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Reactivity Control of an Allylsilane Bearing a 2-(Phenylazo)phenyl Group by Photoswitching of the Coordination Number of Silicon

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Highly coordinated organosilicon compounds are known to exhibit reactivities that are different from those of ordinary organosilicon compounds with a tetracoordinate silicon atom.[1] If the coordination number of the silicon can be reversibly controlled by external stimuli such as magnetism, light, etc., without influencing the reaction conditions or adding external reagents to the reaction system, the reactivities can be altered by such stimuli. Although a change in the coordination number of silicon between five and six in response to heat and light was recently reported in some organosilicon compounds, this change was not applied to switching of the reactivities.[2,3] In this paper, we report the reactivity control of an allyldifluorosilane bearing a 2-(phenylazo)phenyl group by switching of the coordination number of silicon between four and five induced by photoirradiation.

Allyldifluorosilane (*E*)-**1** bearing a 2-(phenylazo)phenyl group was synthesized from 2-iodoazobenzene[2,4] via allyldiethoxy[2-(phenylazo)phenyl]silane. In the ^{29}Si NMR spectrum of (*E*)-**1** in $CDCl_3$ at room temperature (rt), a triplet coupled with two fluorine nuclei ($^1J_{SiF} = 278$ Hz) was observed at δ_{Si} −38.5, which shifted upfield compared with allyldifluorophenylsilane (δ_{Si} −20.4). In the ^{19}F NMR spectrum, a broad singlet at δ_F −140.4 with satellite peaks ($^1J_{SiF} = 278$ Hz) at rt was split into two broad peaks at δ_F −141.27 (1F) and −127.17 (1F) at −90 °C. Such coupling patterns and chemical shifts, which are similar to those of pentacoordinate silanes bearing a 2-(dimethylaminomethyl)phenyl group,[5] indicate nonequivalency of fluorine nuclei due to a trigonal bipyramidal (TBP) geometry around silicon constructed by coordination of a lone pair of nitrogen of the azo group in the solution state. The pentacoordinate state of the silicon atom in (*E*)-**1** in the crystalline state was determined by X-ray crystallographic analysis (Figure 1).[6] The N2 atom of the azo moiety is directed to the Si1 atom despite the steric repulsion of a bulky silyl group.[4a] The intramolecular N2···Si1 distance (2.389(2) Å), which is almost similar to that of difluoro[2-(dimethylaminomethyl)phenyl](methyl)silane (2.346(3) Å), is much shorter than the sum of the corresponding van der Waals radii (3.65 Å).[7] Therefore, the crystal structure of (*E*)-**1** is most likely interpreted as a distorted TBP structure with N2 and F1 atoms at apical positions and C1, C4, and F2 atoms at equatorial positions. In the UV/vis spectra of (*E*)-**1**, an absorption maximum ($\pi-\pi^*$) was observed at 339 nm in $CDCl_3$. The color of (*E*)-**1** is yellow, which is in contrast to the previously reported red of tetracoordinate 2-(phenylazo)phenylsilanes, suggesting the perturbation of the electronic structure of the azo moiety.[4a]

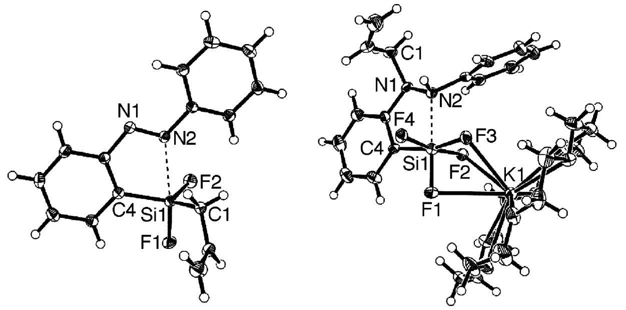
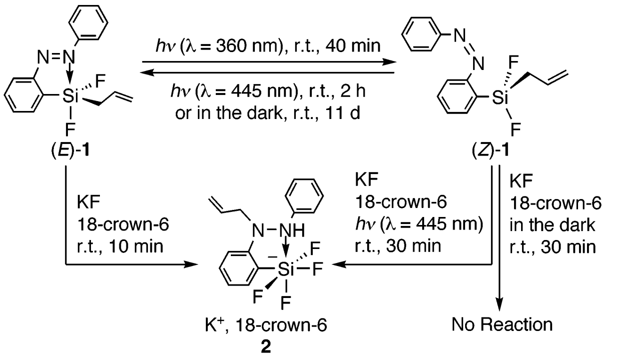


