Complete Intermolecular Ligand Crossover in Hexacoordinate Silicon Dichelates. Establishment of a Ligand Priority Order

Shlomi Sergani, Inna Kalikhman,* Shiri Yakubovich, and Daniel Kost*

Department of Chemistry, Ben Gurion University of the Negev, Beer Sheva 84105, Israel

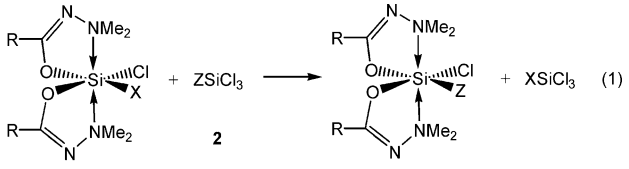
Received July 22, 2007

Hexacoordinate silicon dichelates undergo three unique intermolecular chelate exchange reactions: complete ligand transfer from dichelates to trichlorosilanes, which is formally equivalent to interchange of monodentate ligands between dichelate and $ZSiCl_3$, controlled by a ligand priority order; bidentate ligand interchange between dichelate and trimethylsilyl-hydrazide precursor; complete chelate crossover between different dichelates.

Hexacoordinate silicon complexes[1] are highly flexible molecular systems, undergoing a variety of chemical and geometrical transformations:[2] intramolecular ligand-site exchange processes;[2a,3a] ionic dissociation to pentacoordinate siliconium halides;[2b,3c] an alternative neutral dissociation of the N→Si dative bond,[2c,3a,b] as well as thermal[2g,3a,d] and photochemical[3d,e,4] molecular rearrangements. We now present evidence for complete *inter*molecular mono- and bidentate ligand crossover among different dichelate complexes, further extending the flexible nature of these compounds. Ligand crossover is controlled by priority rules.

Three unique intermolecular exchange reactions are described below: (i) formal exchange of monodentate ligands between a silicon dichelate (**1**) and a trichlorosilane (**2**); (ii) exchange of a chelate ring between **1** and its trimethylsilyl-hydrazide precursor (**3**); (iii) complete chelate-ring scrambling between pairs of hexacoordinate silicon dichelates **1**.

(i) Bidentate Ligand Transfer from Dichelates to Trichlorosilanes (formally constituting exchange of monodentate ligands). When a neutral hexacoordinate silicon dichelate (**1**) reacts with a substituted trichlorosilane (**2**) at ambient temperature in $CDCl_3$ solution, within minutes new signals in the ^1H, ^{13}C, and ^{29}Si NMR spectra (Figure 1) indicate that ligand Z has formally replaced X in complex **1**, while X formed $XSiCl_3$ (**2**, eq 1). The product is identified by its spectral analogy with the independently characterized sample,[2d] and progress of the reaction is monitored by the gradual growth of the $XSiCl_3$-characteristic ^{29}Si and ^{13}C NMR signals.[5] Figure 1 serves to demonstrate the exchange: to a pure sample of **1e** (Figure 1A) was added excess **2g**, and after a few minutes at ambient temperature spectrum B was taken, showing that **1e** had *quantitatively* been replaced by the hydrido complex **1g** (apparent by its typical $^1J_{HSi} = 346$ Hz doublet, at a chemical shift characteristic of hexacoordination), along with formation of **2e**. A small excess of **2g** is evident by its low-field doublet at −9.6 ppm. The volatile components were then removed under reduced pressure, and excess **2e** was added. No reversal of the reaction (formation of **1e**) was observed, as found in Figure 1C.



1a, R = Ph, X = *c*-C_6H_{11} **2a**, Z = *c*-C_6H_{11}
1b, R = Ph, X = *i*-Bu **2b**, Z = *i*-Bu
1c, R = Ph, X = Et **2c**, Z = Et
1d, R = Ph, X = Me **2d**, Z = Me
1e, R = X = Ph **2e**, Z = Ph
1f, R = Ph, X = vinyl **2f**, Z = vinyl
1g, R = Ph, X = H **2g**, Z = H
1h, R = Ph, X = Cl **2h**, Z = Cl
1i, R = *t*-Bu, X = Me
1j, R = X = Me
1k, R = CF_3, X = Me
1l, R = CF_3, X = Ph

Z > X in "priority list", see text

It is highly unlikely that ligand exchange takes place by direct cleavage of the silicon−carbon Si−X and Si−Z bonds, followed

* Author to whom correspondence should be addressed.

