Competitive Molecular Rearrangements in Hexacoordinate Cyano-Silicon Dichelates

Inna Kalikhman,*,[†] Boris Gostevskii,[†,‡] Evgenia Kertsnus,[†] Mark Botoshansky,[§]
Claire A. Tessier,[⊥] Wiley J. Youngs,[⊥] Stephan Deuerlein,[‖] Dietmar Stalke,[‖] and
Daniel Kost*,[†]

Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel, A. E. Favorsky Irkutsk Institute of Chemistry, RAS, Irkutsk, Russian Federation, Department of Chemistry, Technion−Israel Institute of Technology, Haifa 32000, Israel, Department of Chemistry, University of Akron, Akron, Ohio 44325-3601, and Institut für Anorganische Chemie, Universität Göttingen, Göttingen, Germany

Received December 25, 2006

Pentacoordinate siliconium chloride or neutral hexacoordinate silicon complexes with imino-nitrogen donor groups react with cyanotrimethylsilane in two competing reactions, leading either to addition of the cyano group to the imino carbon or to hexacoordinate cyano-silicon complexes. The latter may further transform to a rearranged tricyclic pentacoordinate complex. The common driving force for these reactions seems to be the conversion of one of the two initial N→Si dative bonds, present in the starting complexes, to a shorter formal covalent bond.

Introduction

Hypercoordinate silicon compounds are highly versatile and flexible molecules, capable of a variety of intra- and intermolecular transformations.[1] We have recently prepared and reported on a series of penta- and hexacoordinate hydrazide-based silicon dichelates, in which the ligand donor group is an imino nitrogen atom (**1**).[1p] Complexes **1** readily dissociate to ionic siliconium halide salts (**2**) at ambient temperature in chloroform solutions (eq 1).[2] The ionic **2** was shown to undergo an interchelate molecular rearrangement, consisting of an internal aldol-type condensation, presumably catalyzed by its own halide counterion (eq 2).[3] Surprisingly, the hexacoordinate silacyclobutane complexes (**4**) also undergo this rearrangement, in the absence of counterion, forming **5** (eq 3). These rearrangements take place under mild *thermal* conditions.[4]

The condensation of eq 2 (and eq 3 to give **5a**,**b**) requires the presence of protons in α-position relative to the imino carbon atoms. Only in the *absence* of α-protons did **4** undergo a different molecular rearrangement, namely, ring opening of the four-membered chelate, followed by addition to the imino double bond (**6a**,**b**, eq 3). Both of these reactions (eq 2 and both sides of eq 3) are presumably driven by the conversion of one of the relatively long N→Si dative bonds to a regular (shorter) covalent bond.[4] The present report describes new cyano complexes of silicon, in which these two molecular rearrangements, interchelate condensation and double-bond addition, take place *simultaneously* in a competitive manner, depending on the reaction conditions.

Results

The results of reactions of cyanotrimethylsilane (Me_3SiCN, **7**)[5] with three different silicon complex systems is described. Because of the different courses that these reactions take, each one is detailed separately below.

Reaction of Cyanotrimethylsilane with Methylsiliconium Chloride (2a). 2a was prepared by the reaction of methyl-

---

[†] Ben-Gurion University.

[‡] Favorsky Irkutsk Institute of Chemistry.

[§] Technion−Israel Institute of Technology.

[⊥] University of Akron.

[‖] Universität Göttingen.

(1) 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; *Chem. Rev.* **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*; Kin-ya Akiba, Ed.; Wiley-VCH: Weinheim, Germany, 1999; pp 81−146. (i) Kira, M.; Zhang, L. C. In *The Chemistry of Hypervalent Compounds*; Kin-ya Akiba, 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.

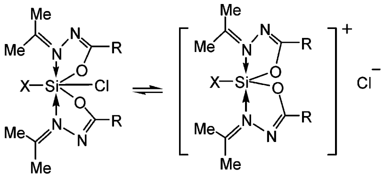
(2) Kost, D.; Kingston, V.; Gostevskii, B.; Ellern, A.; Stalke, D.; Walfort, B.; Kalikhman, I. *Organometallics* **2002**, *21*, 2293.

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

(4) Gostevskii, B.; Kalikhman, I.; Tessier, C. A.; Panzner, M. J.; Youngs, W. J.; Kost, D. *Organometallics* **2005**, *24*, 5786.

(5) (a) Brook, M. A. *Silicon in Organic, Organometallic and Polymer Chemistry*; Wiley: New York, 2000; p 196. (b) Groutas, W. C.; Felker, D. *Synthesis* **1980**, 861. (c) Voronkov, M. G.; Keiko, N. A.; Kuznetsova, T. A.; Tsetlina, E. O. *Zh. Obsh. Khim.* **1978**, *48*, 2138. (d) Voronkov, M. G.; Keiko, N. A.; Kuznetsova, T. A.; Kalikhman, I. D. *Metalloorg. Khim.* **1991**, *4*, 906.

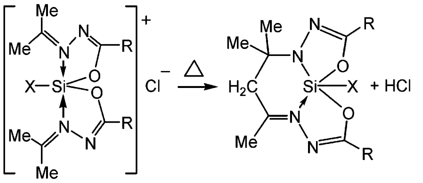
10.1021/om061176y CCC: $37.00



(1)

1 **2**

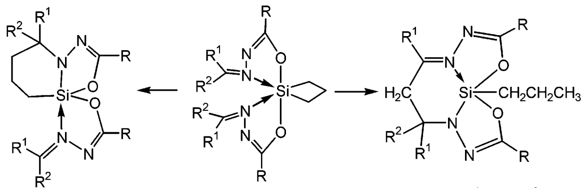
a, R = X = Me
b, R = Ph; X = C_6H_{11}
c, R = CF_3; X = Me
d, R = Me, X = Cl



+ HCl (2)

2 **3**

a, R = X = Me
b, R = Ph; X = C_6H_{11}
c, R = CF_3; X = Me
d, R = Me, X = Cl



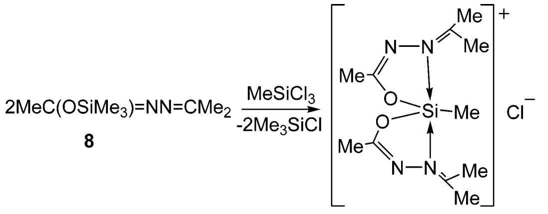
(3)

