 295 K): *δ* 1.62−2.63 (br m, 16H, (CH$_2$)$_4$), 2.21 (s, 6H, Me), 7.06−7.42 (m, 10H, Ph). $^{13}$C NMR (CDCl$_3$, 295 K): *δ* 19.0 (CMe), 23.3, 25.4, 32.4, 33.7 ((CH$_2$)$_4$), 125.9, 126.4, 133.9, 151.6 (Ph), 167.2, 178.3 (C═N). $^{29}$Si NMR (CDCl$_3$, 295 K): *δ* −135.9. Anal. Calcd for $C_{26}H_{32}N_4O_2Si$: C, 67.79; H, 7.00; N, 12.16. Found: C, 68.00; H, 7.16; N, 12.10.

**Bis[*N*-(cyclopentylideneimino)acetimidato-*N,O*]dimethylsilicon(IV) (8).** A mixture of 0.357 g (2.77 mmol) of $Me_2SiCl_2$ and 1.216 g (5.72 mmol) of **10** in 5 mL of trichloromethane was stirred for 28 h at 65 °C. The volatiles were removed under reduced pressure, leaving a yellow precipitate, which was recrystallized by the addition of 10 mL of *n*-hexane, yielding pale yellow crystals: 0.473 g (51% yield) of **8**; mp 90−92 °C. $^1$H NMR (CDCl$_3$, 300 K): *δ* 0.45 (s, 6H, SiMe), 1.64−2.50 (m, 16H, (CH$_2$)$_4$), 1.99, 2.01 (2s, 6H, CMe). $^{13}$C NMR (CDCl$_3$, 295 K): *δ* 3.69 (SiMe), 16.1, 19.1 (C*Me*), 23.9, 24.5, 24.7, 24.9, 25.0, 29.5, 30.9, 31.3, 32.9 ((CH$_2$)$_4$), 164.1, 164.2, 174.2, 175.3 (C═N). $^{29}$Si NMR (CDCl$_3$, 300 K): *δ* −31.5. Two isomers were observed at lower temperature. $^1$H NMR (CD$_2$Cl$_2$, 170 K): major isomer, *δ* 0.40 (s, SiMe) 1.64−2.9 (m, (CH$_2$)$_4$), 1.91, 2.00 (2s, CMe); minor isomer, *δ* 0.20 (s, SiMe) 1.64−2.9 (m, (CH$_2$)$_4$), 1.91, (s, CMe). $^{13}$C NMR (CD$_2$Cl$_2$, 170 K): isomer mixture, *δ* 4.65, 11.0 (SiMe), 16.3, 19.0, 19.3 (CMe), 24.0, 24.1, 24.8, 25.1, 25.5, 30.9, 31.3, 32.2, 33.0, 33.1, 33.7 ((CH$_2$)$_4$), 165.5, 166.1, 166.5, 175.7, 176.2, 176.8 (C═N). $^{29}$Si NMR (CD$_2$Cl$_2$, 170 K): *δ* −44.3, −119.8. CPMAS solid-state $^{29}$Si NMR (300 K): −115.9. Anal. Calcd for $C_{16}H_{28}N_4O_2Si$: C, 57.11; H, 8.39; N, 16.65. Found: C, 57.20; H, 7.98; N, 16.51.

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**Supporting Information Available:** Tables of crystallographic data for compounds **4**−**6** and **8**; data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] Gostevskii, B.; Pestunovich, V.; Kalikhman, I.; Sivaramakrishna, A.; Kocher, N.; Deuerlein, S.; Leusser, D.; Stalke, D.; Kost, D. *Organometallics* **2004**, *23*, 4346.

[16] Majchrzak, M. W.; Bekhazi, M.; Tse-Sheepy, I.; Warkentin, J. *J. Org. Chem.* **1989**, *54*, 1842.