(1) Selected reviews: (a) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371−1448. (b) Verkade, J. G. *Coord. Chem. Rev.* **1994**, *137*, 233−295. (c) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927−950. (d) Bassindale, A. R.; Glin, S. J.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig Y., Eds.; Wiley: Chichester, U. K, 1998; vol. 2, pp 495−511. (e) Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig Y., Eds.; Wiley: Chichester, U. K, 1998; vol. 2, pp 1339−1445. (f) 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. (g) Kira, M.; Zhang, L. C. In *The Chemistry of Hypervalent Compounds*; Akiba, K., Ed.; Wiley-VCH: Weinheim, Germany, 1999; pp 147−169. (h) Tacke, R.; Pülm, M.; Wagner, B. *Adv. Organomet. Chem.* **1999**, *44*, 221−273. (i) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 2000; pp 97−114. (j) 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. (k) Kost, D.; Kalikhman, I. *Adv. Organomet. Chem.* **2004**, *50*, 1−106.

(2) Relevant publications from this group: (a) Kost, D.; Kalikhman, I.; Krivonos, S.; Stalke, D.; Kottke, T. *J. Am. Chem. Soc.* **1998**, *120*, 4209−4214. (b) Kost, D.; Kingston, V.; Gostevskii, B.; Ellern, A.; Stalke, D.; Walfort, B.; Kalikhman, I. *Organometallics* **2002**, *21*, 2293−2305. (c) Gostevskii, B.; Silbert, G; Adear, K.; Sivaramakrishna, A.; Stalke, D.; Deuerlein, S.; Kocher, N.; Kalikhman, I.; Kost, D. *Organometallics* **2005**, *24*, 2913−2920. (d) Kost, D.; Kalikhman, I.; Raban, M. *J. Am. Chem. Soc.* **1995**, *117*, 11512−11522. (e) Kost, D.; Gostevskii, B.; Kocher, N.; Stalke, D.; Kalikhman, I. *Angew. Chem., Int. Ed.* **2003**, *42*, 1023−1026. (f) Kalikhman, I.; Gostevskii, B.; Botoshansky, M.; Kaftory, M.; Tessier, C. A.; Panzner, M. J.; Youngs, W. J.; Kost, D. *Organometallics* **2006**, *25*, 1252−1258. (g) Gostevskii, B.; Pestunovich, V.; Kalikhman, I.; Sivaramakrishna, A.; Kocher, N.; Deuerlein, S.; Leusser, D.; Stalke, D.; Kost, D. *Organometallics* **2004**, *23*, 4346−4348.

(3) (a) Wagler, J.; Böhme, U.; Brendler, E.; Roewer, G. *Organometallics* **2005**, *24*, 1348−1350. (b) Wagler, J.; Hill, A. F. *Organometallics* **2007**, *26*, 3630−3632. (c) Schley, M.; Wagler, J.; Roewer, G. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2914−2918. (d) Wagler, J.; Böhme, U.; Roewer, G. *Organometallics* **2004**, *23*, 6066−6069. (e) Wagler, J.; Doert, T.; Roewer, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 2441−2444.

(4) (a) Kano, N.; Komatsu, F.; Yamamura, M.; Kawashima, T. *J. Am. Chem. Soc.* **2006**, *128*, 7097−7109. (b) Yamamura, M.; Kano, N.; Kawashima, T. *J. Organomet. Chem.* **2007**, *692*, 313−325. (c) Kano, N.; Komatsu, F.; Kawashima, T. *J. Am. Chem. Soc.* **2001**, *123*, 10778−10779.

