Donor-Stabilized Silyl Cations. 8. Carbon−Carbon Bond Formation through a Novel Interchelate Molecular Rearrangement in Pentacoordinate Siliconium-Ion Salts[1]

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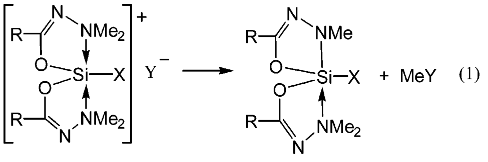
Summary: Tricyclic neutral pentacoordinate silicon complexes are formed by a novel intramolecular rearrangement of pentacoordinate bis(imino nitrogen)-chelated siliconium halide salts. The rearrangement consists of an interchelate aldol-type condensation of imine moieties, forming a new carbon−carbon bond and a third chelate ring.



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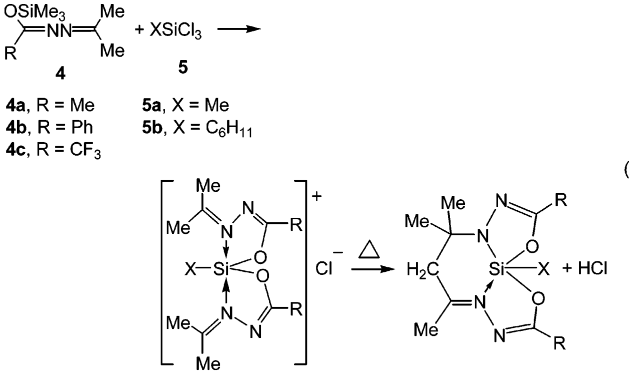
Within the chemistry of hypercoordinate silicon complexes, which has attracted considerable interest recently,[2] the least studied subgroup consists of pentacoordinate siliconium ion salts.[2d,3] These were described as highly reactive;[3c,d] however, little has been reported about their reactions. We have developed a straightforward synthesis for pentacoordinate siliconium ion salts (**1**)[4] and have reported that sterically congested **1** (X = *t*-Bu, cyclohexyl) undergoes facile nucleophilic attack by the halide anion at one of the *N*-methyl groups, to eliminate methyl halide (eq 1).[5]

More recently, we have studied the chemistry of isopropylideneimino-coordinated ions (**2**; eq 2)[3f] and were surprised to find that, like **1**, these also underwent a smooth quantitative transformation upon heating in solution, despite the obvious absence of *N*-methyl groups. This paper reports the unusual interchelate rearrangement of siliconium ions **2**.



4 **5**

4a, R = Me
4b, R = Ph
4c, R = CF$_3$

5a, X = Me
5b, X = C$_6$H$_{11}$

(2)

2

2a, R = X = Me
2b, R = Ph; X = C$_6$H$_{11}$
2c, R = CF$_3$; X = Me

3

3a, R = X = Me
3b, R = Ph; X = C$_6$H$_{11}$
3c, R = CF$_3$; X = Me

The novel transformation **2** → **3** outlined in eq 2 was only identified when crystal structures of the products (**3a**·HI·CH$_3$CN, Figure 1; **3b**, Figure 2) were obtained.[6] The product results from an unexpected intramolecular, interchelate-ring rearrangement. **3a**,**b** have a new C−C bond, which closes a third chelate cycle such that the silicon occupies the bridgehead position in the new tricyclic complex. The product **3** is identified by the characteristic upfield shift of the ^{29}Si resonance by ca. 8 ppm relative to the starting material **2** (Table 1). Likewise, one of the imino carbons of **2** transforms to a saturated quaternary carbon in **3**, accompanied by an upfield shift of the ^{13}C resonance by more than 100 ppm. One isopropyl methyl group in **2** changes to a methylene group, which is immediately recognized by its typical AB quartet in the ^{1}H NMR spectrum.

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(1) Dedicated to the memory of the late Professor Vadim Pestunovich. Part 7: Reference 3f.

