

Equilibrium between neutral hexacoordinate silicon complexes and ionic pentacoordinate siliconium salts through fast dissociation–recombination of the Si–Cl bond

Vijeyakumar Kingston, Boris Gostevskii, Inna Kalikhman* and Daniel Kost*

Department of Chemistry, Ben-Gurion University, Beer-Sheva 84105, Israel.
 E-mail: kostd@bgumail.bgu.ac.il

Received (in Cambridge, UK) 14th March 2001, Accepted 25th May 2001
 First published as an Advance Article on the web 21st June 2001

Equilibrium between neutral hexacoordinate silicon complexes and ionic siliconium chlorides, which is highly temperature, solvent, counterion, ligand and substituent dependent, was observed by low temperature ^{29}Si NMR and confirmed by crystal analysis.

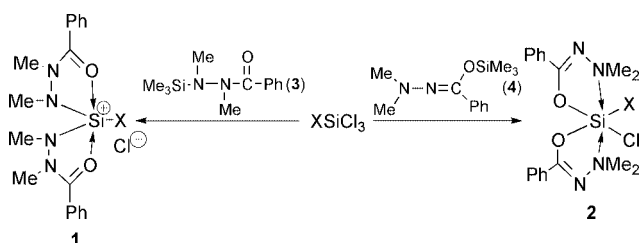
Numerous well established neutral octahedral silicon complexes¹ are now shown to undergo unusual ionic (Si–Cl) dissociation in suitable solvents upon cooling, and consist of equilibrium mixtures with pentacoordinate siliconium chlorides. The only reported similar equilibria are between neutral pentacoordinate and ionic tetra-² or pentacoordinate complexes.^{3,4} This appears to be the first report of a dissociation–recombination of the Si–Cl bond in hexacoordinate silicon compounds. Substantial temperature, solvent, substituent and counterion effects on the neutral-hexacoordinate/ionic-pentacoordinate population ratio are found.

We have recently reported the unexpected spontaneous formation of ionic pentacoordinate siliconium complexes (**1**), stabilized by two O→Si dative bonds,⁵ where neutral hexacoordinate complexes were expected, based on the chemistry of the isomeric N→Si analogs (**2**) (Scheme 1).¹

In search for dissociation of **2**, to form siliconium complexes analogous to **1**, the ^{29}Si NMR spectra of **2a** in CD_2Cl_2 were measured at low temperature. Line broadening over a large temperature range was observed, followed by the emergence of two signals, at -73.0 and -135.6 ppm, below 200 K, assigned to **5a** and **2a**, respectively (Fig. 1).[†] Thus, a reversible equilibrium reaction between neutral hexacoordinate complexes (**2a–d**) to ionic pentacoordinate complexes (**5a–d**) is demonstrated (Scheme 2).

The equilibrium constant $K = [\mathbf{5a}]/[\mathbf{2a}]$ changes quite dramatically with temperature, as is shown by the ^{29}Si NMR spectra below 190 K, when *both* signals are narrow (Table 1, Fig. 1). K values above the coalescence temperature were assessed by the temperature dependence of the weighted-average ^{29}Si chemical shift, and are listed in Table 1. Interestingly, the K values cross over from $K < 1$ to $K > 1$ upon a decrease in temperature, *i.e.* at higher temperatures **2a** is predominant, and at lower temperatures **5a** predominates. The K values obtained directly and from the weighted averages (below and above T_c) were used to calculate ΔH° and ΔS° (Table 1).

A similar measurement of the temperature dependence of $\delta^{29}\text{Si}$ of **2b** showed, likewise, line broadening and splitting of