10.1021/om700739b CCC: $37.00
Publication on Web 10/24/2007

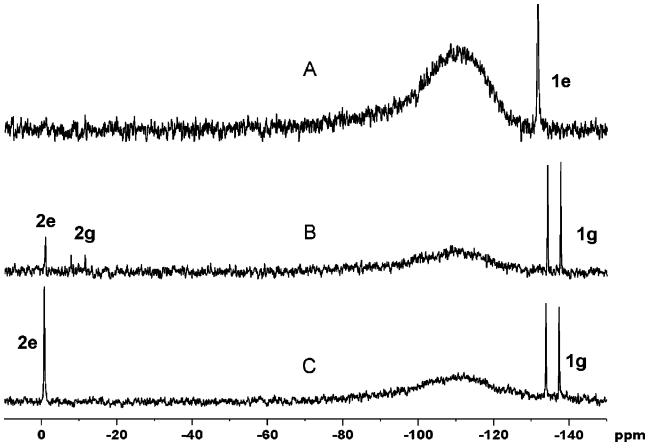


Figure 1. ^{29}Si NMR spectra ($CDCl_3$) for the reaction **1e** + **2g**: (A) **1e**. (B) After addition of **2g**: **1g** and **2e** are formed, the former recognized by the typical $^1J_{SiH}$ doublet. (C) After vacuum removal of volatiles and addition of excess **2e**: no reversal to **1e** or **2g**. Broad signal around −112 ppm is due to glass tube.

Table 1. ^{29}Si NMR Chemical Shifts (ppm) of Trichlorosilanes $ZSiCl_3$ (2)[6] and Complexes 1 (with R = Ph) in $CDCl_3$ Solution, as a Function of Ligand Z (X, Respectively)

Z (X)	C_6H_{11}	*i*-Bu	Et	Me	Ph	vinyl	H	Cl
2	12.9	12.4	14.6	12.2	−0.9	−3.0	−9.6	−20.0
1	−65.2[a]	−106.0	−122.7	−126.2	−131.8	−137.2	−137.2	−145.9

[a] Alkyl ligands, in particular bulky ones, cause partial or complete ionic dissociation, leading to a lower-field ^{29}Si resonance due to pentacoordinate siliconium halides.[2b] However, ionization does not seem to interfere with ligand exchange reactions.

by mixing and re-formation of the exchanged bonds. Exchange probably starts by cleavage of the dative N−Si bond, followed by nucleophilic attack of the loose nitrogen donor group on the electrophilic silicon of an adjacent $ZSiCl_3$ molecule.

Ligand exchange follows the priority order: Cl > H > vinyl > Ph > Me > Et > *i*-Bu > cyclohexyl, such that X is replaced only by a ligand Z *listed before it*. Thus, Z = Me replaces X = Et, and Z = Cl replaces all other ligands in the list.

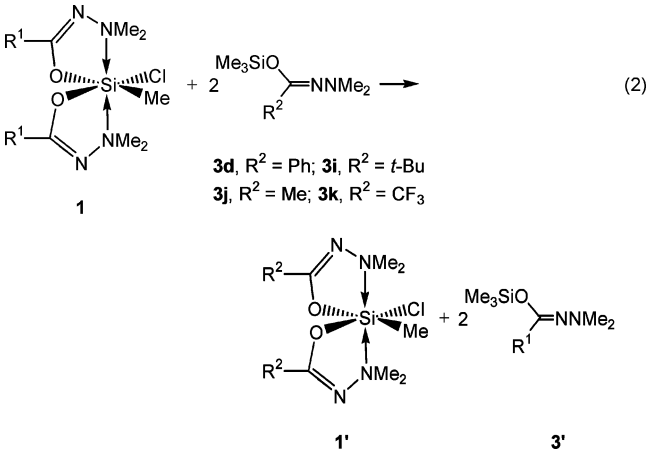
The priority list correlates well with the ^{29}Si chemical shifts of the corresponding $ZSiCl_3$ (**2**)[6] and complexes **1** (Table 1), suggesting that ligand priority is controlled primarily by the electron-withdrawing power of the ligand Z from the silicon atom. This order of ligands apparently follows the thermodynamic stability of complexes: the better electron-withdrawing ligands cause stronger N→Si coordination and hence more stable hexacoordinate complexes.

A closer examination of the ligand priority list and Table 1 shows that chemical-shift differences in the *alkyl*-trichlorosilane series (**2a**−**d**) are too small and irregular to account for the experimental priorities. In this series, priorities seem to follow the steric bulk of the alkyl ligand, the smaller alkyl being the more effective ligand (displacing the bulkier ligand from its complex). Bulky ligands were shown previously to destabilize hexacoordinate complexes and cause them to expel one of their ligands, either halide[2b] or the dimethylamino donor group,[2c] forming pentacoordinate dichelates. Thus, this alkyl priority order is in accord with the rest of the list, from Cl to CH_3, in that *overall priority is determined essentially by complex stability* which, in the absence of a significant polar effect in the alkyl series follows steric bulk, and for all other ligands follows electron-withdrawing ability.