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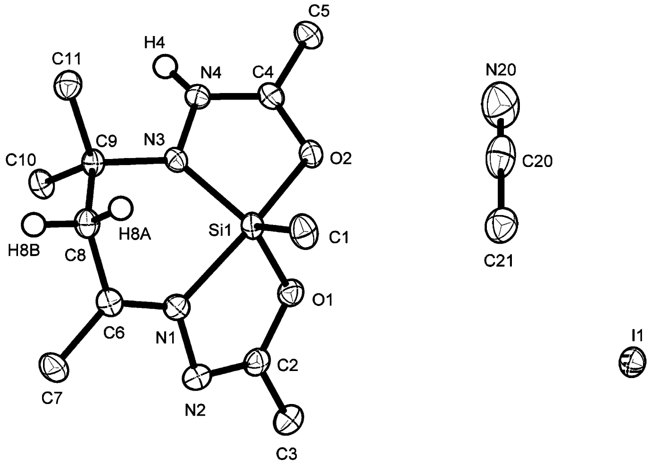
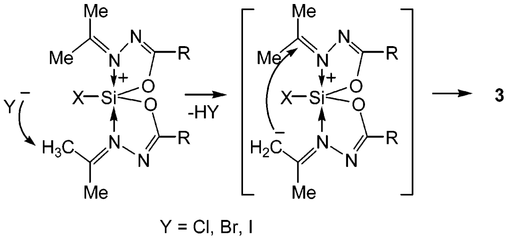


Figure 1. Solid-state structure of **3a**·HI·CH_3CN, asymmetric unit. Hydrogen atoms, except for H4, H8A, and H8B, are omitted for clarity. The anisotropic displacement parameters are depicted at the 50% probability level (MeI was used to replace Cl^-, to assist in crystallization from CH_3CN). Selected bond lengths (Å) and angles (deg): Si1−O1 = 1.7134(13), Si1−O2 = 1.7843(12), Si1−N1 = 1.9372(14), Si1−N3 = 1.7434(14), Si1−C = 1.8492(18), N1−C6 = 1.283(2) N3−C9 = 1.4724(19) Å; N1−Si1−O2 = 161.93, N3−Si1−O1 = 131.41(7), N1−Si1−N3 = 89.52(6)°.

A plausible reaction pathway is shown in eq 3, involving initial deprotonation of one of the isopropylidene methyl groups in **2**, presumably by the halide counterion. The resulting allylic carbanion attacks the electrophilic imino carbon *located at the opposite chelate ring*, despite the apparent long distance and possible interference of equatorial ligands. Apparently the allylic protons are sufficiently acidic, and their acidity may even be increased by coordination of the imino nitrogen to silicon as an electron-donor group. The reaction is similar to an aldol-type condensation of imines.[7] Formation of transition-metal compounds with an analogous chelate ring bridging by condensation of acetone and metal−amine complexes has been reported.[8] However, the present condensation is unique in that it is intramolecular within a silicon complex and catalyzed by mild halide anion. The following results support the proposed mechanism and provide some insight.



(3)