Scheme 1

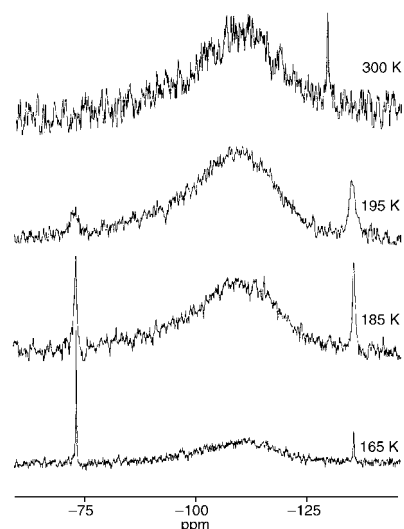
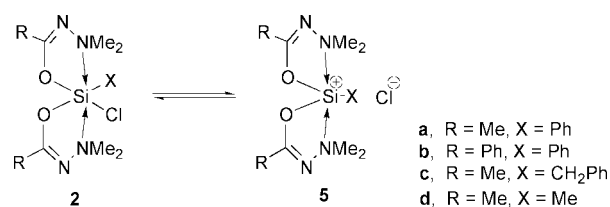


Fig. 1 ^{29}Si NMR spectra (99.325 MHz) of **2a**⇌**5a** in CD_2Cl_2 solution at various temperatures.



Scheme 2

the signal, at the slow exchange limit temperature (180 K), to two signals characteristic of hexa- and pentacoordinate silicon complexes (Table 1). However, in sharp contrast with **2a**, the population ratio $K = [\mathbf{5b}]/[\mathbf{2b}]$ is barely temperature dependent over the range 180–300 K. It follows that by changing the remote substituent (R) alone, a vast change in equilibrium constant and in its temperature dependence is generated.

An even more dramatic manifestation of this effect is found in the equilibrium $K = [\mathbf{5c}]/[\mathbf{2c}]$: K changes from 1:25 at 300 K to 30:1 at 165 K, *i.e.* from an essentially all hexacoordinate to an essentially all pentacoordinate species (Table 1).

In **2d** the exchange rate is too fast to permit full splitting of the broad signal and evaluation of K down to 165 K. However, the huge temperature dependence of K is evident by the continuous change in $\delta^{29}\text{Si}$, from -123.9 at 300 K, to -66.5 (br) at 165 K. Like in **2c**, this change indicates an essentially complete turnover from a hexacoordinate to a pentacoordinate complex upon cooling.

The wide temperature ranges over which line broadening took place in the equilibria **2**⇌**5** provided approximate barrier heights, which are summarized in Table 1. It appears that while the equilibrium constant and its temperature dependence are

Table 1 ^{29}Si Chemical shifts and thermodynamic and activation parameters for the mixtures $2 \rightleftharpoons 5$ in CD_2Cl_2 solution at selected temperatures

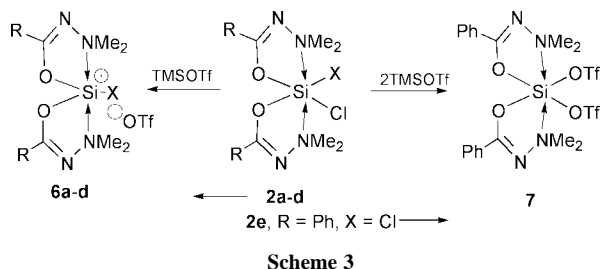
Comp.	^{29}Si Chemical shift (ppm)			Equilibrium constant $K = [5]/[2]$			$\Delta H^{\circ b/}$ kcal mol $^{-1}$	$\Delta S^{\circ b/}$ cal mol $^{-1}$ K $^{-1}$	T_c (± 5)/K a	$\Delta G_{T_c}^*$ (± 0.5) $^a/$ kcal mol $^{-1}$
	300 K	253 K	165 K	300 K	180 K	165 K				
2a \rightleftharpoons 5a	−131.3	−128.9	−73.0; −135.6	0.08	1.38	4.00	−2.8	−15.0	215	8.4
2b \rightleftharpoons 5b	−133.7	−132.8	−73.2; −137.0	0.05	0.13		−0.8	−8.6	215	8.4
2c \rightleftharpoons 5c	−125.4	−118.1	−66.0 c	0.04		30.0	−3.9	−17.5	195	7.5
2d \rightleftharpoons 5d	−123.9	−120.7	−66.5 br d						170	6.5

a The large chemical shift difference causes line broadening over a large temperature range, preventing accurate barrier determination. b Obtained from plots of $\ln K$ vs. T^{-1} . $R > 0.99$. c At this temperature only the major component can be observed. d Barrier too low to permit resolution of the components.

affected primarily by the remote substituent R, the exchange rate constants strongly depend on the ligand X.