Table 1 enables prediction of the behavior of other Z ligands toward given complexes **1**, based on their ^{29}Si chemical shifts: thus, Z = $CHCl_2$ (δ^{29}Si −6.3 ppm) is expected to displace the vinyl ligand (δ^{29}Si −3.0 ppm) from its complex, while the latter may displace CH_2Cl (δ^{29}Si −2.0 ppm) from its dichelate **1**.

Perhaps the most striking feature of this exchange is its apparent irreversibility: within NMR detection limits, the replacement of any X by another ligand Z is *quantitative* and *irreversible*. This is true even for the exchange of relatively similar X and Z, such as isobutyl and cyclohexyl, respectively, and is demonstrated here by the example shown in Figure 1, in which addition of a large excess of **2e** did not result in reversal of the reaction and detection of even a trace of **1e** or **2g**.

(ii) Ligand Interchange between Dichelate and TMS-hydrazide. Exchange of *bidentate* ligands takes place between complexes **1** and their hydrazide precursors **3** as outlined in eq 2. This apparent exchange of R^1 and R^2 substituents involves complete removal of the bidentate chelating ligand from **1**, and its replacement by the ligand from **3**.



(2)

Exchange is observed in the ^{1}H, ^{13}C, and ^{29}Si NMR spectra and is best followed by the change in relative intensities of the Si-*Me* signals of **1** and **1′**. The measured progress of the exchange reactions, expressed in terms of the product/reactant (**1′**/**1**) signal intensity ratio, is presented in Table 2.

Examination of the data in Table 2 reveals that, like the exchange described in (i) above, this reaction is controlled by priority rules, which seem to coincide with thermodynamic complex stabilities. Among the four dichelates studied, **1d**, **1i**, **1j**, and **1k**, sharing a methyl ligand and differing only in the chelate-ring substituents R (= Ph, *t*-Bu, Me, CF_3, respectively), CF_3 (**1k**) has clearly the lowest priority and is driven out quantitatively by all of the other R^2 substituents in **3d**, **3i**, and **3j** (Ph, Me, *t*-Bu, respectively). The reverse reactions, replacement of either one of Ph, Me, or *t*-Bu by $R^2 = CF_3$, was not observed. This observation agrees with reported results on CF_3-substituted hexacoordinate complexes, in which the N→Si coordination is relatively weak and readily dissociates.[2c] Electron-withdrawing substituents such as CF_3 and, to a lesser extent,

(5) The reactions of eq 1 are carried out by addition of a 10−20% molar excess of **2** to a $CDCl_3$ solution of **1** with stirring under argon at ambient temperature for 15 min. The disappearance of the ^{29}Si NMR signal of **1** accompanied by the growth of the corresponding Z-substituted **1** is monitored by NMR, as well as the formation of $XSiCl_3$ along with the excess of unreacted $ZSiCl_3$. To ensure that exchange is complete and irreversible, this procedure is followed by addition of a large excess of $XSiCl_3$. No reversal of the reaction, or any traces of the starting X-substituted **1**, could be detected. Most of the reactants (**1** and **3**) were reported previously,[2b,d] and others are described in the Experimental Section.

(6) Kintzinger, J.-P.; Marsmann, H. *NMR* **1981**, *17*, 65−235.

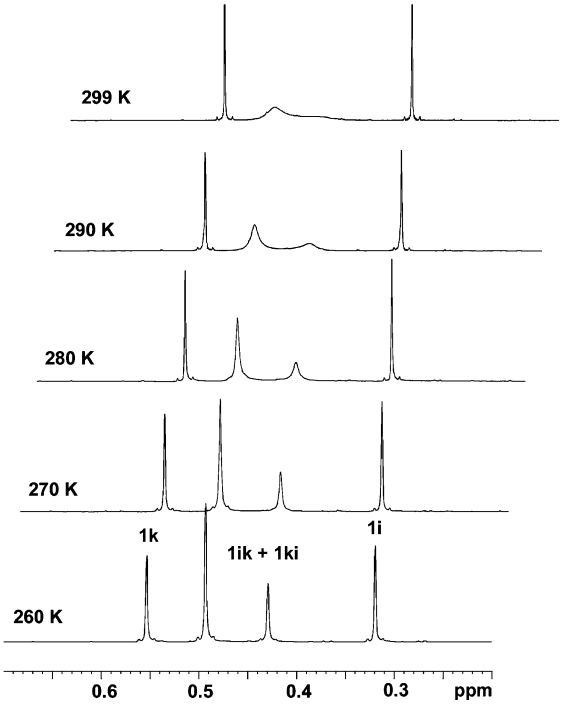


Figure 2. Temperature-dependent ^{1}H NMR spectra (toluene-d_8) of a mixture of **1i** and **1k**. The exchanging internal signals belong to the mixed **1ik** and **1ki** diastereomers.