6a, R = Me, R^1= Ph, R^2= H
6b, R = CF_3, R^1 = Ph, R^2 = H

4

5a, R = Me, R^1 = H, R^2 = Me
5b, R = Ph, R^1 = R^2 = Me

trichlorosilane and the *O*-(trimethylsilyl)hydrazide derivative (**8**) as described previously and shown in eq 4.[3]

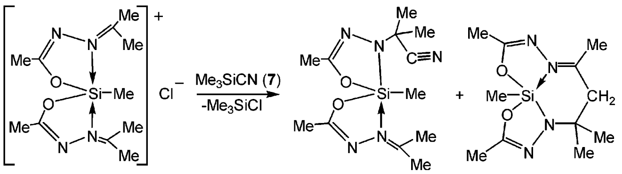


(4)

8 **2a**

This class of silicon complexes (**2**), with the relatively strong isopropylidenimino donor groups, is known to exist as the ionic siliconium salt at room temperature, in CD_2Cl_2 or $CDCl_3$ solution.[3,6] When **2a** is reacted with an equimolar amount of **7** for 1 h in chloroform solution at ambient temperature, it is converted nearly quantitatively to the cyano derivative **9**, with a trace of the rearrangement product **3a** (eq 5). **9** is identified by its typical NMR spectra (Table 2): the ^{29}Si resonance (−75.9 ppm) confirms that it is a pentacoordinate complex; in the ^{1}H and ^{13}C spectra of **9**, the required six C-methyl and one Si-methyl resonances are found; the original isopropylidene imino-carbon resonance of **2a** at 165.6 ppm[3] has turned in **9** to a saturated quaternary carbon resonance at 53.3 ppm. The cyano carbon signal is found in its typical region, 124.5 ppm. In addition, the initial two equivalent pairs of C═N carbon atoms in **2a**, giving rise to two resonances, have turned to three signals, two of which are at low field due to conjugation, whereas the third one lost its conjugation and is found at a higher field, 146.2 ppm.

The appearance of **3a** as a minor byproduct could result from rearrangement of either the starting material **2a**,[3] or its transient (not observed) anion-exchanged cyanide analogue, or as a secondary reaction of **9**. The latter option may be ruled out since no further **9** to **3a** conversion was observed upon prolonged standing. It could not be established with certainty which of the former two possibilities caused formation of **3a**.

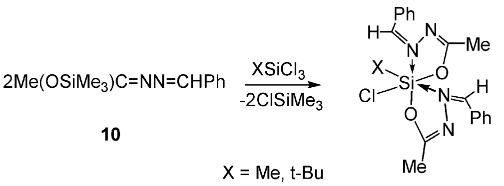


(5)

2a **9** (90%) **3a** (10%)

The facile formation of **9** is in contrast to previous transsilylation reactions,[6] in that the incoming cyano ligand does not bind directly to silicon, but instead adds to the imino carbon. **7** has been reported previously to readily add to imino[7] and carbonyl[8] double bonds, and in that sense the result is not surprising. However, this is not a complete addition to the double bond, since the trimethylsilyl group does not bind to nitrogen but rather forms chlorotrimethylsilane with the chloride counterion. Instead, the existing dative N→Si bond is upgraded to a formal covalent bond. The reaction is reminiscent of a thermal migration of silicon from a Si−Si bond to the adjacent imino carbon observed by Roewer,[9] as well as a similar but photochemical alkyl migration from silicon to the imino carbon.[10]

Reaction of Cyanotrimethylsilane with Benzaldimino Complexes (11). Complexes **11a** and **11b** were prepared by transsilylation of the *O*-(trimethylsilyl)benzaldiminoacethydrazide (**10**)[4] with the corresponding methyl- and *tert*-butyltrichlorosilanes, respectively (eq 6).



(6)

10

X = Me, t-Bu

11a, X = Me
11b, X = t-Bu

The structure of **11b** has been confirmed by an X-ray crystal analysis and is depicted in Figure 1. Selected bond lengths and angles are listed in Table 1. One of the two possible isomers was characterized; however both are found in the NMR spectra (see Experimental Section). The molecular geometry of **11b**, as shown in Figure 1, features a hexacoordinate complex with near octahedral geometry. This is rather surprising, in view of a previously reported *tert*-butyl complex (**1**, R = Ph, X = t-Bu) that ionized to **2** to reduce steric congestion.[6b] The resistance of **11b** to dissociate must result from the relative instability of the pentacoordinate siliconium ion, due to weak electron donation by the benzaldimino ligand groups. The hydrogen and phenyl groups attached to the imino carbon in **11b** are strong

---

(6) (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.

(7) (a) Cainelli, G.; Giacomini, D.; Treré, A.; Galletti, P. *Tetrahedron, Asymmetry* **1995**, *6*, 1593. (b) Merchan, F. L.; Merino, P.; Tejero, T. *Tetrahedron Lett.* **1995**, *36*, 6949.

(8) (a) Gostevskii, B. A.; Vyazankina, O. A.; Vyazankin, N. S. *Zh. Obsh. Khim.* **1983**, *53*, 1843. (b) Kruglaya, O. A.; Gostevskii, B. A.; Kalikhman, I. D.; Vyazankin, N. S. *Zh. Obsh. Khim.* **1979**, *49*, 354. (c) Cunico, R. F.; Kuan, C. P. *J. Org. Chem.* **1992**, *57*, 3331.

(9) (a) Wagler, J.; Böhme, U.; Roewer, G. *Organometallics* **2004**, *23*, 6066. (b) Wagler, J. *Organometallics* **2007**, *26*, 155.

(10) Wagler, J.; Doert, T.; Roewer, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 2441.

(11) (a) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933. (b) *E,Z* isomerization of the imino double bond would have required much higher temperature.