Figure 1. ORTEP drawing of (*E*)-**1** (left) and **2** (right) with thermal ellipsoid plots (50% probability). Selected bond lengths (Å) and angles (deg). (*E*)-**1**: Si1−F1, 1.6228(12); Si1−F2, 1.5955(13); Si1−C1, 1.8640(18); Si1−C4, 1.8578(18); N1−N2, 1.2595(18); Si1−N2, 2.389(2); F1−Si1−F2, 97.28(6); F1−Si1−C1, 102.89(7); F1−Si1−C4, 99.81(7). **2**: Si1−F1, 1.6487(13); Si1−F2, 1.6865(12); Si1−F3, 1.6790(13); Si1−F4, 1.7062(12); Si1−C4, 1.9003(18); Si1−N2, 2.1664(17); N1−N2, 1.442(2); F1−Si1−F2, 88.36(6); F1−Si1−F3, 94.48(6); F1−Si1−F4, 94.64(7); F1−Si1−C4, 100.15(7).

Scheme 1



Isomerization of (*E*)-**1** to (*Z*)-**1** in $CDCl_3$ was carried out quantitatively by irradiation ($\lambda = 360$ nm) for 40 min (Scheme 1).[8] A solution of (*Z*)-**1** showed its absorption maximum ($n-\pi^*$) at 443 nm. Irradiation ($\lambda = 445$ nm) of (*Z*)-**1** at rt for 2 h caused regeneration of (*E*)-**1** (72%).[8] (*Z*)-**1** was thermally isomerized to (*E*)-**1** quantitatively after 11 days, during which it was maintained at rt in the dark. In the ^{29}Si NMR spectrum of (*Z*)-**1** in $CDCl_3$ at −70 °C, a triplet ($^1J_{SiF} = 299$ Hz) was observed at δ_{Si} −20.0, which significantly shifted downfield compared to (*E*)-**1**. These results suggest that (*Z*)-**1** possesses a tetracoordinate silicon atom in the absence of Si···N interaction. The configuration of the lone pair of nitrogen atom, which is at a great distance from the silicon atom, is responsible for these spectral features of (*Z*)-**1**.

Reaction of (*E*)-**1** with an excess amount of KF in the presence of 18-crown-6 in $CDCl_3$ at rt for a period of 10 min afforded 82% yield of tetrafluorosilicate **2**. A similar reaction in benzene-d_6 at rt for 30 min gave 98% yield of **2**. The octahedral structure of **2** with a hexacoordinate silicon atom was determined by NMR spectroscopy and X-ray crystallographic analysis (Figure 1).[7] Conversely, no change was observed on treatment of (*Z*)-**1** with an excess amount of KF in the presence of 18-crown-6 in $CDCl_3$ at rt for 30 min in the dark, which is in contrast to the case of (*E*)-**1**. Silicate **2** was obtained in 36% yield after a period of 2 days. However, photoirradiation ($\lambda = 445$ nm) of tetracoordinate (*Z*)-**1** with an

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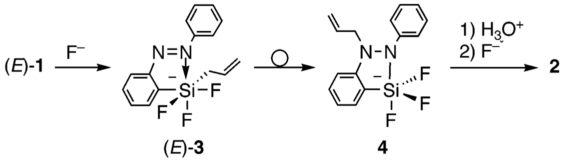
Scheme 2



excess amount of KF in $CDCl_3$ at rt for 30 min gave 91% yield of **2**. Isomerization of (*Z*)-**1** to (*E*)-**1** and the successive formation of **2** should have occurred instead of direct formation of **2** from (*Z*)-**1**. These results clearly illustrate the change in reactivities of **1** induced by photoirradiation.

Considering that the allylation of azobenzene with allylmagnesium chloride yields 1-allyl-1,2-diphenylhydrazine (89%) and that the nucleophilicity of an allyl group in allyl-substituted silicon compounds is raised as the coordination number of silicon increases,[1] the main formation mechanism of **2** is described as follows: The silicon atom of (*E*)-**1** is fluorinated by fluoride ion to generate intermediary silicate (*E*)-**3**. The nitrogen of (*E*)-**3** is allylated to obtain **4** (Scheme 2).[9] Protonation at the other nitrogen of **4** with water contained in the reaction solution and additional fluorination at silicon with fluoride ion resulted in the formation of **2**. Monitoring the reaction solution revealed complete disappearance of the absorbance due to the azo unit in UV/vis spectroscopy and downfield shift of methylene protons of the allyl group (δ 3.56 (brs, 1H), 4.32 (brs, 1H)) compared to those of (*E*)-**1** (δ 1.87−1.94 (m, 2H)) in ^{1}H NMR spectroscopy. These results indicate that migration of the allyl group from silicon to nitrogen proceeded to completion.