phenyl, acting through the carbon−nitrogen double bond, reduce the electron density on the nitrogen donor atom and make it effectively a weaker donor and hence decrease overall complex stability.[2c]

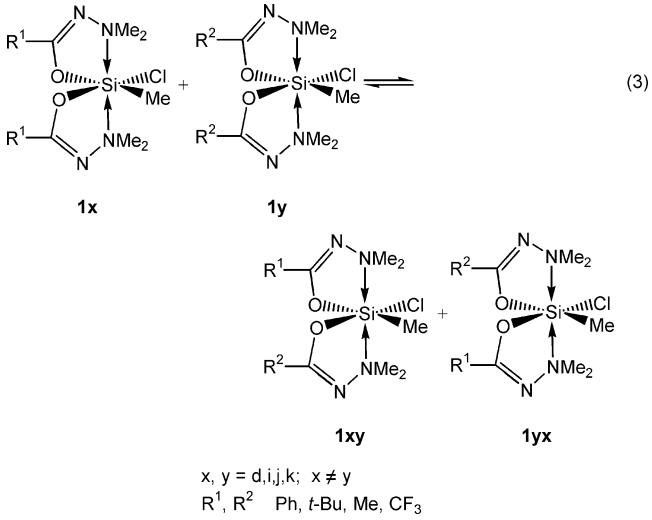
In contrast to the essentially irreversible exchange of eq 1, this exchange (eq 2) is an equilibrium reaction: both dichelates **1** and **1′**, as well as **3** and **3′**, are observed in the NMR spectra.

(iii) Bidentate Ligand Crossover between Different Dichelates. In the third type of exchange, equimolar amounts of any two of the differently substituted methyl complexes **1d**, **1i**, **1j**, **1k** are mixed in toluene-d_8 or chloroform solution at room temperature, and complete crossover of chelate rings is observed (eq 3). All four possible dichelates are found in the NMR spectra: the original **1x** and **1y**, and the two diastereomeric mixed dichelates **1xy** and **1yx**. This is seen in the ^{29}Si NMR spectra of the mixture of **1i** and **1k**, in which signals for all four species are well resolved, and is best viewed by the changes in the Si-*Me* signals in the ^{1}H NMR spectra (Figure 2).

The temperature-dependent ^{1}H NMR spectra depicted in Figure 2 feature line-broadening and dynamic exchange *only*

Table 2. Extent of Exchange in Eq 2 Expressed as 1′:1 Product Ratio, Using 2.2−2.5 Mol of 3 for Each Mole of 1

O-trimethylsilyl-hydrazide, **3**		complex, **1**		
label	R^2	label	R^1	**1′**:**1** ratio
3d	Ph	**1i**	*t*-Bu	0:1
3d	Ph	**1j**	Me	1:1
3d	Ph	**1k**	CF_3	1:0
3i	*t*-Bu	**1j**	Me	3:1
3i	*t*-Bu	**1d**	Ph	2:1
3i	*t*-Bu	**1k**	CF_3	1:0
3j	Me	**1i**	*t*-Bu	0:1
3j	Me	**1d**	Ph	1:1
3j	Me	**1k**	CF_3	1:0
3k	CF_3	**1i**	*t*-Bu	0:1
3k	CF_3	**1j**	Me	0.1:1
3k	CF_3	**1d**	Ph	0:1



(3)

of the internal signals representing the mixed chelates **1ik** and **1ki**. This observation, that mixed chelates equilibrate rapidly, while homodichelates do not, agrees with a previous report on the mechanism of intramolecular ligand exchange in hexacoordinate complexes,[2a,4b] which takes place in two distinct steps, with substantially different activation barriers: the faster of the two processes constitutes exchange of monodentate ligands (Me, Cl) which, in the present case, would account for the interchange **1ik** ⇆ **1ki**. The exchange activation free energy, estimated by the coalescence method (T_c = 299 K), is 14.7 ± 0.2 kcal/mol, in good agreement with previously measured intramolecular exchange barriers.[2d] Clearly, intramolecular ligand-site exchange is substantially faster than the intermolecular, complete chelate exchange, described in this report.