Table 1. Selected Bond Lengths and Angles for 11b, 12a, and 14

11b		12a		14	
		Bond Lengths, Å			
Si−O2	1.7591(18)	Si−O2	1.7787(16)	Si−O1	1.7332(11)
Si−O1	1.7926(17)	Si−O1	1.7358(16)	Si−O1A	1.7332(11)
Si−C7	1.959(3)	Si−N1	1.765(2)	Si−N2	1.9289(12)
Si−N1	1.977(2)	Si−C20	1.863(3)	Si−N2A	1.9289(12)
Si−N2	2.033(2)	Si−N4	1.958(2)	Si−Cl(1)A	2.245(3)
Si−Cl(1)	2.214(1)			Si−C6	1.964(15)
		Angles, deg			
O2−Si−N1	166.14(9)	O1−Si−O2	153.47(9)	O1−Si−O1A	180.0
C7−Si−N2	174.44(10)	N1−Si−N4	145.03(10)	N2−Si−N2A	180.0
O1−Si−Cl	165.26(7)	O1−Si−N1	85.17(8)	C6−Si−C6A	180.0
O2−Si−O1	89.79(8)	N1−Si−O2	91.10(8)	O1A−Si−N2A	83.98(5)
O2−Si−C7	94.06(11)	O1−Si−C20	105.16(1)	O1−Si−N2A	96.02(5)
O1−Si−C7	97.58(10)	N1−Si−C20	114.33(11)	O1A−Si−N2	96.02(5)
O1−Si−N1	80.90(8)	O2−Si−C20	100.30(10)	O1−Si−N2	83.98(5)
C7−Si−N1	97.31(10)	O1−Si−N4	87.73(8)	O1A−Si−C6A	89.2(6)
O2−Si−N2	80.53(8)	O2−Si−N4	80.37(8)	O1A−Si−C6	90.8(6)
N1−Si−N2	88.23(9)	C20−Si−N4	100.58(11)	O1−Si−C6	89.2(6)
O2−Si−Cl	94.55(6)			N2A−Si−C6	92.5(6)

Table 2. Selected ^{1}H, ^{13}C, and ^{29}Si Chemical Shift Data Leading to Structural Assignments of 9, 12a, 12b, 13, and 17[a]

compd	Si	*H*C−N	*C*−C≡N	*C*≡N	Me*C*=NN=C	MeC=NN=*C*	Me*C*=NN−C
9	−75.9		53.3	124.5	169.4	165.6	146.2
12a	−83.6	5.87,	53.3	126.8	172.5	158.5	153.2
	−84.9	5.93	53.5	126.9	172.6	158.3	153.0
12b	−82.7	5.87,	53.3	119.6	172.6	158.9	153.1
	−83.8	5.89	53.7	120.1	172.7	159.0	153.0
13	−102.3		52.9	124.1	174.6	165.2	145.4
17	−43.8		51.8	121.4			150.1

[a] Data for two diastereomers are listed in the spectra of each of **12a** and **12b**.

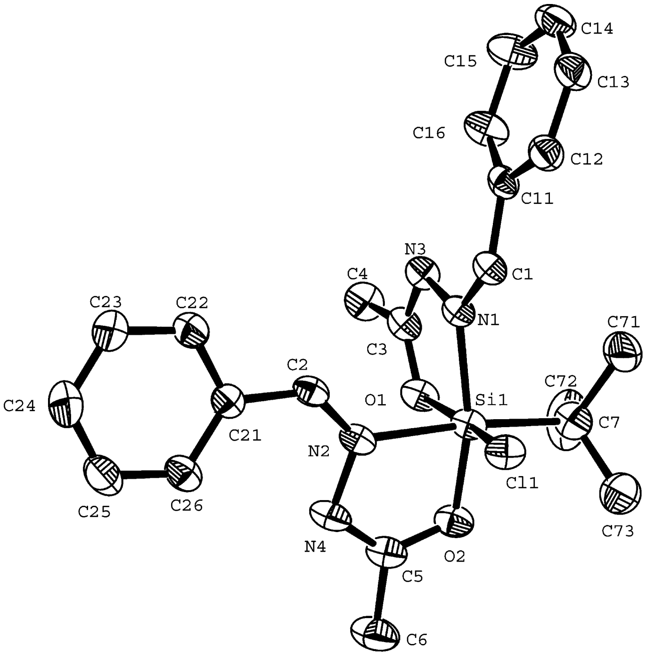


Figure 1. Molecular structure of **11b** in the crystal.

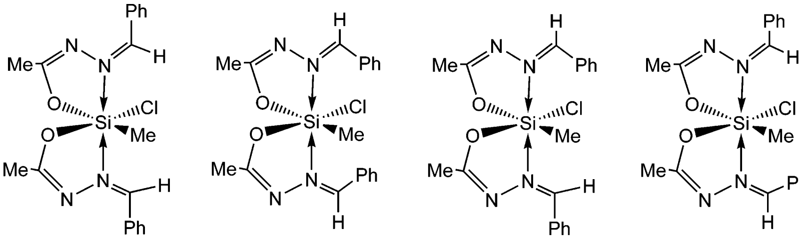
electron-withdrawing substituents and make the imino groups too weak donors so as not to stabilize a forming cation and thus avoid ionization at room temperature. However, at lower temperatures (270 K), ionization was observed (see Experimental Section). The ligand arrangement around the silicon is also uncommon: most of the hexacoordinate hydrazide-based silicon dichelates studied so far have the nitrogen ligands in trans arrangement relative to each other.[1p] In contrast, **11b** has the unique arrangement of cis nitrogen atoms, cis oxygen atoms, and cis monodentate ligands (chloro and *tert*-butyl groups). This geometry may be justified by the steric requirement of the bulky *tert*-butyl ligand, pushing away the relatively bulky nitrogen ligand in favor of the smaller oxygen ligand. This is not the case in **11a**, which is assumed to have the more common trans-nitrogen geometry. In principle, several geometrical isomers are possible for **11b**, differing in the *E*,*Z* arrangement about the imino double bonds. The room-temperature NMR spectra of **11b** showed two isomers at approximately 1:4 ratio, but no isomers could be isolated other than the one shown in Figure 1.

The ^{29}Si NMR chemical shift of **11a** indicates that it is also (like **11b**) hexacoordinate in $CDCl_3$ solution at ambient temperature. This is expected, in view of the structure of **11b**, since there is less steric bulk and weaker electron release to the silicon in **11a** than in **11b**, and hence the former is even less likely to ionize than the latter. **11a** features *four* hexacoordinate isomers, as clearly observed by the low-temperature (220 K) ^{29}Si NMR spectra (see Experimental Section). The possible stereoisomers are shown in Figure 2. Upon gradual increase of temperature, the pair of higher-field signals in the ^{29}Si NMR spectrum coalesce to a singlet, as a result of rapid exchange of *only two* of the four isomers. Equilibrium exchange of isomers in hexacoordinate silicon complexes was studied previously, and it was suggested that nondissociative exchange of monodentate ligands takes place at rates that are compatible with the NMR time scale.[12] It is thus concluded that the intramolecular exchange of methyl and chloro ligands produces the rapid interchange and coalescence of corresponding signals of the *E*,*Z* and *Z*,*E* isomers.

