Fluxional Behavior of Alkoxy-Bridged Bis(silylene)ruthenium Complexes $Cp^*(Me_3P)Ru\{SiMe_2\cdots O(R)\cdots SiMe_2\}$ (R = Me, ^tBu) Caused by Rotation of the Silylene Ligands

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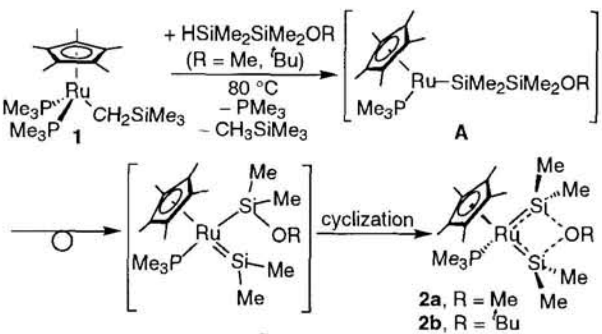
The exchange of Si-Me groups caused by silylene ligand rotation in alkoxy-bridged bis(silylene)complexes $Cp^*(Me_3P)Ru\{SiMe_2\cdots O(R)\cdots SiMe_2\}$ (R = Me, ^tBu) is observed by the variable temperature ^1H NMR (VT ^1H NMR) spectroscopy. This fluxionality is considered to be due to the weakened Si···O partial bonds caused by the strong electron-releasing effect of Cp* and PMe_3 ligands.

We have reported the syntheses[1] of various donor-bridged bis(silylene) complexes $L_nM\{SiMe_2\cdots Do\cdots SiMe_2\}$ (M = Fe, Mn, Ru, Ir, W; Do = OMe, O^tBu, NEt_2) as well as their germanium analogs for iron complexes.[2,3] Although a fluxional behavior caused by the rotation of the germylene ligand in alkoxy bridged bis(germylene)iron complex and germylene(silylene)iron complexes was observed in solution,[2,3] a similar behavior caused by the rotation of the silylene ligand in bis(silylene) complexes has not been observed except in the case of tungsten complexes.[1g] In this paper, we report the first observation of a fluxional behavior in alkoxy-bridged bis(silylene) complexes of a group 8 metal.

Alkoxy-bridged bis(silylene)ruthenium complexes $Cp^*(Me_3P)Ru\{SiMe_2\cdots O(R)\cdots SiMe_2\}$ (**2a**, R = Me; **2b**, R = ^tBu) were prepared by a method similar to that for $Cp(Ph_3P)Ru\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$.[1e] Heating a hexane solution of $Cp^*(Me_3P)_2RuCH_2SiMe_3$ (**1**)[4] and $HSiMe_2SiMe_2OR$ (R = Me, ^tBu[5]) at 80 °C overnight in a sealed tube followed by cooling the tube to -70 °C (R = Me) or -50 °C (R = ^tBu) gave alkoxy-bridged bis(silylene)ruthenium complexes **2a** and **2b** as air sensitive yellow crystals in 77% (**2a**) and 39% (**2b**) yields, respectively (Scheme 1).[6,7] In ^{29}Si NMR, doublets were observed at 108.4 ppm (**2a**, $^2J_{Si\text{-}P}$ = 30.5 Hz) and 119.0 ppm (**2b**, $^2J_{Si\text{-}P}$ = 28.7 Hz). Their chemical shifts are near or slightly downfield shifted compared to those reported for crystallographically determined bis(silylene)ruthenium complexes $CpLRu\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$ (108.7 ppm, doublet, $^2J_{Si\text{-}P}$ = 25.0 Hz, for L = PPh_3;[1e] 104.2 ppm for L = CO[1h]). These spectral data support the double bond character of Ru-Si bonds in **2a** and **2b**.

A possible formation mechanism for **2a,b** is given in Scheme 1. This mechanism is essentially the same as that for $Cp(Ph_3P)Ru\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$.[1e] The reaction is initiated by PMe_3 dissociation and following oxidative addition of $HSiMe_2SiMe_2OR$ at the Si-H bond and reductive elimination of CH_3SiMe_3 generate a coordinately unsaturated intermediate **A**. Finally, the 1,2-migration of the $SiMe_2OR$ group followed by cyclization gives complexes **2a,b**.

