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Kinetic Study of Interconversion between Two Geometrical Isomers of the Methoxy-Bridged Bis(silylene)iron Complex, $(\eta\text{-}C_5Me_5)(OC)Fe\{(SiMe_2)\cdots OMe\cdots(SiMeOMe)\}$

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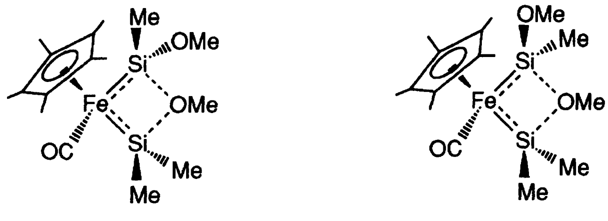
Isomerization between two geometrical isomers of the methoxy-bridged bis(silylene)iron complex, *anti*- and *syn*-$Cp^*(OC)Fe\{(SiMe_2)\cdots OMe\cdots(SiMeOMe)\}$ ($Cp^*=\eta^5$-C_5Me_5), was investigated by means of a variable-temperature ^1H NMR experiment. The equilibrium constant (K) for the isomerization and its thermodynamic parameters were determined to be $K=[syn\text{-isomer}]/[anti\text{-isomer}]=0.53$ at 293 K in toluene-d_8, $\Delta G^\circ_{298}=1.5\pm0.5$ kJ mol^{-1}, $\Delta H^\circ=3.8\pm0.2$ kJ mol^{-1}, and $\Delta S^\circ=7.7\pm1.0$ J mol^{-1} K^{-1}. Computer simulation of the VT spectra and calculation using Eyring equation yielded activation parameters, $\Delta H^\ddagger=83.8\pm3.2$ kJ mol^{-1}, $\Delta S^\ddagger=42.3\pm9.6$ J mol^{-1} K^{-1}, and $\Delta G^\ddagger_{298}=71.2\pm6.0$ kJ mol^{-1}, for the isomerization from the *anti*-isomer, in which the terminal OMe group is located on the opposite side of the Cp^* group with respect to the Fe–Si–O(bridged)–Si ring, to the *syn*-isomer. A mechanism in which the bridging OMe group is replaced by the terminal OMe group is proposed for the isomerization.

Study on the reactivity of the silylene complexes is important since the silylene complexes have been postulated as intermediates in a number of transition-metal-mediated processes of silicon compounds, namely Rochow's direct process,[1)] catalytic redistribution of silanes,[2)] various silylene-transfer reactions,[3)] and dehydrogenative silane couplings.[4)] The synthesis and isolation of the donor-stabilized[5—11)] and donor-free silylene complexes[12—15)] which have been recently achieved have made it possible to investigate the reactivities of the silylene complexes directly. One of the most basic reactions of the donor-stabilized silylene complexes is a donor-exchange reaction on the silylene ligand.[5b,6f,6h,9)] However, kinetic studies of the donor-exchange reactions on the silylene ligands are quite rare.[5b,6f,6h)]

We have reported the synthesis, structure, and properties of alkoxy-bridged bis(silylene)iron, manganese, and ruthenium complexes and an amino-bridged bis(silylene)iron complex.[7)] The donor-bridged bis(silylene)metal complexes are unique among the known base-stabilized silylene complexes since the two M–Si bonds of the bis(silylene)metal complexes take on partial double-bond character and the bridging donor-group stabilizes the bis(silylene) structure by coordination to the two electron-deficient silylene units. In the previous paper,[7a,7b)] we found that the methoxy-bridged bis(silylene)iron complex, $Cp^*(OC)Fe\{(SiMe_2)\cdots OMe\cdots(SiMeOMe)\}$ (**1**: $Cp^*=\eta^5$-C_5Me_5), exists as a mixture of two geometrical isomers, *anti*-isomer **1a** and *syn*-isomer **1b** (Chart 1), in a C_6D_6 solution and a rapid interconversion between **1a** and **1b** occurs in the solution. This paper describes the details of the kinetic study on the isomerization reaction of **1** by means of a variable-temperature ^1H NMR spectroscopy.



anti-isomer **1a**

syn-isomer **1b**

Chart 1.

Experimental

All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques or under high vacuum using vacuum line techniques. Toluene-d_8 was dried over a potassium mirror and distilled directly into the reaction vessel before use. Details of the preparation of $Cp^*Fe(CO)_2SiMe_2SiMe(OMe)_2$ and complex **1** were reported previously.[7a,7b)] Variable-temperature ^1H NMR spectra were recorded on a Bruker ARX-300 Fourier transform spectrometer.