The reaction of **11a** with **7** leads exclusively to addition of the cyano group to the imino carbon (**12a**, eq 7), opening the C=N double bond and converting the hexacoordinate to a pentacoordinate silicon complex. **12a** has two equally populated

---

(12) (a) Kost, D.; Kalikhman, I.; Raban, M. *J. Am. Chem. Soc.* **1995**, *117*, 11512. (b) Kost, D.; Kalikhman, I.; Krivonos, S.; Stalke, D.; Kottke, T. *J. Am. Chem. Soc.* **1998**, *120*, 4209.



E,E-**12a** *Z,Z*-**12a** *E,Z*-**12a** *Z,E*-**12a**

Figure 2. Four geometrical isomers associated with the geometry about the imino double bonds of **12a**.

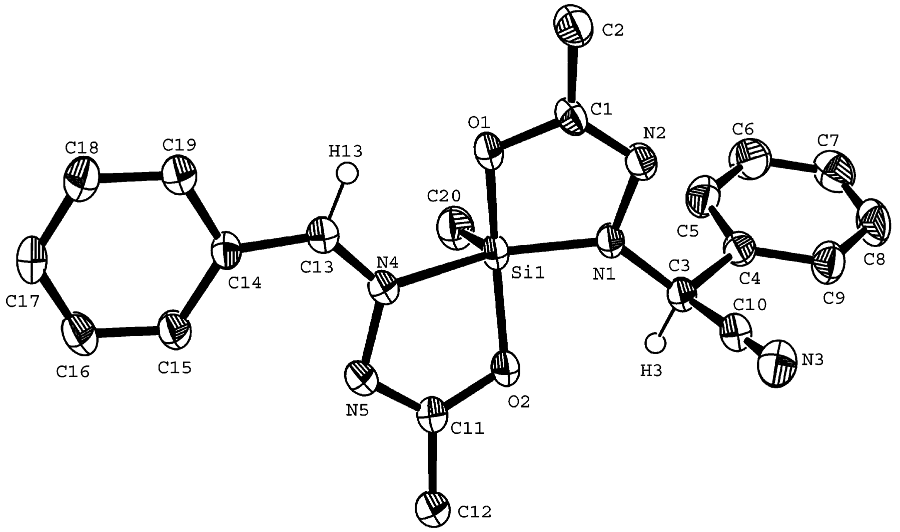


Figure 3. Molecular structure of **12a** in the crystal.

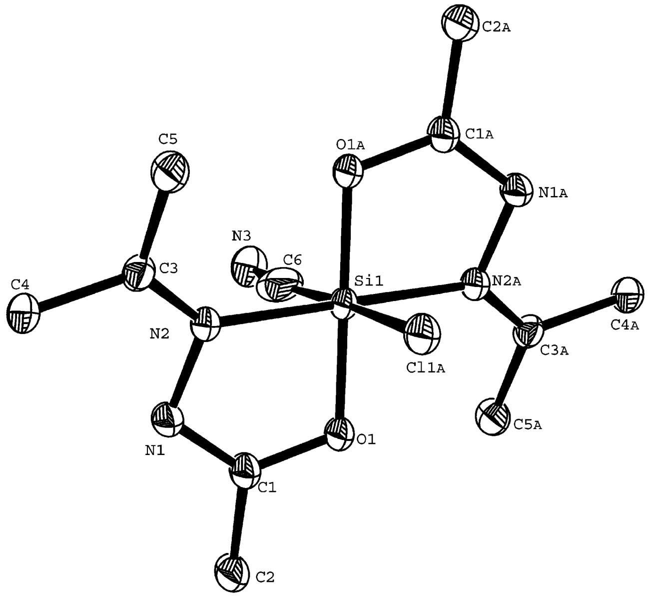
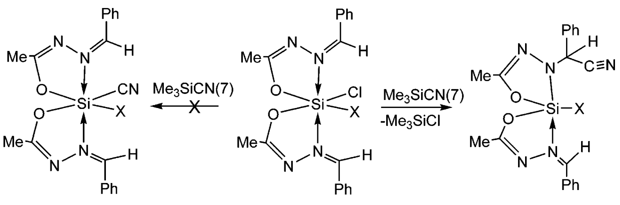


Figure 4. Molecular structure of **14** in the crystal.

isomers in $CDCl_3$ solution, as evident from the various NMR spectra, showing doubling of all signals in a 1:1 ratio (Table 2). This ratio suggests that the isomers result from the presence of two chiral centers in the molecule, rather than from *E*,*Z* relationships at the imino double bonds: in the latter one might expect the isomers with hydrogen atoms pointing toward silicon (*E*) to be substantially more stable, and hence more abundant, than those with a phenyl group pointing toward silicon. One of the possible diastereoisomers of **12a** has been crystallized from a diethylether−THF mixture, and its crystal structure has been determined. The resulting molecular structure of **12a** in the crystal is shown in Figure 3, and selected bond lengths and angles are listed in Table 1. It is evident from the bond lengths in Table 1 that one of the two N−Si dative bonds present in **11a** transformed in **12a** to a fully covalent bond.

Upon reaction of **11b** with **7** in chloroform solution at ambient temperature, the ^{29}Si NMR chemical shift changed from the typically hexacoordinate −132.1, −135.4 ppm in **11b** to the distinctly pentacoordinate −82.7, −83.8 ppm in the product (**12b**, eq 7). Analysis of the NMR spectra of **12b** (Table 2) reveals that, like in **12a**, a cyano group has added to the imino carbon. The initial product consists of a 1:3 mixture of two stereoisomers, as determined from the various NMR spectra. Upon evaporation of the solvent at room temperature under reduced pressure, the isomer population ratio changed to 1:1. This population ratio remains constant under further manipulations, and no individual components have been isolated. The observation that the initial uneven population ratio changed to a 1:1 ratio in solution suggests that isomerization takes place by epimerization at the chiral pentacoordinate silicon center, presumably by the Berry pseudorotation mechanism.[11] It follows that the isomers are apparently due to the two diastereomers (RΛ, LΔ and RΔ, LΛ) resulting from the presence of chiral carbon and silicon centers, respectively, and that their equilibrium constant at room temperature is near 1.