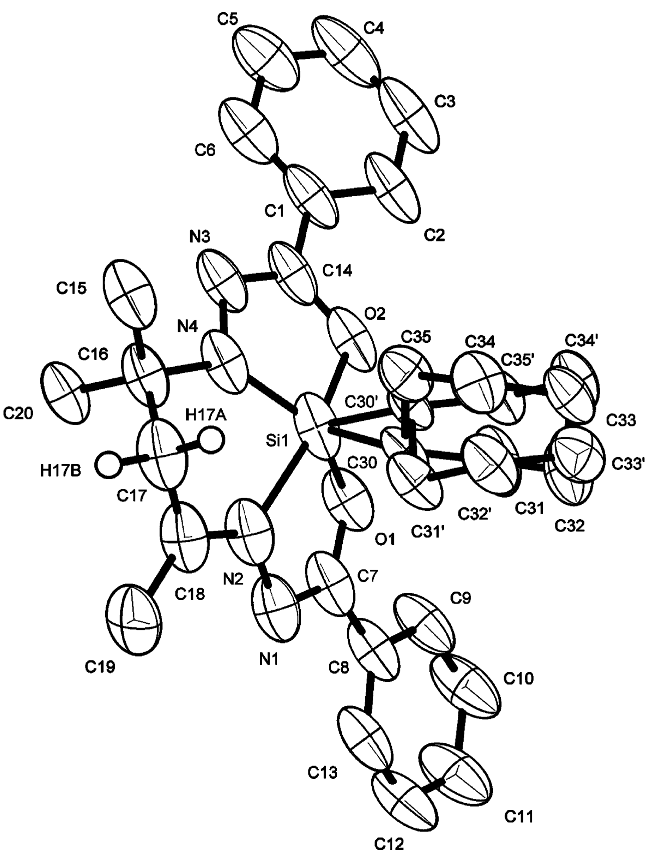


Figure 2. Solid-state structure of **3b**, asymmetric unit. Hydrogen atoms, except for H17A and H17B, are omitted for clarity. The anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths (Å) and angles (deg): Si1−O1 = 1.7444(14), Si1−O2 = 1.7396(16), Si1−N2 = 1.9895(19), Si1−N4 = 1.744(2), Si1−C30 = 1.907(4), Si1−C30′ = 1.914(4), N2−C18 = 1.291(2), N4−C16 = 1.479(2) Å; N2−Si1−O2 = 158.79, N4−Si1−O1 = 135.83(7), N2−Si1−N4 = 89.03(8)°.

Table 1. Comparison of ^{29}Si NMR Data for Siliconium Cations and Rearranged Products and ^{13}C NMR Data (ppm)

	Si cation	rearrangement product (**3a**−**c**, **7**)			
			$\delta(^{13}C)$		
	Si cation (**2a**−**c, 6**) $\delta(^{29}Si)$	$\delta(^{29}Si)$	quat C	CH_2(CH) carbon	$\delta(^1H)$ CH_2 ($^2J_{AB}$, Hz)
2a−**3a**	−82.9	−88.7	53.4	45.5	2.72, 2.83 (15.9)
2b−**3b**	−80.2	−86.1	53.5	47.1	2.59, 2.82 (15.5)
2c−**3c**	−75.8	−83.9	54.0	46.3	2.70, 2.77 (15.8)
6−**7**	−96.9	−99.4	67.9	(52.0)	

(a) The effect of halide ion on the rearrangement rate is *opposite* to that observed previously in the elimination reaction of eq 1[5] and follows the order $Cl^- > Br^- > I^-$.[9] This reactivity order is the order of basicity toward

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[6] (a) The hydrogen halide acid can either form a hydrohalide salt of **3**, as in the crystal of **3a**·HI·CH_3CN (Figure 1), or it may be removed during crystallization to form neutral **3**, as in **3b**, depending on the conditions. (b) **3a**·HI·CH_3CN: $T = 100(2)$ K, triclinic, space group $P\bar{1}$, $a = 8.832(2)$ Å, $b = 9.853(2)$ Å, $c = 10.885(2)$ Å; $\alpha = 98.806(3)°$, $\beta = 93.522(3)°$, $\gamma = 101.601(3)°$, $Z = 2$, $V = 912.9(4)$ Å^3, $R_F = 0.0164$ ($R_{wF} = 0.0432$) for $I > 2\sigma(I)$, 18 873 reflections collected, 3724 independent reflections. Full-matrix least squares on F^2 was used for refinement. The N4-bonded hydrogen atom was refined freely. **3b**: $T = 100(2)$ K, orthorhombic, space group $Pca2_1$, $a = 23.345(4)$ Å, $b = 9.6561(17)$ Å, $c = 10.7969(19)$ Å, $Z = 8$, $V = 2433.8(7)$ Å^3, $R_F = 0.0357$ ($R_{wF} = 0.0904$) for $I > 2\sigma(I)$, 32 267 reflections collected, 5003 independent reflections. Full-matrix least squares on F^2 was used for refinement. The cyclohexyl group was refined to split site occupation factors of 0.56 and 0.44, respectively, corresponding to two chair conformations. The crystal data for **3a**,**b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-232790 and CCDC-232791, respectively. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk). Data tables and figures can be found in the Supporting Information.

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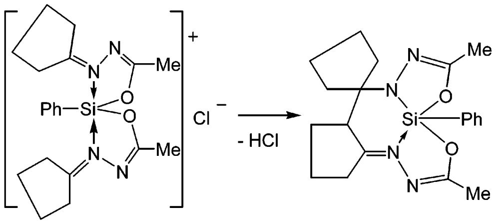
proton and supports the proposed initial deprotonation step (eq 3).

