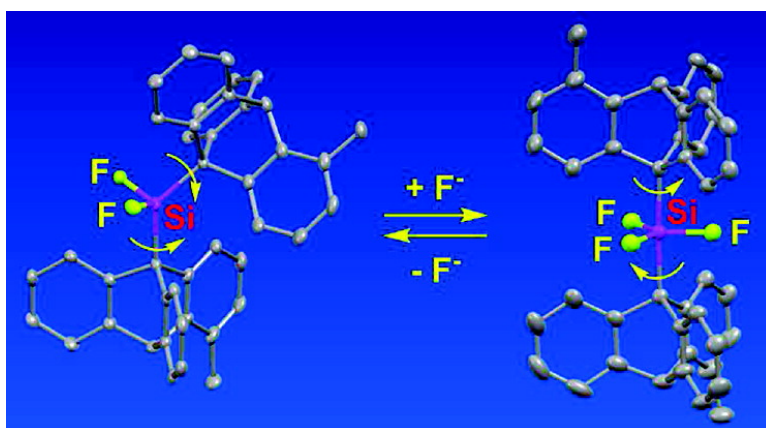


Introduction of Clutch Function into a Molecular Gear System by Silane#Silicate Interconversion

Wataru Setaka, Takayoshi Nirengi, Chizuko Kabuto, and Mitsuo Kira

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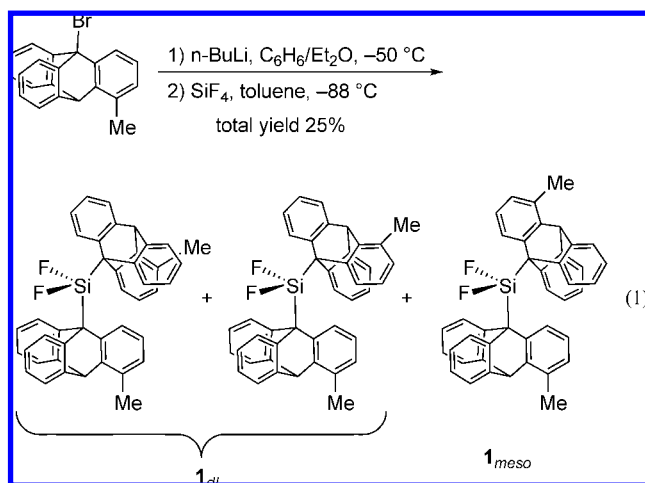
Wataru Setaka,^{*,†,‡} Takayoshi Nirengi,[†] Chizuko Kabuto,[†] and Mitsuo Kira^{*,†}

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan, and PRESTO, JST, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

Received July 23, 2008; E-mail: setaka@mail.tains.tohoku.ac.jp; mkira@mail.tains.tohoku.ac.jp

Since pioneering studies of Mislow et al. and Iwamura et al.,¹ bis(9-triptycyl)X systems (X = CH₂, O, NH, SiH₂, PH, etc.) are known as well-designed bevel gear systems. To use the gear systems as a molecular machine,² it is desirable to introduce a clutch–declutch mechanism controllable by external stimuli. Silane–silicate interconversion using reversible attachment of a fluoride ion may be a promising option for this purpose.^{3,4} We report herein that the introduction of the clutch–declutch mechanism into a new gear system, a bis(9-triptycyl)difluorosilane derivative, is achieved by the reversible attachment of a fluoride ion and that the corresponding pentacoordinate silicate adopts an unusual trigonal bipyramid (TBP) structure having both the two 9-triptycyl groups at the apical positions against the Muetterties rule.^{5,6}

A new bevel gear system, bis(4-methyl-9-triptycyl)difluorosilane **1**, was synthesized as a mixture of phase isomers [*dl* (**1_{dl}**) and *meso* isomers (**1_{meso}**)] by the reaction of SiF₄ with the corresponding triptycylithium.⁷



The structure of **1** (**1_{dl}** + **1_{meso}**) was determined by NMR spectroscopy and mass spectrometry of the mixture.⁷ X-ray analysis of a single crystal obtained by recrystallization of the mixture from benzene revealed that only **1_{dl}** (racemic mixture) exists in the crystal with a disorder of methyl positions as shown in Figure 1a.⁸ The C1–Si1–C2 angle of **1** (128.99(11)°) is remarkably larger than 109.5° that is expected for normal tetrahedral silane, probably due to the steric repulsion between two bulky triptycyl groups. NMR analysis showed the existence of two phase isomers **1_{dl}** and **1_{meso}** in a 2:1 ratio at room temperature in solution expectedly. Rapid gear rotation within each phase isomer of **1** is evidenced by rather simple ¹H NMR patterns of these compounds: seven aromatic