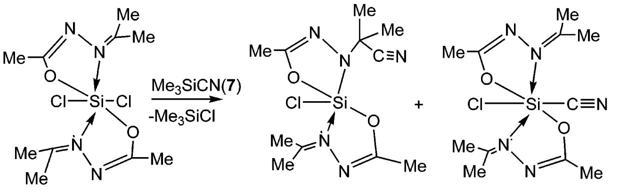


(7)

11a, X = Me
11b, X = t-Bu

12a, X = Me
12b, X = t-Bu

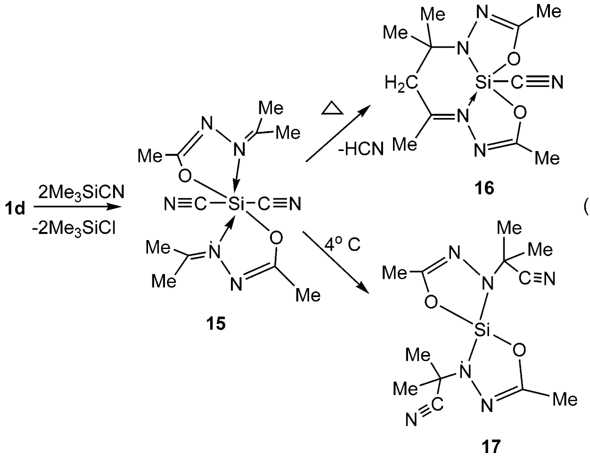
Reaction of Cyanotrimethylsilane with the Dichloro Complex (1d). 1d was synthesized by transsilylation of **8** with tetrachlorosilane, as described previously for similar compounds with different chelate-ring substituents.[6] When 1 molar equiv of cyanotrimethylsilane (**7**) is added at ambient temperature to a chloroform solution of **1d**, the NMR spectra (Table 2 and Experimental Section) reveal nearly quantitative formation of **13**, the addition product of the cyano group to the imino double bond (eq 8). **14**, the expected "normal" hexacoordinate transsilylation product, formed only as a minor byproduct, in no more than 10% of the total yield. Nevertheless, upon prolonged standing at 4 °C (30 days), **14** (and not **13**) crystallized out of the mixed solution. **13** was obtained from the mother liquor as a viscous oil. The crystal structure of **14** has been determined (Figure 4, Table 1). Like similar dichloro and dibromo dichelates that had molecular C_{2h} symmetry,[6b] **14** has the monodentate chloro and cyano ligands in trans positions, in a 50% disordered crystal arrangement.



1d **13** **14** (8)

It is noteworthy that the formation of the hexacoordinate transsilylation product **14** is observed only in this case, where **1d** has two electronegative chloro ligands. When one of the monodentate ligands was an alkyl (methyl in **2a** and t-Bu in **11b**), the reaction with **7** led *only* to the rearranged products, analogues of **13** and **16**.

Reaction of **1d** with excess **7** leads to **15**, the trans (C_{2h}) dicyano complex, characterized by its NMR spectra (eq 9). **15** is remarkably more stable (kinetically) than the monocyano **14** and rearranges to **16** after prolonged heating at chloroform reflux temperature. Addition to the imino double bonds takes place at 4 °C, only after several days, producing the *tetra*coordinate compound **17**. **17** was characterized by its very typical NMR spectra (δ^{29}Si, −43.8 ppm, see following discussion), but could not be isolated and purified.



(9)

The reaction pathways and some of the products outlined in eqs 8 and 9 are based on complete NMR spectral assignments and analysis. Table 2 lists the relevant NMR spectral data. The assignment of **13** is based on its ^{1}H and ^{13}C NMR spectra: the molecular symmetry of the starting material **1d** has been lost in **13**, as seen from the presence of six, rather than the original three, methyl signals. The ^{1}H chemical shifts of two of these methyl signals turned from allylic (δ > 2.0 ppm) to saturated (1.67, 1.70 ppm), as required by the N−C(CN)*Me*$_2$ group. In analogy to **9**, the imino-carbon signal shifted to 52.9 ppm, following saturation due to the addition of CN, and the typical cyano-carbon signal has appeared at 124.1 ppm. **15** is hexacoordinate, as shown by its remarkably high-field ^{29}Si chemical shift (−193.3 ppm), and it retains the C_{2h} symmetry of its precursor **1d**, evident in the ^{1}H and ^{13}C NMR spectra. The characteristic spectral feature of **16** is the appearance of the CH_2-AB quartet (δ 2.62, 2.84, J_{AB} = 16.3 Hz) in the ^{1}H NMR spectrum, in agreement with previously reported analogues,[3] as well as the cyano-carbon signal in the ^{13}C NMR spectrum. The chemical shift of the new quaternary carbon at 53.25 ppm is also typical and confirms the structural assignment. Finally, **17** is identified by its tetracoordinate silicon chemical shift (δ(^{29}Si) = −43.7 ppm) and by its 2-fold symmetry. The chemical shifts of the cyano and methyl protons and carbons in **17** are similar to those observed in **13** (Table 2).