Finally, to ensure that indeed *complete* chelate scrambling takes place in eq 3, it was necessary to have maximum labeling, i.e., two dichelate complexes differing not only in the ring-substituents R, but also in the monodentate X ligands. To this end, equimolar amounts of **1b** (R^1 = Ph, X = *i*-Bu) and **1k** (R^2 = CF_3, X = Me) were mixed and allowed to react at $CDCl_3$ reflux temperature for 5 min, and the resulting ^{29}Si NMR spectrum of the solution was measured (Figure 3). Complete statistical distribution of chelates and X-ligands is expected to form eight different complexes. Figure 3 clearly shows that at least six of these dichelates were present in solution and not just the four suggested by eq 3, evidence that each chelate ring is transferred individually between the two silicon atoms.

One can only speculate on the mechanisms of the three intermolecular chelate exchange reactions reported above. It appears that all three reactions start by dissociation of either the Si−Cl or the N→Si dative bond in **1**, followed by nucleophilic attack of the Cl^- or loose NMe_2 on a neighboring silicon atom. This is another important manifestation of the flexible nature of hypercoordinate silicon compounds, which undergo a variety of changes depending on conditions: elimination of methyl halide;[2e] *two* dynamic intramolecular ligand-site exchange processes observed by NMR spectroscopy;[2d] ionic[2b,3c] as well as nonionic[2c,3a,3b] dissociation leading to penta-hexacoordination exchange; geometrical diversity of pentacoordinate complexes in the solid-state resulting in a complete crystallographic reaction coordinate[2e] representing the Berry pseudorotation;[7] dramatic geometrical changes (octahedral to tetrahedral) in hexacoordinate complexes.[2f]

(7) Berry, S. *J. Chem. Phys.* **1960**, *32*, 933−938; Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318−3326.

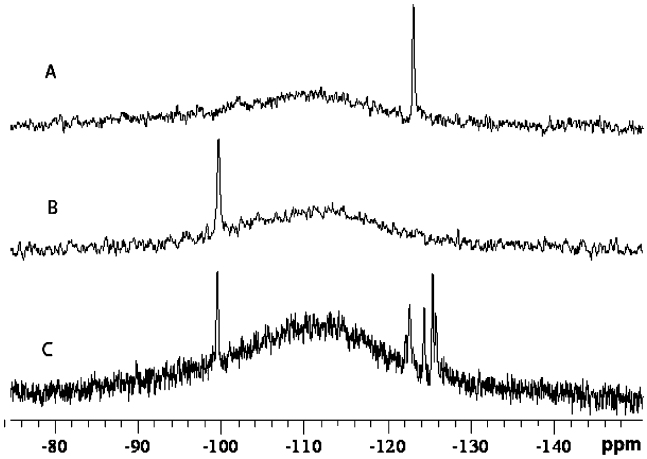


Figure 3. ^{29}Si NMR spectra ($CDCl_3$) of (A) **1k**; (B) **1b** (this complex is in equilibrium with its dissociated chloride, resulting in the relatively low-field resonance);[2b] (C) a mixtrue of **1b** and **1k** after 5 min reflux in $CDCl_3$ solution, causing complete chelate crossover.

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.

The procedures below relate only to the syntheses of previously unknown compounds. Other complexes (**1**) and their precursors (**3**) used in this study have been reported in earlier publications: **1d**, **1e**, **1g**, **1j**−**l**;[2d] **1i**.[2b] Compounds **2** were obtained from commercial sources.

Chlorocyclohexylbis[*N*′-(dimethylamino)benzimidato-*N,O*]-silicon(IV) (1a). To a solution of **3d**[8] (1.156 g, 4.89 mM) in 10 mL of *n*-hexane was added **2a** (0.732 g, 3.36 mM), and the mixture was stirred for 1 h at RT. The volatiles were removed under vacuum and the residue washed with 10 mL of *n*-hexane, leaving a white powder of **1a** (0.99 g, 2.10 mM, 88%) mp 131−2 °C. ^{1}H NMR ($CDCl_3$, 300 K): δ 0.60−1.11 (m, 11H, C_6H_{11}), 2.87 (s, 12H, NMe_2), 6.97−7.48 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, 300 K): δ 21.5, 24.5, 25.7, 26.4 (C_6H_{11}), 49.1, 49.5 (NMe_2), 124.5, 126.4, 126.6, 127.8, 132.5 (Ph), 163.7 (C═N). ^{29}Si NMR ($CDCl_3$, 300 K): δ −65.2. Anal. Calcd for $C_{24}H_{33}ClN_4O_2Si$: C 61.06, H 7.05, N 11.87. Found: C 61.00, H 6.99, N 11.76.