(b) The remote substituent R has a substantial effect on the reaction rate: when R = CF_3 (**2c**), the rearrangement was so rapid that the starting siliconium cation could only be detected as an intermediate (in the ^{29}Si and ^{13}C NMR spectra), with immediate formation of the rearranged product **3c** at ambient temperature and completion of the reaction within 1 h. The rate enhancement is likely due to the increased acidity of the allylic protons, on one hand, and the increased electrophilicity of the imino carbon of the opposite chelate ring, on the other, both caused by electron withdrawal by the CF_3 groups through the conjugated π system.

(c) An excess of **4** causes a dramatic enhancement (ca. 10-fold) of the **2** → **3** reaction rate (eq 2). This may be due to the basicity of **4** causing more facile proton removal.

(d) The concentration of **2** in solution had no noticeable effect on reaction rate, indicating that halide attack on the cation occurs "intramolecularly" within an ion-pair cage.

The reaction is quite general and is not restricted to isopropylideneimino complexes **2**, as demonstrated by the variety of differently substituted diiminosiliconium complexes listed in Table 1, including the cyclopentylideneimino complexes **6** → **7** (eq 4). This skeletal rearrangement is another case of the unusual reactivity of siliconium ion salts, following the reported methyl halide elimination (eq 1).[5] It is interesting to note that in both of these reactions one of the N→Si dative bonds is converted to a regular covalent bond (evidenced by the tricoordinate nitrogen). This could be the common driving force for both reactions.



6 **7** (4)

Experimental Section. NMR spectra, recorded on a Bruker DMX-500 spectrometer, are reported in ppm relative to TMS in $CDCl_3$ solutions. Siliconium complexes **2** and **6** were prepared by the method described previously,[3f] except for **2c**, which rearranged before it could be isolated and was identified by its NMR spectra and by the rearrangement product. **2a**: mp 130 °C dec; yield 93%; ^1H NMR δ 0.81 (s, 3H, MeSi), 2.03 (s, 6H, MeCO), 2.32, 2.39 (2s, 12H, $NCMe_2$); ^{13}C NMR δ 3.9 (SiMe), 17.0 (CH_3CO), 23.5, 24.8 ($(CH_3)_2C$), 165.6 (OC=N), 180.8 (C=NN); ^{29}Si NMR δ −82.9. Anal. Calcd for $C_{11}H_{21}N_4O_2ClSi$: C, 43.34; H, 6.94; N, 18.38. Found: C, 43.13; H, 6.80; N, 18.16. **2b** was described previously.[3f] **2c**: ^1H NMR δ 0.88 (s, 3H, MeSi), 2.51, 2.53 (2s, 12H, $NCMe_2$); ^{13}C NMR δ 9.6 (SiMe), 23.3, 24.4 ($(CH_3)_2C$), 117.0 (q, $^1J_{CF}$ = 288 Hz, CF_3), 155.0 (q, $^2J_{CF}$ = 39 Hz, OC=N), 184.0 (C=NN); ^{29}Si NMR δ −75.8. **6**: mp 121 °C dec; yield 93%; ^1H NMR δ 1.50, 1.61, 2.65 (3m, 16H $(CH_2)_4$), 1.99 (s, 6H, Me), 6.95−7.19 (m, 5H, Ph); ^{13}C NMR δ 16.6 (Me), 22.6, 24.4, 33.3, 34.7 ($(CH_2)_4$), 127.8, 128.7, 131.9, 132.1 (Ph), 166.8 (OC=N), 193.7 (C=NN); ^{29}Si NMR δ −96.9. Anal. Calcd for $C_{20}H_{27}N_4O_2ClSi$: C, 57.33; H, 6.50; N, 13.37. Found: C, 56.88; H, 6.29; N, 13.38.