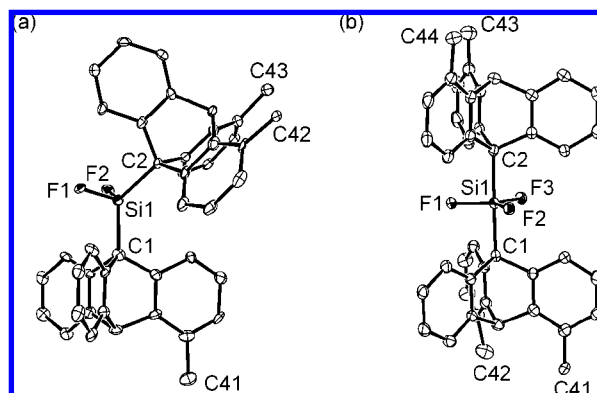


Figure 1. (a) Molecular structure of difluorodi(4-methyl-9-triptycyl)silane **1** (*dl*). (b) Molecular structure of (trifluorodi(4-methyl-9-triptycyl)silicate **2**. Hydrogen atoms and counteranion in the salt of **2** are omitted for clarity. Selected bond lengths (Å), bond angles (deg), and site occupancy factors of methyl carbons: **1**, Si1–C1 1.912(7); Si1–C2 1.932(6); Si1–F1 1.597(4); Si1–F2 1.572(4); C1–Si1–C2 128.99(11); C1–Si1–F1 101.9(3); F1–Si1–F2 102.43(9); C42 0.271(7); C43 0.557(8); C44 0.443(8). **2**, Si1–C1 2.007(4); Si1–C2 2.004(4); Si1–F1 1.639(2); Si1–F2 1.647(3); Si1–F3 1.647(3); C1–Si1–C2 178.09(19); F1–Si1–F2 117.98(14); F2–Si1–F3 121.90(14); F1–Si1–F3 120.12(14); C1–Si1–F1 90.48(15); C41 0.496(12); C42 0.504(12); C43 0.496(12); C44 0.504(12).

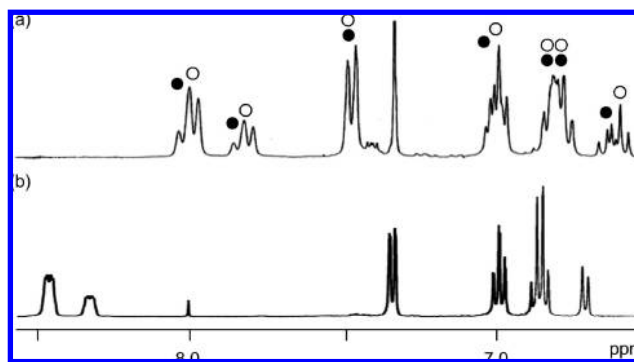


Figure 2. ¹H NMR spectra at 293 K (aromatic region) of (a) a mixture of silanes **1_{dl}** (○) and **1_{meso}** (●) in 1,1,2,2-tetrachloroethane-*d*₂ and (b) silicate **2** in acetone-*d*₆. Apparent broadening of lines may suggest coupling with ¹⁹F nuclei.

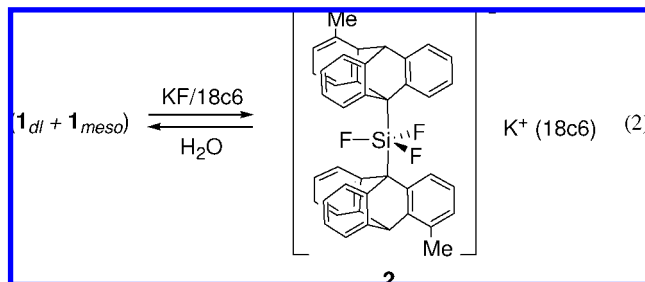
proton signals for **1_{dl}** and **1_{meso}** with reasonable coupling patterns (Figure 2a). These phase isomers cannot be separated at ambient temperature by HPLC, because of the equilibrium via gear slippage. The activation parameters for the slippage or interconversion between **1_{dl}** and **1_{meso}** were determined by analyzing temperature dependent NMR spectra to be $\Delta H^\ddagger = 17.2 \pm 0.2 \text{ kcal} \cdot \text{mol}^{-1}$ and $\Delta S^\ddagger = 0.9 \pm 0.9 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.⁹ Although the activation free energy for the slippage of **1** is relatively low as expected for bis(9-

[†] Tohoku University.

