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Neutral and ionic dissociation patterns in hexacoordinate silicon chelates: a model nucleophilic substitution at pentacoordinate silicon

Boris Gostevskii,[ab] Keren Adear,[a] Akella Sivaramakrishna,[a] Gilad Silbert,[a] Dietmar Stalke,[c] Nikolaus Kocher,[c] Inna Kalikhman*[a] and Daniel Kost*[a]

[a] *Department of Chemistry, Ben-Gurion University, Beer-Sheva 84105, Israel*

[b] *A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk, Russia*

[c] *Institut für Anorganische Chemie der Universität Würzburg, Germany. E-mail: kostd@bgumail.bgu.ac.il, innakal@bgumail.bgu.ac.il*

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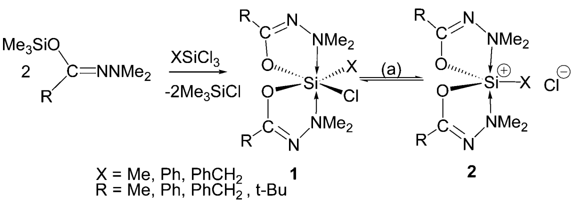
A model nucleophilic-displacement reaction coordinate at pentacoordinate silicon is demonstrated by neutral and ionic dissociation equilibria through a stable hexacoordinate complex.

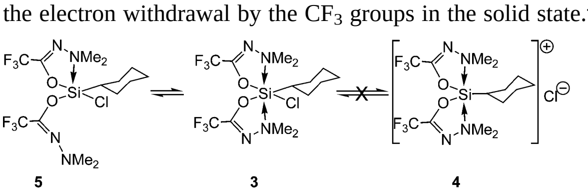
Within a general study of hypervalent silicon complexes,[1] we have reported that neutral hexacoordinate silicon complexes undergo facile, solvent-driven, ionization to pentacoordinate siliconium halide salts [eqn. (1)].[2] This was associated with a dramatic temperature dependence of the ^{29}Si NMR chemical shift (which had not been reported previously for hexacoordinate silicon complexes),[1] indicating increased dissociation at *low* temperature in an apparently counterintuitive process.[2,3] The present communication describes the first observation of an *opposite* temperature-dependence of ^{29}Si chemical shifts in hexacoordinate complexes, resulting from a *nonionic* equilibrium dissociation of the N–Si dative bond exchanging between neutral hexa- and pentacoordinate silicon complexes. The two dissociation patterns offer a model for nucleophilic displacement at a *pentacoordinate* silicon atom.



(1)

The ionization in eqn. (1) is prevented by strong electron-withdrawing groups attached to the complex: when X = halogen or R = CF_3.[2] This was attributed to insufficient stabilization of the cation (**2**) by the donor ligands, resulting from electron-withdrawal by the electronegative R or X groups. On the other hand, it has been shown that ionization is dramatically enhanced by bulky monodentate ligands, such as X = t-Bu[4] or cyclohexyl (**2a**, R = t-Bu, X = C_6H_{11}, this work), in which ionization is complete at ambient temperature, as evident from the low-field ^{29}Si chemical shift at 300 K, −65.1 ppm ($CDCl_3$), characteristic of pentacoordination.[1]

These two opposing effects, prevention of ionization by electron-withdrawing groups, and enhanced ionization in the presence of bulky X ligands, prompted us to investigate the outcome of the combined effect of both features. The essential structural features were incorporated in one molecule, **3**, a modified **1** in which R = CF_3 and X = cyclohexyl. It was expected that one of the opposing effects would prevail, resulting in either the hexacoordinate **3** or the ionic siliconium salt **4**. Indeed, an X-ray crystal analysis (Fig. 1) revealed that the solid product was **3**, suggesting predominance of the electron withdrawal by the CF_3 groups in the solid state.†



(2)

The solution behavior of **3** was surprisingly different: the ^{29}Si NMR spectra of **3** were measured and a remarkable temperature dependence was found (Fig. 2a): a decrease of 170° (from 370 to 200 K) resulted in an upfield shift of the ^{29}Si resonance by nearly 60 ppm, from −63 to −117.8 ppm (characteristic of penta- and hexacoordination, respectively[1b]) in toluene-d_8 solution. A similar trend was observed in $CDCl_3$ solution, though the temperature range was obviously limited (Fig. 2a). This temperature depend-