Discussion

Hexacoordinate silicon dichelates based on hydrazide ligands and sharing the SiN_2O_2XY ligand environment (X, Y = alkyl, halogen) react in a variety of ways,[1p] all of which lead from hexa- to pentacoordination, and usually reduce the number of dative N−Si bonds from two to one. These reactions include equilibrium ionic dissociation[2] and methyl halide elimination,[13] and when the donor group is a ketene−imine, an internal aldol-type condensation between the imine functions takes place.[3] In the present work a new reaction of this family has been studied, the 1,3-shift of a cyano monodentate ligand from silicon to the imino carbon. Previous mono- or dihalo complexes did not undergo this kind of reaction, but instead initiated the elimination or rearrangement reactions, in which dissociated halide ion acted as a base or nucleophile, respectively. In contrast, the cyano group in the present study acts entirely differently: rather than abstract a proton, it attacks the electrophilic imino carbon. This selectivity may be due to the softness of the cyano base, relative to chloride or bromide, causing preferential attack on the "soft" imino carbon rather than abstraction of the "hard" proton.[14]

It has been demonstrated that the addition of a cyano group to the imino carbon takes place instantly, either directly from cyanotrimethylsilane or through transsilylation such that a cyano complex is formed initially but rearranges very rapidly (shifting the cyano group from silicon to the imino carbon) so that it cannot be observed. This was the case in the pentacoordinate isopropylideneimino-siliconium complex **2a**, as well as in the neutral hexacoordinate **11a** and **11b**. Interestingly, transsilylation of the hexacoordinate dichloro complex **1d** with **7**, while leading preferentially to the addition of cyano to the imino carbon like in **2a** and **11**, afforded nevertheless also the hexacoordinate mono- and dicyano complexes (**14** and **15**, respectively), with the CN group attached directly to silicon. Moreover, the hexacoordinate **15** undergoes two competing reactions, as shown in eq 9: at low temperature cyano migrates to the imino carbon, while at boiling chloroform solution it rearranges to the tricyclic complex **16**, with the expulsion of HCN (evident by its distinct signal in the ^{13}C NMR spectrum at 108.8 ppm). This result suggests that **15** reacts in a manner similar to the ionic chloride

---

[13] Kost, D.; Gostevskii, B.; Kocher, N.; Stalke, D.; Kalikhman, I. *Angew. Chem., Int. Ed.* **2003**, *42*, 1023.

[14] (a) Pearson, R. G. *Chem. Br.* **1967**, *3*, 103. (b) Seyden-Penne, J. *Bull. Soc. Chim. Fr.* **1968**, *9*, 3871.

Table 3. Crystal Data and Experimental Parameters for the Structure Analyses of 11b, 12a, and 14

	11b	**12a**	**14**
CCDC number	631486	631487	631488
empirical formula	$C_{22}H_{27}ClN_4O_2Si$	$C_{20}H_{21}N_5O_2Si$	$C_{11}H_{18}ClN_5O_2Si$
form mass, g mol^{-1}	443.02	391.51	315.84
collection T, K	133(2)	230(1)	100(2)
cryst syst	monoclinic	triclinic	triclinic
space group	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$
a, Å	9.1022(18)	8.323(2)	7.4185(14)
b, Å	19.821(4)	11.282(2)	7.4631(14)
c, Å	12.996(3)	11.880(2)	7.8493(15)
α, deg	90	65.24(2)	115.855(3)
β, deg	97.21(3)	78.28(2)	98.022(3)
γ, deg	90	87.60(2)	98.096(3)
V, Å^3	2326.2(8)	990.7(3)	377.20(12)
Z	4	2	1
$\rho_{calc,}$ Mg/m^3	1.265	1.312	1.390
F(000)	936	412	166
θ range, deg	1.88−24.64	2.50−25.20	2.85−28.24
no. of coll reflns	15 409	8164	3313
no. of indep reflns	3899	3384	1735
R_{int}	0.0765	0.0652	0.0243
no. of reflns used	3899	3384	1735
no. of params	276	261	109
Goof	1.030	0.920	1.138
R1, wR2 [$I > 2\sigma(I)$]	0.0428, 0.0972	0.0444, 0.1112	0.0391, 0.1012
R1, wR2 (all data)	0.0654, 0.1059	0.0697, 0.1176	0.0412, 0.1027
max./min. res electron dens (e Å^{-3})	0.307/−0.221	0.345/−0.364	0.393/−0.230

complexes, such as **2a**, whereby the cyano group dissociates, and the cyanide anion abstracts a methyl proton to initiate the skeletal rearrangement to **16**. Likewise, eq 8 represents a competition reaction that **1d** undergoes, whereby the cyano group attaches either to the silicon atom, forming hexacoordinate **14**, or directly to the imino double bond to form **13**. The course of these competition reactions depends primarily on the reaction temperature.

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 (**12a**), a Bruker Apex CCD diffractometer (**14**), and a Bruker Smart Apex on D8-goniometer (**11b**). The data were collected from oil-coated shock-cooled crystals. The diffractometers are equipped with a low-temperature device using graphite-monochromated (Mo Kα) radiation (λ = 71.073 pm).[15] The data were integrated with SAINT.[16] The structures were solved by direct methods (SHELXS-97)[17] and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[18] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were assigned ideal positions and refined using a riding model with U_{iso} constrained to 1.2 times the U_{eq} value of the parent atom. Experimental details are listed in Table 3. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers are listed in Table 3. Copies of the data can be obtained free of charge on application to CCDC; e-mail: deposit@ccdc.cam.ac.uk. The crystal structures in Figures 1, 3, and 4 are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity.

Bis[*N*-(isopropylidenimino)acetimidato-*N,O*]dichlorosilicon(IV) (1d). A solution of 1.000 g (5.37 mmol) of **8**[3] and 0.455 g (2.68 mmol) of $SiCl_4$ in 5 mL of chloroform was kept at room temperature for 10 min, followed by removal of volatiles under reduced pressure (0.2 mmHg). The residue was washed by 15 mL of hexane and vacuum-dried to yield 0.867 g (99%) of **1d**, a white solid, mp 172−173 °C. ^{1}H NMR ($CDCl_3$, 300 K): δ 2.02 (s, 6H, CMe), 2.39 (s, 6H, NMe), 2.60 (s, 6H, NMe). ^{13}C NMR ($CDCl_3$, 300 K): δ 17.8 (CCH_3), 23.8, 25.1 (NMe_2), 164.9, 173.5 ($C{=}N$). ^{29}Si NMR ($CDCl_3$, 300 K): δ −163.7. Anal. Calcd for $C_{10}H_{18}Cl_2N_4O_2Si$: C, 36.93; H, 5.58; N, 17.22. Found: C, 36.63; H, 5.80; N, 17.16.