Preparation of Methoxy-Bridged Bis(silylene)iron Complex 1 for NMR Measurements. A requisite amount of $Cp^*Fe(CO)_2SiMe_2SiMe(OMe)_2$ was placed in a Pyrex NMR sample tube (o.d. 5 mm, i.d. 3 mm) connected to a vacuum line. Toluene-d_8 was transferred into the sample tube using conventional trap-to-trap distillation. The sample tube was then flame-sealed under high vacuum. The sample was irradiated in a water-bath using a medium-pres-

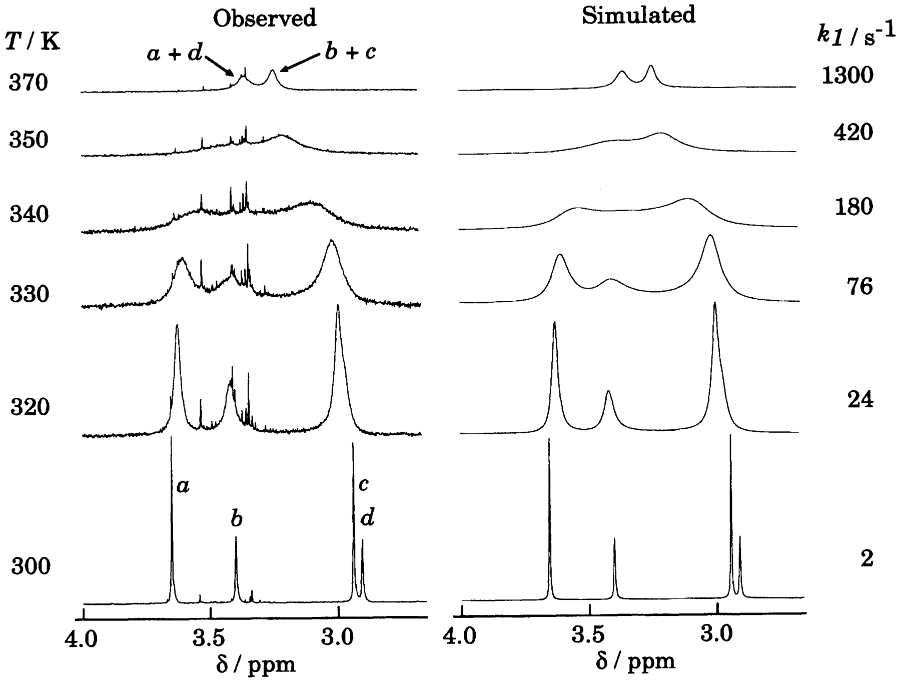


Fig. 1. Variable-temperature 300 MHz ^{1}H NMR line shapes of **1** at the methoxy region (2.7—4.0 ppm) measured in toluene-d_8: Experimental spectra (left); simulated spectra (right).

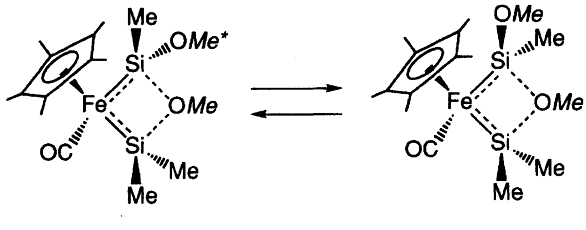
sure mercury lamp (Ushio UV-450) placed in a water-cooled quartz jacket. The course of the reaction was monitored periodically by ^{1}H NMR spectroscopy. Fifteen minutes of irradiation caused the complete conversion of the starting material into **1**.

Determination of Equilibrium Constant (K) for the *anti–syn* Isomerization Reaction. Proton NMR spectra of **1** were measured in 10 K increments from 210 to 290 K. The equilibrium constant K, where $K=$ [*syn*-isomer]/[*anti*-isomer], was determined from the ratio of the peak area of the methoxy signal of **1a** to that of **1b**. Thermodynamic parameters, ΔH° and ΔS°, for the isomerization reaction were obtained by applying a linear least-squares procedure to a plot of $\ln K$ vs. $1/T$.