Synthesis of 3. Vacuum-sealed $CHCl_3$ solutions of compounds **2** were prepared in situ and kept in a 90 °C bath for 20−48 h, followed by removal of volatiles. To the glassy residue was added *n*-hexane, and the mixture was stirred for 1 h. A powder (**3**) formed and was separated from the liquid by decantation. **3a**: mp 177−178 °C; yield 82%; ^1H NMR δ 0.27 (s, 3H, MeSi), 1.33, 1.66 (2s, 6H, Me_2C), 1.83, 2.04 (2s, 6H, 2MeCO), 2.44 (s, 3H, MeC=N), 2.72, 2.83 (ABq, $^2J_{HH}$ = 15.9 Hz, 2H, CH_2); ^{13}C NMR δ 0.8 (SiMe), 15.3, 16.8 (CH_3CO), 22.4, 25.9, 29.1 ($3CH_3CN$), 45.5 ($NCCH_2$), 53.4 (Me_2C), 160.8, 169.7, 172.8 (C=N); ^{29}Si NMR δ −88.7. Anal. Calcd for **3a**·HCl ($C_{11}H_{21}ClN_4O_2Si$): C, 43.34; H, 6.94; N, 18.38. Found: C, 43.49; H, 7.05; N, 18.2. **3b**: mp 115−120 °C; yield 71%; ^1H NMR δ 1.11−1.28, 1.58−1.68 (2m, 11H, C_6H_{11}), 1.20, 1.58, 2.53 (3s, 9H, NCMe), 2.59, 2.82 (ABq, $^2J_{HH}$ = 15.5 Hz, 2H, CH_2), 7.24−8.17 (m, 10H, Ph); ^{13}C NMR δ 22.3 (CH_3CN), 26.8, 30.8 ($(CH_3)_2C$), 26.7, 27.9, 28.1, 28.4, 28.7, 30.4 (C_6H_{11}), 47.1 ($NCCH_2$), 53.5 (Me_2C), 152.0, 167.1, 170.6 (C=N); ^{29}Si NMR δ −86.1. Anal. Calcd for **3b**·$CHCl_3$ ($C_{27}H_{33}Cl_3N_4O_2Si$): C, 55.90; H, 5.73; N, 9.66. Found: C, 55.45; H, 6.18; N, 9.50. **3c**: obtained from **4c** and **5a** in $CHCl_3$ after 20 min at room temperature, light green powder washed with *n*-hexane; mp 99−100 °C; yield 83%; ^1H NMR δ 0.30 (s, 3H, MeSi), 1.11, 1.45 (2s, 6H, Me_2C), 2.51 (s, 3H, N=CMe), 2.70, 2.77 (ABq, $^2J_{HH}$ = 15.8 Hz, 2H, CH_2); ^{13}C NMR δ 1.6 (SiMe), 22.9, 26.2, 30.0 ($3CH_3C$), 46.3 (CH_2), 54.0 (Me_2C), 116.8 (q, $^1J_{CF}$ = 278 Hz, CF_3), 117.9 (q, $^1J_{CF}$ = 278 Hz, CF_3), 142.5 (q, $^2J_{CF}$ = 39 Hz, C=N), 158.9 (q, $^2J_{CF}$ = 39 Hz, C=N), 179.5 (MeC=N); ^{29}Si NMR δ −83.9. Anal. Calcd for **3c** ($C_{11}H_{14}F_6N_4O_2Si$): C, 35.11; H, 3.75; N, 14.89. Found: C, 34.60; H, 3.90; N, 15.20. **7** (prepared similarly from **6**): mp 138−140 °C; yield 75%; ^1H NMR δ 1.48−3.10 (m, 15H, $7CH_2$, CH), 2.12, 2.65 (2s, 6H, Me), 7.16−7.60 (m, 5H, Ph); ^{13}C NMR δ 15.2, 17.0 (Me) 22.8, 24.8, 26.2, 27.4, 33.8, 35.9, 38.4 (CH_2), 52.0 (CH), 67.9 ($C(CH_2)_4$), 127.7, 130.5, 132.2, 132.9 (Ph), 161.4, 171.6, 185.5 (C=N); ^{29}Si NMR δ −99.4. Anal. Calcd for **7**·HCl ($C_{20}H_{27}ClN_4O_2Si$): C, 57.33; H, 6.50; N, 13.37. Found: C, 56.76; H, 6.72; N, 13.37.

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Supporting Information Available: Tables of crystallographic data and figures giving additional views of the structures for **3a** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) A vacuum-sealed chloroform-*d* solution of **2a**(Cl) had completely rearranged after 1 h in a 90 °C bath. However, the bromo and iodo analogues took 36 h under similar conditions to rearrange to 42 and 1.3%, respectively.