[‡] PRESTO.

tritycyl) systems joined by third row elements,^{1c} **1** would still be regarded as meshed molecular gears in solution at room temperature.

When the mixture of silanes **1_{dl}** and **1_{meso}** was treated with potassium fluoride in chloroform in the presence of 18-crown-6 (18c6), the corresponding pentacoordinate silicate **2** was obtained quantitatively as a salt with a K⁺(18c6) ion (eq 2).⁶



The molecular structure of silicate salt **2**·K⁺(18c6) determined by X-ray crystallography is shown in Figure 1b.¹⁰ The most intriguing structural feature of **2** in the crystal is that two triptycyl groups in a molecule occupy the apical positions and three fluorine atoms are in the equatorial plane of the almost ideal TBP structure; C–Si–C angle = 178.09(19)°; F–Si–F angles = 120.00(14)° (av); the sum of the F–Si–F angles = 360.00(14)°. The mean Si–F [1.644(3) Å] and Si–C bond lengths [2.006 (4) Å] of **2** are significantly longer than the corresponding lengths for **1** due to the hypercoordination.

Although R₂SiF₃ and R₃SiF₂ type pentacoordinate silicates are known to adopt a TBP structure with two electronegative fluorine atoms at the apical positions (Muetterties rule),⁵ the structure of **2** is not compatible with the rule. The reason would be ascribed to almost complete relief of the steric repulsion between two bulky 9-triptycyl substituents in the observed structures. To the best of our knowledge, silicate **2** is the first compound against the rule among pentacoordinate silicates without chelating ligands.^{6,11}

The above unusual TBP structure was found to be maintained also in solution. As expected by the pentacoordinate silicate nature, **2** shows the ²⁹Si NMR signal (−109.1 ppm) at much higher field with a larger ¹J_{Si–F} value (quartet, 398 Hz) than silane **1**, whose δ_{Si} and ¹J_{Si–F} are −2.75 and 329 Hz (triplet). ¹⁹F NMR spectra of silicate **2** show only one signal at −86.3 ppm at room temperature. As shown in a ¹H NMR spectrum (Figure 2b), no isomeric structures of **2** exist in solution.¹² These NMR analyses indicate that the two triptycyl groups of **2** are located at the apical positions of the TBP structure and rapidly rotating around Si–C bonds without correlation at room temperature.

All these results indicate that the meshed gear of silanes **1_{dl}** and **1_{meso}** is declutched by the introduction of a F[−] ion forming pentacoordinate silicate **2** with the two triptycyl groups at the apical position. Because silicate **2** is reverted to the corresponding silane mixture (**1_{dl}** + **1_{meso}**) by treating with excess water (eq 2),⁹ the present silane–silicate system constitutes a chemical clutch–declutch mechanism of the gear.

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Supporting Information Available: Details of the synthesis and NMR spectra of silane **1** and silicate **2**, molecular orbital calculations