[*N*-(Isopropylidenimino)acetimidato-*N′*,*O*][*N*-2(2-cyanopropylamino)acetimidato-*N′*,*O*]methylsilicon(IV) (9). Crude **2a**, prepared from 1.058 g (5.68 mmol) of **8** and 0.623 g (4.16 mmol) of $MeSiCl_3$ as described previously,[3] was dissolved in 5 mL of $CHCl_3$, and 0.292 g (2.95 mmol) of Me_3SiCN (**7**) was added. The mixture was stirred for 1 h at room temperature, followed by removal of volatiles under reduced pressure (0.2 mmHg). The solid residue was washed in 10 mL of hexane and dried at 0.2 mmHg, after which 0.747 g (89%) of a white solid, **9**, of mp 106−108 °C, was obtained. ^{1}H NMR ($CDCl_3$, 300 K): δ 0.47 (s, 3H, SiMe), 1.59, 1.61 (2s, 6H, $CCMe_2$), 1.85, 2.03 (2s, 6H, OCMe), 2.26, 2.31 (2s, 6H, $N{=}CMe_2$). ^{13}C NMR ($CDCl_3$, 300 K): δ 6.62 (SiMe), 16.1, 17.7 ($N{-}C(CH_3)_2$), 21.8, 23.5 ($OCCH_3$), 27.5, 27.7 ($N{=}C(CH_3)_2$), 53.3 ($C(C{\equiv}N)Me_2$), 124.5 ($C{\equiv}N$), 146.2, 165.6, 169.4 ($C{=}N$). ^{29}Si NMR ($CDCl_3$, 300 K): δ −75.9. Anal. Calcd for $C_{12}H_{21}N_5O_2Si$: C, 48.79; H, 7.17; N, 23.7. Found: C, 48.54; H, 7.22; N, 23.52.

Bis[*N*-(benzaldimino)acetimidato-*N′*,O]methylchlorosilicon(IV) (11a). A mixture of 0.882 g (3.76 mmol) of **10**[4] and 0.287 g (1.92 mmol) of $MeSiCl_3$ in 5 mL of chloroform was kept at room temperature for 12 h, followed by removal of volatiles under reduced pressure (0.2 mmHg). The residue was washed in hexane to yield 0.729 g of **11a**, a white solid (97% yield), mp 138−140

---

[15] (a) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615. (b) Kottke, T.; Lagow, R. J.; Stalke, D. *J. Appl. Crystallogr.* **1996**, *29*, 465. (c) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171.

[16] *SAINT-NT*; Bruker-AXS Inc.: Madison, WI, 2000.

[17] Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

[18] Sheldrick, G. M. *SHELXL-97*; University of Göttingen, 1997.

°C. ^{1}H NMR ($CDCl_3$, 300 K): δ 0.64 (s, 3H, SiMe), 2.38 (m, 12H, NMe_2), 7.36−8.37 (m, 10H, Ph), 7.6, 9.1 (2 m, 2H). ^{13}C NMR ($CDCl_3$, 300 K): δ 15.1 (SiMe), 18.6 (C*C*H_3), 127.1−134.0 (Ph), 149.8, 172.0 (C═N). ^{29}Si NMR ($CDCl_3$, 300 K): δ −148.8, −139.5. ^{29}Si NMR ($CDCl_3$, 220 K): δ −140.1, −144.4, −145.5, −149.0. Anal. Calcd for $C_{19}H_{21}ClN_4O_2Si$: C, 36.93; H, 5.58; N, 17.22. Found: C, 37.22; H, 5.62; N, 17.02.

Bis[*N*-(benzaldimino)acetimidato-*N′*,*O*]*tert*-butylchlorosilicon(IV) (11b). A mixture of 1.063 g (4.54 mmol) of **10**,[4] 0.490 g (2.56 mmol) of t-Bu$SiCl_3$, and 5 mL of chloroform was kept at room temperature for 1 h, followed by removal of volatiles at 0.2 mmHg. The white residue was recrystallized from 10 mL of *n*-hexane to yield 0.974 g (97%) of **11b**, mp 154−155 °C. A single crystal was grown from a THF + Et_2O mixture. ^{1}H NMR for two isomers ($CDCl_3$, 300 K): δ 0.89, 0.94 (2s, 9H, t-Bu), 2.29, 2.45 (2 br m, 6H, CMe), 7.36−8.63 (m, 12H, Ph, CH). ^{13}C NMR ($CDCl_3$, 270 K): δ 18.4, 19.6 (OC*C*H_3), 27.1, 28.6 (*C*(CH_3)$_3$), 31.3, 31.6 (C(*C*H_3)$_3$), 127.9−138.0 (Ph), 148.3, 150.6, 160.9, 170.8, 171.2, 172.3 (C═N). ^{29}Si NMR ($CDCl_3$, 300 K): δ −132.1, −135.4. ^{29}Si NMR ($CDCl_3$, 270 K): δ −81.8, −136.1. Anal. Calcd for $C_{22}H_{27}ClN_4O_2Si$: C, 59.65; H, 6.14; N, 12.65. Found: C, 59.70; H, 6.32; N, 12.55.

12a. A mixture of 0.911 g (3.89 mmol) of **10**[4] and 0.362 g (2.42 mmol) of $MeSiCl_3$ in 5 mL of chloroform was stirred at room temperature for 10 min, followed by removal of volatiles under reduced pressure (0.2 mmHg). The solid residue was washed with 10 mL of *n*-hexane and dried under reduced pressure. This product was stirred with 0.216 g (2.18 mL) of **7** in 5 mL of $CHCl_3$ for 30 min at room temperature. After removal of volatiles under vacuum the residue was washed with 10 mL of hexane. The yellow solid **12a** was isolated by decantation and vacuum drying, to yield 0.714 g (94%), mp 147−149 °C. Crystals for X-ray diffraction analysis were grown from Et_2O−THF solution. NMR for two diastereomers (1:1.1): ^{1}H NMR ($CDCl_3$, 300 K): δ 0.31, 0.37 (2s, 3H, SiMe), 1.96, 2.15 (s, 3H, OCMe), 2.00, 2.17 (s, 3H, OCMe), 5.87, 5.93 (s, 1H, *H*CPh), 7.32−7.64, 8.44 (2m, 11H, Ph, CH═N). ^{13}C NMR ($CDCl_3$, 300 K): δ 2.5, 3.0 (Si*C*H_3), 16.7, 16.1 (O*C*Me), 53.3, 53.5 (C*C*HPh), 126.8, 126.9 (C≡N), 127.6, 129.0, 134.5, 137.1, 137.4 (Ph), 153.0, 153.2, 172.6 (C═N), 158.3, 158.5 (HC═N). ^{29}Si NMR ($CDCl_3$, 295 K): δ −83.6, −84.9. Anal. Calcd for $C_{20}H_{21}N_5O_2Si$: C, 61.36; H, 5.41; N, 17.89. Found: C, 60.91; H, 5.23; N, 17.70.