In the ^1H NMR of **2b**, two broad signals assignable to the Si-Me groups appeared at room temperature. In the VT ^1H NMR, the two signals sharpened at 263 K, but when the temperature was raised, they gradually broadened and coalesced at 307 K. In the ^1H NMR of **2a**, two SiMe signals did not appear so broad as those of **2b** at room temperature, but, on raising the temperature, a similar spectral change was observed and the signals coalesced at 335 K. Kinetic and thermodynamic parameters for the fluxional process were quantitatively evaluated by computer simulation[8] and visual fitting to the experimental spectra (Figure 1). This gave



Scheme 1.

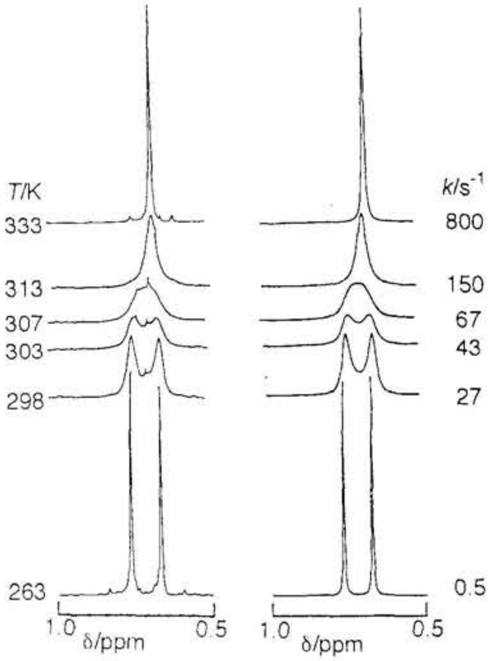
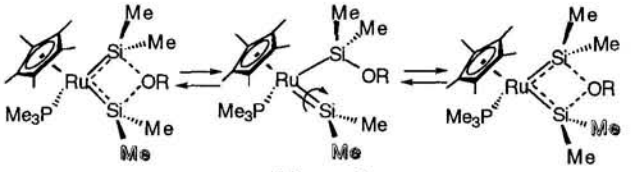


Figure 1. Experimental and computer simulated variable-temperature ^1H NMR spectra (300 MHz, toluene-d_8) and rate constants, k, in the Si-Me region of **2b**.

values of the exchange rate, k, for which Eyring plots (ln (k/T) vs $1/T$) afforded thermodynamic parameters, $\Delta H^{\ddagger} = 73.6 \pm 2.2$ kJ mol^{-1}, $\Delta S^{\ddagger} = 12.6 \pm 6.9$ J mol^{-1} K^{-1}, $\Delta G^{\ddagger}_{298} = 69.8 \pm 4.3$ kJ mol^{-1} for **2a**, and $\Delta H^{\ddagger} = 75.4 \pm 1.7$ kJ mol^{-1}, $\Delta S^{\ddagger} = 36.2 \pm 5.6$ J mol^{-1} K^{-1}, $\Delta G^{\ddagger}_{298} = 64.6 \pm 3.4$ kJ mol^{-1} for **2b**, respectively.

The exchange of Si-Me groups is considered to proceed via a mechanism shown in Scheme 2. It involves cleavage of a Si···O partial bond, followed by rotation of the resulting coordinated silylene moiety about the Ru=Si double bond to interchange the methyl group environments. This mechanism is essentially the same as those of the exchange of Ge-Me groups in Cp*(OC)Fe{GeMe$_2$···O(R)···EMe$_2$} (E = Si, Ge; R = Me, ^{t}Bu)[2,3] and Si-Me groups in Cp(OC)$_2$W{SiMe$_2$···Do···SiMe$_2$} (Do = OMe, NEt$_2$).[1g]



Scheme 2.