Complete Lineshape Analysis. The lineshape analysis was performed for the spectra measured in 10 K increments from 300 to 370 K using the DNMR5 program.[16] The rate constants of the isomerization reaction were determined by least-squares curve fitting of the simulated spectra to the observed spectra. The activation parameters and the errors for the isomerization reaction were calculated from the Eyring equation using an unweighted linear least-squares procedure. The transmission coefficient in the Eyring equation was assumed to be unity. All calculations were performed on an Apple Macintosh personal computer.

Results and Discussion

The metoxy-bridged bis(silylene)iron complex **1** exists as an equilibrium mixture of two geometrical isomers in toluene-d_8. The molar ratio of the two isomers is approximately 2 : 1 at 300 K, and the major component is presumed to be *anti*-isomer **1a** which has less steric repulsion between the substituent of the asymmetric silicon atom and bulky Cp* ligand than *syn*-isomer **1b**.[7a,7b] Figure 1 (left) shows the variable-temperature 300 MHz ^{1}H NMR spectra at the methoxy group region (2.7—4.0 ppm) of the bis(silylene)iron complex **1**. At 300 K, **1** shows four singlet peaks at 3.65, 3.40, 2.95, and 2.92 ppm with 2 : 1 : 2 : 1 intensity, which are designated as *a*, *b*, *c*, and *d*, respectively. These four signals are assignable to the terminal methoxy groups of **1a** and **1b** and the bridging methoxy groups of **1a** and **1b**, respectively. As the temperature is raised, these resonances broaden, then coalesce, and finally become two singlet peaks with equal intensity at high temperature. The fact that these two signals appear at the weight averaged position of the signals *a* and *d* and that of the signals *b* and *c* clearly shows that exchange occurs between the terminal OMe group of **1a** and the bridging OMe group of **1b** and between the bridging OMe group of **1a** and the terminal OMe group of **1b** (Eq. 1).



1a **1b**

(1)

Spectral changes in the Si–Me region upon raising the temperature are rather complicated since accidental overlaps of signals happen on warming up the solution (Fig. 2). The ^{1}H NMR spectrum at 230 K exhibits three

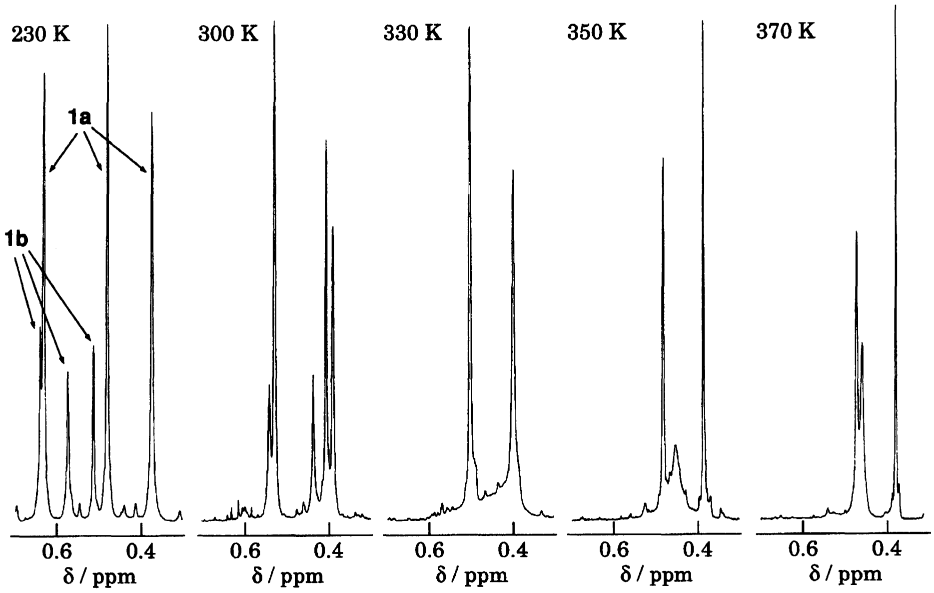
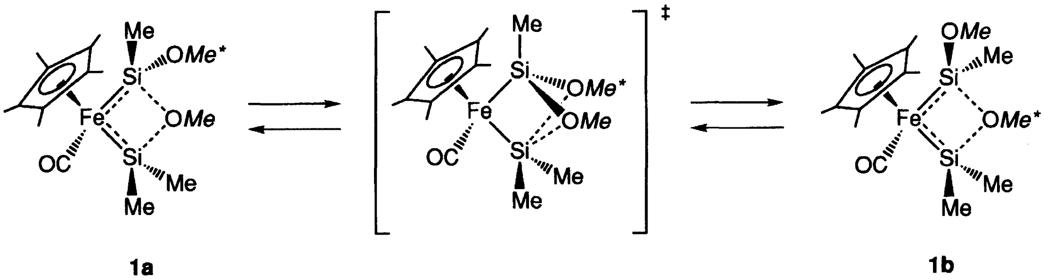


Fig. 2. Variable-temperature 300 MHz ^{1}H NMR spectra of **1** at the SiMe region (0.3—0.7 ppm) measured in toluene-d_8.