The remarkable counter-intuitive temperature dependence of the equilibria (*i.e.* dissociation upon cooling) may result from increased solvent organization around the ions. Alternatively, the N \rightarrow Si coordination may strengthen upon cooling, in agreement with some observations in pentacoordinate complexes,^{1e,2a,b} driving the chloro ligand away as a chloride anion.

Solvent and counterion effects shift the equilibrium: when the apolar toluene- d_8 was used as solvent instead of CD_2Cl_2 , the equilibrium shifted toward the hexacoordinate side and only **2** could be observed. \ddagger When the chloro ligand in **2** was replaced by triflate (OTf), using trimethylsilyl triflate (TMSOTf),^{3,4,6} only the pentacoordinate **6a–d** were observed (Scheme 3).



The crystal structure of **6a** (Fig. 2a) features a well separated triflate anion and a distorted trigonal bipyramid geometry, confirming the assigned pentacoordinate siliconium complex structure. \S

The pentacoordination of **6** in solution is confirmed by the large downfield changes in ^{29}Si chemical shifts (**6a**, −73.2; **6b**, −72.3; **6c**, −65.3 and **6d**, −61.7 ppm) relative to the parent hexacoordinate **2**. Moreover, these shifts correspond almost exactly to those found for **5a–d** at 165 K (Table 1), also confirming the structural assignments of the latter.

A notable exception from the behaviour of **2a–d** was found in the low temperature ^{29}Si NMR spectra of **2e** (Scheme 3).

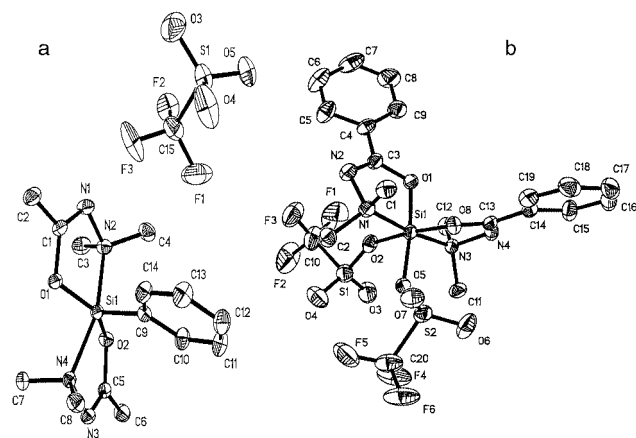


Fig. 2 Crystal structures of **6a** (a) and **7** (b) at 50% probability level. Hydrogen atoms have been omitted for clarity.

Temperature independent ^{29}Si chemical shift, and the absence of exchange phenomena upon cooling, indicated that in this case no ionization took place. Even replacement of the Cl ligands by OTf, which drove the $2 \rightleftharpoons 5$ equilibrium completely to the ionic side in **2a–d**, failed for **2e** and resulted in the covalent **7**, which was characterized by its crystal structure (Fig. 2b). \S This different behaviour of **2e** relative to **2a–d** may be accounted for by the greater electron withdrawing power of the chloro ligand, causing a greater electron deficiency at silicon and hence stabilizing the hexacoordinate relative to the pentacoordinate complex.

We thank Dr Arkady Ellern for the crystallographic analyses. Financial support from the Israel Science Foundation and the German Israeli Foundation (GIF) is gratefully acknowledged.

Notes and references

\dagger These chemical shifts are highly characteristic, respectively, of penta- and hexacoordination in silicon chelates.^{1e} The ^1H and ^{13}C NMR spectra featured only line broadening, but no splitting.