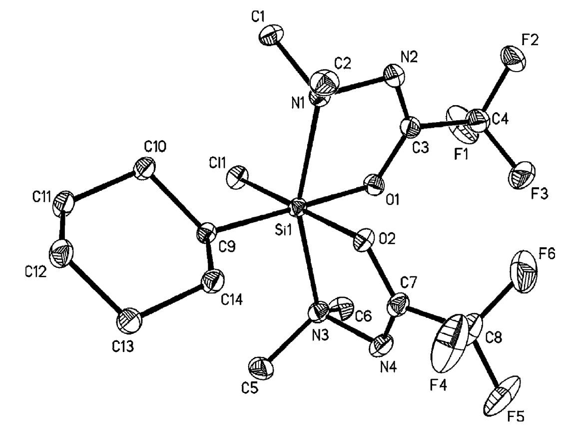


Fig. 1 Crystallographic molecular structure of **3**. Thermal ellipsoids represent 50% probabilities. Hydrogens are omitted for clarity. Selected bond lengths: Si–O1, 1.8027(10); Si–O2, 1.8022(10); Si–C1, 2.1963(6); Si–C9, 1.9304(13); Si–N1, 2.1015(12); Si–N3, 2.0968(13) Å.

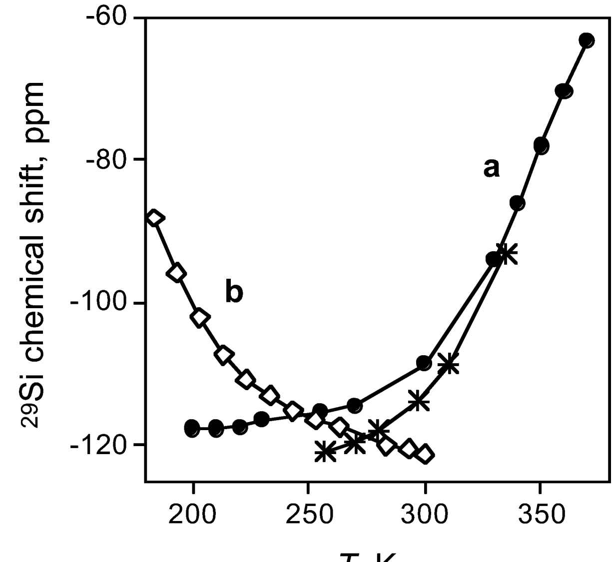


Fig. 2 Temperature dependence of ^{29}Si chemical shift (a) for **3** in toluene-d_8 (●) and $CDCl_3$ (*) solutions, and (b) for **1b** ⇄ **2b** (R = X = Me) in CD_2Cl_2 solution (◇).

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Table 1 Calculated absolute and relative energies, and ^{29}Si NMR chemical shifts for **3** and **5**

	3		**5**		ΔE(**3** − **5**)
Basis set	Total E^a/Hartree molecule^{-1}	$\delta(^{29}Si)^b$ (ppm)	Total E^a/Hartree molecule^{-1}	$\delta(^{29}Si)^b$ (ppm)	Relative E^c/ kcal mol^{-1}
6-31G(d) (ZPE, kcal/mol)	−2265.592207 (249.27289)		−2265.590312 (247.63071)		0.42
6-311G(2d)	−2266.082159	−115.41	−2266.081621	−68.63	1.27
6-311G(3d)	−2266.112900	−118.67	−2266.112571	−72.61	1.40
6-311G(3d,p)	−2266.142569	−116.46	−2266.142288	−70.30	1.43

^{a} Total calculated B3LYP-energies at the given basis set, at //B3LYP/6-31G(d) optimized geometry, without zero-point vibrational energy correction. ^{b} Chemical shifts calculated using the GIAO method at the given basis sets, relative to TMS chemical shift calculated at the same level. ^{c} The difference between total energies of **5** and **3**, with ZPVE corrections scaled by 0.9804 according to ref. 8.