Scheme 1.

large signals at 0.63, 0.47, and 0.37 ppm and three small signals at 0.64, 0.57, and 0.51 ppm, which are assignable to the three SiMe groups of **1a** and those of **1b**, respectively. As temperature is raised, these resonances broaden, coalesce, and, at 370 K, become three singlet signals with equal intensity. This is consistent with the exchange scheme shown in Eq. 1 and indicates that intramolecular exchange of the Si–Me groups, such as rotation of $SiMe_2$ group or scrambling of methyl groups between two silicon atoms, does not occur during the isomerization.

Complete lineshape analysis was performed using methoxy signals to evaluate the rate constants for the isomerization reaction at the different temperatures (Fig. 1). Satisfactory simulation of the variable-temperature spectra (Fig. 1, right) was obtained using the exchange scheme shown in Eq. 1 and the rate constants k_1 given in Fig. 1 which correspond to the isomerization from **1a** to **1b**. The activation parameters were determined to be $\Delta H^{\ddagger}=83.8\pm3.2$ kJ mol^{-1}, $\Delta S^{\ddagger}=42.3\pm9.6$ J mol^{-1} K^{-1}, and $\Delta G^{\ddagger}_{298}=71.2\pm6.0$ kJ mol^{-1}.

The relatively small values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ indicate that the isomerization occurs through an intramolecular and concerted process. Thus, we propose the mechanism given in Scheme 1 for the isomerization of **1**: The terminal OMe group in **1a** bridges two silicon atoms from the opposite side of Cp* ligand with respect to the Fe–Si–O–Si four-membered ring to become the bridging OMe group in **1b** and simultaneously the bridging OMe group in **1a** changes to the terminal OMe group in **1b** (vice versa).

We have reported that the methoxy-bridged bis(germylene)- and germylene(silylene)iron complexes $Cp^*(OC)Fe\{(GeMe_2)\cdots OMe\cdots(EMe_2)\}$ (E = Ge, Si) show fluxional behavior due to germanium–oxygen bond cleavage and dimethylgermylene rotation around $Fe{=}GeMe_2$ bond in the complexes.[17)] However, for the methoxy-bridged bis(silylene)iron complexes[7a,7b)] and the germylene(silylene)iron complex,[17b)] no silylene rotation has been observed. Therefore, it is difficult to consider that the isomerization of **1** proceeds through a mechanism involving silylene rotation.

There have been two reports on the kinetic studies of the donor-exchange reactions in the donor-stabilized silylene complexes. Tilley et al. reported that the coordinated acetonitrile in $[Cp^*(Me_3P)_2Ru{=}SiPh_2{\cdot}NCMe](BPh_4)$ (**2**) exchanges with free acetonitrile (1 equiv) in CH_2Cl_2 via a dissociative mechanism with $\Delta H^{\ddagger}=59.74$ kJ mol^{-1}, $\Delta S^{\ddagger}=57.68$ J K^{-1} mol^{-1}, and $\Delta G^{\ddagger}_{298}=42.5$ kJ mol^{-1}.[5b)] Zybill et al. reported the intramolecular "flip-flop" coordination of two amino groups to the silicon atom in $(OC)_5Cr{=}Si[2\text{-}(Me_2NCH_2)C_6H_4]_2$ (**3**) ($\Delta G^{\ddagger}_{252}=54.4$ kJ mol^{-1}).$^{6f,6h)}$ The Gibbs energies of activation $\Delta G^{\ddagger}$ for these reactions are smaller than that for the donor-exchange process of **1**. This suggests that the bond between the bridging methoxy group and each silicon atom in **1** is much stronger than those between donors and the silylene ligands in **2** and **3**. This may be rationalized by considering that the bonds in **2** and **3** are weak and purely dative ones, but the Si···OMe(bridging) bonds in **1** are a hybrid of covalent and dative bonding.$^{7)}$

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