\ddagger The use of toluene- d_8 as solvent prevented earlier detection of the dissociation reported here.^{1b}

\S *Crystal data for 6a*: $\text{C}_{15}\text{H}_{23}\text{F}_3\text{N}_4\text{O}_5\text{SSi}$, $M = 456.52$, triclinic, space group $P\bar{1}$, $a = 8.4678(15)$, $b = 11.032(2)$, $c = 11.517(2)$ Å, $V = 1033.7(3)$ Å 3 , $Z = 2$, $\mu(\text{Mo-K}\alpha) = 0.118$ mm $^{-1}$, 12650 reflections measured, 5128 unique ($R_{\text{int}} = 0.0241$) which were all used in calculations. Final $R_1 = 0.0365$ and $wR_2 = 0.1016$ (all data). For **7**: $\text{C}_{20}\text{H}_{22}\text{F}_6\text{N}_4\text{O}_8\text{S}_2\text{Si}$, $M = 652.63$, monoclinic, space group $P2_1/n$, $a = 16.466(5)$, $b = 8.193(3)$, $c = 20.861(7)$ Å, $V = 2748.3(15)$ Å 3 , $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.330$ mm $^{-1}$, 26602 reflections measured, 3920 unique ($R_{\text{int}} = 0.0500$) which were all used in calculations. Final $R_1 = 0.0506$ and $wR_2 = 0.1258$ (all data). Data were measured at 173(2) K on a Bruker SMART CCD 1000 diffractometer [$\lambda(\text{Mo-K}\alpha) = 0.711069$ Å, graphite monochromator, a scan width of 0.3° in ω and exposure time of 10 s frame $^{-1}$, detector–crystal distance = 4.95 cm]. Bruker SHELX software was used. CCDC 157088 (**6a**) and 157089 (**7**). See <http://www.rsc.org/suppdata/cc/b1/b102427m/> for crystallographic data in CIF or other electronic format.

- (a) A. O. Mozhukhin, M. Yu. Antipin, Yu. T. Struchkov, B. A. Gostevskii, I. D. Kalikhman, V. A. Pestunovich and M. G. Voronkov, *Metalloorg. Khim.*, 1992, **5**, 658; *Chem. Abstr.*, 1992, **117**, 234095w; (b) D. Kost, I. Kalikhman and M. Raban, *J. Am. Chem. Soc.*, 1995, **117**, 11 512; (c) I. Kalikhman, S. Krivonos, D. Stalke, T. Kottke and D. Kost, *Organometallics*, 1997, **16**, 3255; (d) D. Kost, I. Kalikhman, S. Krivonos, D. Stalke and T. Kottke, *J. Am. Chem. Soc.*, 1998, **120**, 4209; (e) D. Kost and I. Kalikhman, in *The Chemistry of Organic Silicon Compounds, Vol 2*, ed. Z. Rappoport and Y. Apeloig, Wiley, Chichester, 1998, pp. 1339–1445.
- (a) D. Kummer, S. C. Chaudhry, J. Seifert, B. Deppisch and G. Mattern, *J. Organomet. Chem.*, 1990, **382**, 345; (b) D. Kummer and S. H. Abdel Halim, *Z. Anorg. Allg. Chem.*, 1996, **622**, 57; (c) A. R. Bassindale and M. Borbaruah, *J. Chem. Soc., Chem. Commun.*, 1991, 1499.
- (a) M. Chauhan, C. Chuit, R. J. P. Corriu and C. Reyé, *Tetrahedron Lett.*, 1996, **37**, 845; (b) M. Chauhan, C. Chuit, R. J. P. Corriu, A. Mehdi and C. Reyé, *Organometallics*, 1996, **15**, 4326.
- (a) J. Belzner, D. Schär, B. O. Kneisel and R. Herbst-Imer, *Organometallics*, 1995, **14**, 1840; (b) D. Schär and J. Belzner, in *Organosilicon Chemistry III*, ed. N. Auner and J. Weis, VCH, Weinheim, 1997, p. 429.
- I. Kalikhman, S. Krivonos, L. Lameyer, D. Stalke and D. Kost, *Organometallics*, 2001, **20**, 1053.
- U.-H. Berlekamp, P. Jutzi, A. Mix, B. Neumann, H.-G. Stammer and W. W. Schoeller, *Angew. Chem., Int. Ed.*, 1999, **38**, 2048.