12b (identified by the NMR spectra of its two diastereomers (1:1)). ^{1}H NMR ($CDCl_3$, 300 K): δ 0.35 (s, 3H, SiMe), 0.87, 0.94 (2s, 9H, $SiCMe_3$), 1.96, 2.00 (2s, 3H, OCC*H$_3$*), 2.14, 2.18 (2s, 3H, OCC*H$_3$*), 5.87, 5.89 (2s, 1H, *H*CPh), 7.30−7.64, 8.44 (2 m, 11H, Ph+CH═N). ^{13}C NMR ($CDCl_3$, 300 K): δ 16.5, 16.6, 17.8, 17.9 (O*C*Me), 21.8, 22.0 (*C*(CH_3)$_3$), 27.5, 27.7 (C(*C*H_3)$_3$), 53.3, 53.7 (C*C*HPh), 119.6, 120.1 (C≡N), 126.9−137.3 (Ph), 153.0, 153.1, 172.6, 172.7 (C═N), 158.9, 159.0 (CH═N). ^{29}Si NMR ($CDCl_3$, 300 K): δ −82.7, −83.8.

Synthesis of 14 and 13. Crude **1d**, prepared from 1.088 g (5.80 mmol) of **8** and 0.497 g (2.93 mmol) of $SiCl_4$ as described above, was allowed to react with 0.323 g (3.26 mmol) of **7** in 5 mL of $CHCl_3$ for 30 min at room temperature. The partly concentrated solution was placed in the refrigerator for 30 days, after which crystals of **14** had separated, mp 110 °C (dec). Evaporation of the mother liquor afforded an oily mixture of **13** (90%) and **14** (10%). **13** was identified by its NMR spectra.

[*N*-(Isopropylidenimino)acetimidato-*N′*,*O*][*N*-2(2-cyanopropylamino)acetimidato-*N′*,*O*]chlorosilicon(IV) (13). ^{1}H NMR ($CDCl_3$, 300 K): δ 1.61, 1.70 (2s, 6H, $CNCMe_2$), 1.92, 2.14 (2s, 6H, OCMe), 2.35, 2.47 (N═CMe_2). ^{13}C NMR ($CDCl_3$, 300 K): δ 16.1, 17.4 (N−C*Me$_2$*), 23.4, 24.4 (OC*Me*), 27.2, 27.7 (C═N*Me$_2$*), 52.9 (N−*C*Me_2), 124.1 (C≡N), 145.4, 165.2, 174.6 (C═N). ^{29}Si NMR ($CDCl_3$, 300 K): δ −102.3.

Bis[*N*-(isopropylideneimino)acetimidato-*N′*,*O*]chlorocyanosilicon(IV) (14). ^{1}H NMR ($CDCl_3$, 300 K): δ 2.06 (s, 6H, MeCO), 2.40, 2.61 (s, 6H, N═CMe_2). ^{13}C NMR ($CDCl_3$, 300 K): δ 17.8 (*Me*CO), 23.8, 25.1 (N═C*Me$_2$*), 133.6 (C≡N), 169.9, 173.6 (C═N). ^{29}Si NMR ($CDCl_3$, 300 K): δ −179.6. Anal. Calcd for $C_{11}H_{18}ClN_5O_2Si$: C, 41.83; H, 5.74; N, 22.17. Found: C, 42.04; H, 5.83; N, 22.07.

15. To crude **1d**, obtained from 1.244 g (6.68 mmol) of **8** and 0.606 g (3.57 mmol) of $SiCl_4$ were added 0.670 g (6.75 mmol) of Me_3SiCN (**7**) and 5 mL of $CHCl_3$. The volatiles were removed at 0.2 mmHg, and the solid residue was washed by 10 mL of hexane to yield 0.942 g (82%) of **15**, mp 124−127 °C. ^{1}H NMR ($CDCl_3$, 300 K): δ 2.06 (s, 6H, MeCO), 2.41, 2.58 (s, 6H, N═CMe_2). ^{13}C NMR ($CDCl_3$, 300 K): δ 17.8 (*Me*CO), 24.3, 24.9 (N═C*Me$_2$*), 133.2 (C≡N), 167.0, 176.6 (C═N). ^{29}Si NMR ($CDCl_3$, 300 K): δ −193.9. Anal. Calcd for $C_{12}H_{18}N_6O_2Si$: C, 47.04; H, 5.92; N, 27.43. Found: C, 46.73; H, 6.08; N, 26.90.

16. 16 was obtained by heating a chloroform solution of **15** to boiling for 2 h. It was characterized by its NMR spectra. ^{1}H NMR ($CDCl_3$, 300 K): δ 1.07, 1.42 (2s, 6H, Me_2C), 1.93, 2.14 (2s, 6H, MeCO), 2.42 (s, 3H, N═CMe), 2.64, 2.82 (ABq, $^2J_{HH}$ = 16.3 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 300 K): δ 15.8, 17.8, 23.1, 26.7, 29.9 (Me), 46.8 (CH_2), 53.3 (*C*Me_2), 124.5 (C≡N), 153.2, 169.8, 176.5 (C═N). ^{29}Si NMR ($CDCl_3$, 300 K): δ −126.5.

17. A $CHCl_3$ solution of **15** was kept at 4 °C for 7 days. Evaporation of the solvent afforded a 2:1 mixture of **15** and **17**. **17** was characterized by its typical NMR spectra. ^{1}H NMR ($CDCl_3$, 300 K): δ 1.62, 1.63, 2.02 (3s, 9H, Me). ^{13}C NMR ($CDCl_3$, 300 K): δ 16.0, 26.2, 27.1 (Me), 51.8 (C*C*Me_2), 121.4 (C≡N), 150.1 (C═N). ^{29}Si NMR ($CDCl_3$, 300 K): δ −43.8.

Acknowledgment. Financial support from the Israel Science Foundation, grant No. ISF-139/05, and from INTAS, project 03-51-4164, is gratefully acknowledged.

Supporting Information Available: Crystallographic data for **11b**, **12a**, and **14** in the form of CIF files are available free of charge via the Internet at http://pubs.acs.org.

OM061176Y