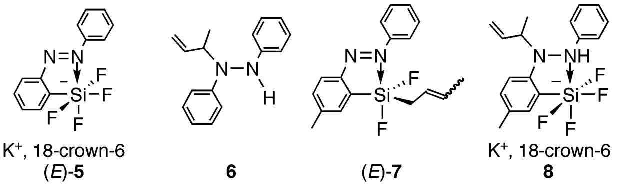
The fluorination proceeded easily in both (*E*)-**1** and the intermediate with a pentacoordinate silicon atom[2] because the Si···N interaction could increase the electrophilicity of the silicon atom in analogy with trifluoro[2-(phenylazo)phenyl]silane. Contrary to the behavior of (*E*)-**1**, neither allyldifluorophenylsilane nor (*Z*)-**1** reacted with fluoride ion under the same reaction conditions. The tetracoordinate state of (*Z*)-**1** is obviously responsible for the reluctant reactivities.

Differences in the reactivity of (*E*)-**1** and (*Z*)-**1** toward fluoride ion also indicate the importance of activation of the azo moiety induced by coordination to silicon in the N-allylation of the azo group.[9] The importance of this activation is further revealed by the following experiments: allylation of hexacoordinate potassium (*E*)-tetrafluorosilicate (*E*)-**5**[2] with crotyltrifluorosilane and CsF in refluxing THF for 24 h and successive hydrolysis, which yielded hydrazine **6** (59%) (Chart 1), and the treatment of azobenzene with crotyltrifluorosilane and CsF in THF at 90 °C for 4 days, which resulted in no reaction, contrary to the previous experiment.

A labeling experiment using a mixture of (*E*)-**1** and its dimethyl-substituted derivative, (*E*)-**7**, yielded a mixture of only silicates **2** and **8** (Chart 1). This result reveals that the allylic rearrangement reaction proceeds regiospecifically and intramolecularly at the γ-position of its allyl group.[9] The migration of the allyl group from silicon to nitrogen is superficially like the Claisen rearrangement in the point of γ-allylic migration onto an atom with a double bond.

To summarize, we have achieved control of a series of reactions yielding silicate **2** from allylsilane **1** based on change of the coordination number of silicon induced by photoirradiation. To promote the reaction, it is important that both the nucleophilic and electrophilic parts are activated by the Si···N interaction immediately. Such a type of reaction control can lead to new ways of starting or stopping a reaction without changing any other conditions that are suitable for a certain reaction.

Chart 1



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Supporting Information Available: Synthetic procedures and spectral data for (*E*)-**1**, (*Z*)-**1**, **2**, (*E*)-**5**, and **6** (PDF) and X-ray crystallographic files in CIF format for (*E*)-**1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Crystal data for (*E*)-**1**: $C_{15}H_{14}F_2N_2Si$, triclinic, *P*-1, $a = 7.192(4)$, $b = 9.719(5)$, $c = 10.504(6)$ Å, $\alpha = 74.203(18)$, $\beta = 87.53(3)$, $\gamma = 75.58(2)°$, $V = 684.0(6)$ Å^3, $Z = 2$, MW = 288.37, $D_c = 1.400$ Mg m^{-3}, $T = 120$ K, R_1 ($I > 2\sigma(I)$) = 0.038, wR_2 (all data) = 0.092, GOF = 1.051. Crystal data for **2**·$2CHCl_3$: $C_{29}H_{41}Cl_6F_4KN_2O_6Si$, triclinic, *P*-1, $a = 9.511(8)$, $b = 11.179(9)$, $c = 20.257(20)$ Å, $\alpha = 86.65(4)$, $\beta = 76.72(3)$, $\gamma = 67.81(2)°$, $V = 1940(3)$ Å^3, $Z = 2$, MW = 869.53, $D_c = 1.489$ Mg m^{-3}, $T = 120$ K, R_1 ($I > 2\sigma(I)$) = 0.038, wR_2 (all data) = 0.088, GOF = 1.157.

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