for trifluorodi(9-triptycyl)silicates, and X-ray crystallographic data for **1** and **2** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) For the synthetic details of **1** and **2**, see the Supporting Information. A mixture of **1_{dl}** and **1_{meso}**: colorless crystals; mp 128–130 °C; ¹H NMR (400 MHz, CDCl₃, δ) 2.448 (s, 6H), 5.579 (s, 2H), 6.513 (t, *J* = 7.6 Hz, 2H, **1_{dl}**), 6.578 (t, *J* = 7.6 Hz, 2H, **1_{meso}**), 6.68–6.79 (m, 6H, **1_{dl}** and **1_{meso}**), 6.85–6.93 (m, 4H, **1_{dl}** and **1_{meso}**), 7.336 (d, *J* = 7.2 Hz, 4H, **1_{dl}** and **1_{meso}**), 7.690 (d, *J* = 7.6 Hz, 2H, **1_{dl}**), 7.745 (d, *J* = 7.6 Hz, 2H, **1_{meso}**), 7.878 (d, *J* = 7.6 Hz, 2H, **1_{dl}**), 7.935 (d, *J* = 7.6 Hz, 2H, **1_{meso}**); ¹³C NMR (100 MHz, CDCl₃, δ) 19.1, 51.5, 55.3 (t, ²J_{C–F} = 14 Hz), 124.1, 124.2, 124.7, 124.8, 125.1, 125.6, 126.9 (t, ³J_{C–F} = 4 Hz), 127.1 (t, ³J_{C–F} = 4 Hz), 127.4, 132.0, 143.3, 143.6, 144.2, 144.5, 145.1, 145.2, 146.9, 147.0; ²⁹Si NMR (59 MHz, CDCl₃, δ) −2.75 (t, ¹J_{Si–F} = 329 Hz); ¹⁹F NMR (282.41 MHz, CDCl₃, δ) −110.2; HRMS (EI) calcd for C₄₂H₃₀SiF₂, 600.2045 (M⁺); found, 600.2087 (M⁺). **2**·K⁺(18c6): colorless crystals; mp 233–234 °C (decomp.); ¹H NMR (400 MHz, acetone-*d*₆, δ) 2.530 (s, 6H), 3.522 (s, 24 H, 18c6), 5.661 (s, 2H), 6.701 (d, *J* = 7.2 Hz, 2H), 6.842 (t, *J* = 7.2 Hz, 4H), 6.862 (t, *J* = 7.2 Hz, 2H), 6.982 (t, *J* = 7.2 Hz, 4H), 7.332 (d, *J* = 7.2 Hz, 4H), 8.33 (brd, 2H), 8.47 (brd, 4H); ¹³C NMR (100 MHz, acetone-*d*₆, δ) 19.09, 53.12, 60.62 (q, ²J_{C–F} = 73 Hz), 71.06 (18c6), 123.53, 123.62, 123.92, 124.45, 125.26, 128.11, 130.06, 130.61, 149.45, 151.22, 154.45, 155.10; ²⁹Si NMR (79 MHz, acetone-*d*₆, δ) −109.1 (q, ¹J_{Si–F} = 398 Hz); ¹⁹F NMR (282 MHz, acetone-*d*₆, δ) −86.3; HRMS (ESI, negative) calcd for C₄₂H₃₀SiF₃, 619.2074 (M[−]); found, 619.2076 (M[−]); HRMS (ESI, positive) calcd for C₁₂H₂₄O₆K⁺, 303.1204 (K⁺·18c6); found, 303.1203 (K⁺·18c6).
- (8) Crystal data for **1**: C₄₂H₃₀F₂Si + C₆H₆; FW 678.86. At 100 K; monoclinic; space group Cc; *a* = 11.810(5) Å, *b* = 21.803(9) Å, *c* = 13.251(6) Å, β = 90.155(6)°, *V* = 3412(2) Å³, density (calculated) 1.322 Mg/m³, *Z* = 4, 470 parameters. Final *R* indices *R* = 0.044 [*I* > 2 σ (*I*)], *wR*2 = 0.1218 for all data, 5624 unique reflections.
- (9) See the Supporting Information for the details.
- (10) Crystal data for **2**·K⁺(18c6): C₄₂H₃₀F₃KSi + C₁₂H₂₄O₆ + 2(CH₂Cl₂); FW 1093.01, 90 K; orthorhombic; space group P2₁2₁2₁; *a* = 12.461(3) Å, *b* = 18.925(5) Å, *c* = 22.839(6) Å, *V* = 5386(2) Å³, density (calculated) 1.348 Mg/m³, *Z* = 4, 823 parameters. Final *R* indices *R*1 = 0.078 [*I* > 2 σ (*I*)], *wR*2 = 0.218 for all data, 12 234 unique reflections.
- (11) DFT calculations for trifluorodi(9-triptycyl)silicate at the B3LYP/B1 level (B1: Si and F for 6-31+G*, C and H for 3-21G (except for C–Si; 3-21+G)) using GAUSSIAN 03 program packages revealed that the optimized molecular structure is similar to that observed by X-ray crystallography: Frisch, M. J. et al. *Gaussian 03*, revision D.01. The unusual TBP structure is 3.9 kcal mol^{−1} more stable than a normal TBP structure having the two 9-triptycyl groups at the equatorial positions. See the Supporting Information for the details of theoretical calculations.
- (12) For example, two ¹⁹F resonances are observed at δ −100.5 (d, *J*_{F–F} = 2.58 Hz, 2F_{ap}) and δ −133.9 (t, *J*_{F–F} = 2.58 Hz, 1F_{eq}) for Ph₂SiF₃.^{3a}

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