There is not a significant difference between the $\Delta H^{\ddagger}$ values of **2a** and **2b**, but the $\Delta S^{\ddagger}$ value of **2b** is slightly larger by 23.6 J mol^{-1} K^{-1} than that of **2a**. The trend in $\Delta S^{\ddagger}$ values resembles that of Cp*(OC)Fe{GeMe$_2$···O(R)···SiMe$_2$} (R = Me, 28.5 J mol^{-1} K^{-1}; R = ^{t}Bu, 117.7 J mol^{-1} K^{-1}),[3] and this can be understood by the interpretation that the greater degree of freedom is gained at the transition state with a bulkier alkoxy group.

Such a fluxionality was not observed in CpLRu{SiMe$_2$···O(Me)···SiMe$_2$} (L = PPh$_3$,CO)[1e,h] nor in the iron analogues.[1a,b,d] The difference may be caused by the electron-releasing ability of supporting ligands. Strongly electron-releasing PMe$_3$ and Cp* ligands in **2a,b** make the ruthenium center electron rich, and enhance the back donation to the σ^* orbital of Si···O partial bonds to weaken them. The electron-rich ruthenium center also lowers the activation energy by stabilizing the proposed transition state in Scheme 2, through back donation to the empty p-orbital of the silylene ligand. This explanation is similar to that of Cp(OC)$_2$W{SiMe$_2$···Do···SiMe$_2$} (Do = OMe, NEt$_2$) which contains an electron rich metal center.[1g,9]

These results clearly demonstrate that, in alkoxy-stabilized bis(silylene) complexes, the electron richness of the metal center adjusted by supporting ligands strongly influences the strength of Si···O partial bonds probably through back donation to the σ^* orbital of the bonds, which in turn determines the activation energy of the exchange of Si-Me groups.

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5 HSiMe$_2$SiMe$_2$O^{t}Bu was prepared by a similar method to that of HSiMe$_2$SiMe$_2$OMe described in Ref. 1g. The Et$_2$O solution of HSiMe$_2$SiMe$_2$NEt$_2$ and 4.1 equiv. of ^{t}BuOH was stirred at room temperature for 2 days and the solution was distilled to give HSiMe$_2$SiMe$_2$O^{t}Bu as a colorless liquid in 67% yield. Selected data for HSiMe$_2$SiMe$_2$O^{t}Bu: ^{1}H NMR (300 MHz, benzene-d_6) δ 0.18 (6H, d, $^3J_{\text{H-H}} = 4.5$ Hz, Si(H)Me), 0.30 (6H, s, Si(O^{t}Bu)Me), 1.20 (9H, s, O^{t}Bu), 3.97 (1H, septet, $^3J_{\text{H-H}} = 4.5$ Hz, Si(H)Me). ^{29}Si NMR (59.6 MHz, benzene-d_6) δ -41.2 (SiO^{t}Bu), 3.8 (SiH). Exact mass m/z Found: 175.0968. Calcd for $C_7H_{19}OSi_2$ (M$^+$-Me): 175.0974.

6 Selected data for **2a**: ^{1}H NMR (300 MHz, benzene-d_6) δ 0.39 (6H, s, SiMe), 0.52 (6H, s, SiMe), 1.34 (9H, d, $^2J_{\text{H-P}} = 7.5$ Hz, PMe$_3$), 1.96 (15H, d, $^3J_{\text{H-P}} = 1.2$ Hz, Cp*), 2.81 (9H, s, OMe). ^{31}P NMR (122 MHz, benzene-d_6) δ 10.3. Anal. Found: C, 47.37; H, 8.73%. Calcd for $C_{18}H_{39}OPRuSi_2$: C, 47.02; H, 8.57%.

7 Selected data for **2b**: ^{1}H NMR (300 MHz, toluene-d_8) δ 0.65 (6H, br, SiMe), 0.74 (6H, br, SiMe), 1.17 (9H, s, O^{t}Bu), 1.38 (9H, d, $^2J_{\text{H-P}} = 7.4$ Hz, PMe$_3$), 1.94 (15H, d, $^3J_{\text{H-P}} = 1.2$ Hz, Cp*). ^{31}P NMR (122 MHz, toluene-d_8) δ 13.5. Exact mass m/z Found: 502.1802. Calcd for $C_{21}H_{45}OPRuSi_2$ (M$^+$): 502.1791.

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