ence is in sharp contrast with previously reported temperature dependencies of equilibrating silicon complexes [eqn. (1), R, X = alkyl, aryl], a typical example of which is depicted in Fig. 2b for comparison.[2] In these compounds, as in the example (**1b** ⇄ **2b**) of Fig. 2, cooling was accompanied by a substantial *downfield* shift of the ^{29}Si resonance, associated with increased solvent-driven ionization at low temperature (no such shift could be observed in toluene-d$_8$ solution of **1b**, in which no ionization takes place). The clearly opposite temperature dependence of the ^{29}Si chemical shift of **3**, relative to other compounds **1** (**2**), indicates that a different process, other than ionization, must take place in the solution of **3**. The only other reasonable process leading smoothly and reversibly to formation of a pentacoordinate silicon complex (as evident by the low-field ^{29}Si NMR chemical shift[1b]) is the non-ionic dissociation of the N–Si dative bond, shown in eqn. (2) (**3** ⇄ **5**). This is the first reported *neutral* equilibrium dissociation of a dative bond in hexacoordinate silicon complexes.

Support for the assignment of **5** comes from the ^{1}H and ^{13}C NMR spectra, which feature one singlet for all four *N*-methyl groups (δ in toluene-d$_8$, at 350 K, ^{1}H 2.67; ^{13}C 48.2 ppm): the two dimethylamino groups in **5** exchange rapidly by a reversible internal nucleophilic displacement (sometimes referred to as "flip-flop"),[5] and this renders all four *N*-methyl groups equivalent. Observation of individual *N*-methyl resonances at the slow exchange limit temperature is obscured by the predominance of **3** at ambient or lower temperatures.

Rigorous characterization of **5** was prevented by its equilibrium with **3**, which did not enable crystallization. Additional support for the structure of **5** was obtained from *ab initio* quantum-mechanical calculations: **3** and **5** were fully optimized at the B3LYP/6-31G* level, using the Gaussian-03W software.[6] Both structures occupy minima on the potential energy hypersurface, as evident from frequency calculations, indicating that both are feasible molecules. The total energies and ^{29}Si chemical shifts of **3** and **5** have been calculated and compared at several larger basis sets (Table 1). The energies of the two species at the various levels and including zero point vibrational corrections are nearly equal, with a slight (1.3–1.4 kcal mol^{-1}) preference for the pentacoordinate structure **5** in agreement with the observation of an equilibrium population ratio in solution.

The calculated ^{29}Si NMR chemical shifts (Table 1) are in excellent agreement with experiment (Fig 2): at temperatures near 200 K, the equilibrium is shifted completely towards **3**, and the chemical shift is within 2 ppm from the calculated values. Similar agreement is found for the high-temperature values with the chemical shifts calculated for **5**.

The formation of **5** satisfies the tendencies of both functional groups: that of the bulky cyclohexyl to expel a ligand, and that of the electron-withdrawing CF_3 to avoid ionization.

Eqn. (2) can also be viewed from a different angle, as a model for a nucleophilic displacement reaction at *pentacoordinate* silicon.[7] It is a model, rather than a real nucleophilic substitution, because in order to realize the complete sequence as outlined in eqn. (2), the CF_3 substituent must be replaced by an alkyl or aryl group, to obtain the ionic structure **4** or its analog. The sequence models attack by the neutral dimethylamino nucleophile in **5** on pentacoordinate silicon, to form the neutral hexacoordinate "intermediate" **3** (which may well be the most stable molecule along the reaction coordinate). This is followed by departure of the chloride leaving group, forming the ionic siliconium salt **4**. Thus a complete nucleophilic substitution coordinate is demonstrated. The model reaction coordinate differs, however, from previous S_N2 reaction-coordinate models[7] in that it is an attack on *pentacoordinate* silicon, *via hexacoordinate* intermediate forming a substituted (and ionic) pentacoordinate product.

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Notes and references

† *Crystal data* for **3**: $C_{14}H_{23}ClF_6N_4O_2Si$, M = 456.90, monoclinic, space group $P2_1/c$, a = 7.806(2), b = 9.205(3), c = 28.156(8) Å, β = 94.228(6)°, V = 2017.7(10) Å^3, T = 100(2) K, Z = 4, μ(Mo–Kα) = 0.320 mm^{-1}, 26321 reflections collected, 4098 unique (R_{int} = 0.0295) which were all used in calculations. Final wR_2 = 0.0776 (all data). Data were measured on a Bruker SMART CCD 1000 diffractometer, and solved using Bruker SHELX software. CCDC 225181. See http://www.rsc.org/suppdata/cc/b4/b404157g/ for crystallographic data in .cif format.

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