Chlorobis[*N*′-(dimethylamino)benzimidato-*N,O*]isobutylsilicon(IV) (1b). The procedure for **1a** was used to prepare **1b**, using 1.023 g (4.32 mM) of **3d** and 0.441 g (2.30 mM) of **2b**. **1b** (0.92 g, 2.06 mM, 95%) was obtained, mp 154−5 °C. ^{1}H NMR ($CDCl_3$, 300 K): δ 0.89 (d, ^3J = 6.4 Hz, 6H, $C(CH_3)_2$), 1.32 (br.s, 2H, CH_2), 1.95 (m, 1H, $CH_2CH(CH_3)_2$), 3.30 (s, 12H, NMe_2), 7.20−7.80 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, 300 K): δ 24.7, 25.4, 28.4 (*i*-Bu), 50.3 (NMe_2), 126.2, 126.9, 127.3, 131.8 (Ph), 163.4 (C═N). ^{29}Si NMR ($CDCl_3$, 300 K): δ −106.0. Anal. Calcd for $C_{22}H_{31}ClN_4O_2Si$: C 59.11, H 6.99, N 12.53. Found: C 59.08, H 7.00, N 12.51.

Chlorobis[*N*′-(dimethylamino)benzimidato-*N,O*]ethylsilicon-(IV) (1c). **1c** was synthesized by the method described for **1a**, from **3d** (1.273 g, 5.38 mM) and **2c** (0.472 g, 2.88 mM). A 1.06 g amount of **1c** was obtained (2.53 mM, 92%), mp 182−4 °C. ^{1}H NMR ($CDCl_3$, 300 K): δ 1.01 (t, ^3J = 7.6 Hz, 3H, CCH_3), 1.33 (m, 2H, CH_2), 3.15 (m, 12H, NMe_2), 7.31−7.80 (10H, Ph). ^{13}C NMR ($CDCl_3$, 300 K): δ 12.4, 20.3 (Et), 51.2, 51.6 (NMe_2), 127.3, 128.0, 130.5, 131.1 (Ph), 163.7 (C═N). ^{29}Si NMR ($CDCl_3$, 300 K): δ −122.7. Anal. Calcd for $C_{20}H_{27}ClN_4O_2Si$: C 57.33, H 6.50, N 13.37. Found: C 57.30, H 6.42, N 13.31.

Chlorobis[*N*′-(dimethylamino)benzimidato-*N,O*]vinylsilicon-(IV) (1f). The same procedure was applied for this synthesis, using **3d** (1.274 g, 5.39 mM) and **2f** (0.448 g, 2.77 mM). **1f** (1.12 g, 2.68 mM, 98% yield) was obtained as a white powder, mp 176−177 °C. ^{1}H NMR ($CDCl_3$, 300 K): δ 3.0, 3.1 (2s, 12H, NMe_2), 5.8 (dd, ^2J = 3.6, ^3J = 19.8 Hz, 1H, vinyl trans), 5.9 (dd, ^2J = 3.6, ^3J = 13.8 Hz, 1H, vinyl cis), 6.45 (dd, ^3J = 19.8, ^3J = 13.8 Hz, 1H, vinyl), 7.3−7.9 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, 300 K): δ 51.2, 51.8 (NMe_2), 127.3, 128.1, 130.5, 131.2 (Ph), 129.9, 150.0 (vinyl). ^{29}Si NMR ($CDCl_3$, 300 K): δ −137.2.

Mixed Complexes 1xy, 1yx. These compounds were characterized by their ^{1}H, ^{13}C, and ^{29}Si NMR spectra but could not be isolated because of rapid equilibration with their precursors **1x** and **1y**.

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

OM700739B

(8) Kalikhman, I. D.; Bannikova, O. B.; Volkova, L. I.; Gostevskii, B. A.; Yushmanova, T. I.; Lopirev, V. A.; Voronkov, M. G. *Bull. Akad. Nauk SSSR* **1988**, 460−461; *Chem. Abstr.* **1989**, *110*, 75608c.