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Synthesis and Properties of a Silyl(silylene)ruthenium Complex: Activation Barrier of the Ru=Si Bond Rotation and Facile Replacement of the Methyl Groups with Alkoxy Groups of a Silyl Ligand

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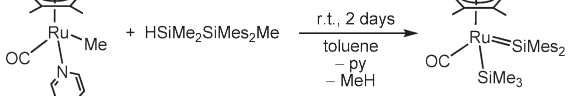
*Summary: A silyl(silylene)ruthenium complex, Cp*Ru(CO)(=SiMes$_2$)SiMe$_3$ (**2**), was synthesized by the reaction of Cp*Ru(CO)(py)Me with HSiMe$_2$SiMes$_2$Me (Mes = 2,4,6-trimethylphenyl). In contrast to its iron analogue Cp*Fe(CO)(=SiMes$_2$)SiMe$_3$ (**1**), which we reported previously, **2** exhibits a fluxional behavior that involves rotation around the Ru=Si and Si−C(mesityl) bonds. The activation parameters for the M=Si bond rotation were determined for the first time using line-shape analysis of the variable-temperature ^{1}H NMR spectra of **2**. Complex **2** underwent a facile alkoxylation reaction on the silyl ligand with ROH (R = Me or Et) in the presence of R′NC (R′ = ^{t}Bu or Xyl = 2,6-dimethylphenyl) to afford Cp*Ru(CO)(CNR′)[Si(OR)$_3$] and Mes$_2$Si(OR)H in high yields at room temperature, with cleavage of all three Si−C bonds.*

Transition-metal silyl(silylene) complexes have been postulated as important intermediates for the scrambling of substituents and dehydrogenative coupling of hydrosilanes.[1] Recently, several base-free silyl(silylene) complexes of Pt,[2] Pd,[2] W,[3a] Fe,[4] and Mo[3b] have been successfully isolated. Of these, the isolated Fe complex Cp*Fe(CO)(=SiMes$_2$)SiMe$_3$ (**1**, Mes = mesityl)[4] was employed as a probe to investigate the mechanisms of the above reactions. Specifically, the scrambling of substituents and Si−Si bond formation can be attributed to the 1,2- and 1,3-group migrations on the silyl(silylene) complex.[5] However, because **1** was found to be only weakly reactive toward external organic substrates, we focused our attention on the ruthenium analogue, Cp*Ru(CO)(=SiMes$_2$)SiMe$_3$ (**2**), which possesses a larger and a more electron-rich metal center. Accordingly, the behavior of **2** was noticeably different from that of **1**. First, the fluxional behavior involved rotations around the Ru=Si double and the Si−C(mesityl) single bonds; accordingly, line-shape analysis of the variable-temperature ^{1}H NMR spectra of **2** allowed for the first experimental evaluation of the activation parameters for the M=Si bond rotation. Second, **2** exhibited facile replacement of all alkyl groups by alkoxy groups on the silyl ligand, with cleavage of all three Si−C bonds at room temperature. Such a complete alkoxylation reaction on the silyl ligands under mild conditions is very rare.[6,7] As a representative example, Maitlis has reported the alkoxylation of all ethyl groups of one of the silyl ligands on Cp*RhH$_2$(SiEt$_3$)$_2$ with alcohol under photochemical conditions.[6] Herein, we report the synthesis and X-ray structural analysis of **2** along with details on its alkoxylation reaction.

The synthesis of **2** was based on the thermal synthetic methodology of **1**:[4b] Cp*Ru(CO)(py)Me (py = pyridine)[8] reacted with HSiMe$_2$SiMes$_2$Me at room temperature to afford **2** as yellow crystals, which were isolated in 75% yield (eq 1).



2

(1)

The ^{29}Si NMR spectrum of **2** exhibited signals at 346.8 ppm, of which the large downfield shift is characteristic of the silylene ligand,[9] and at 17.3 ppm, which corresponds to the

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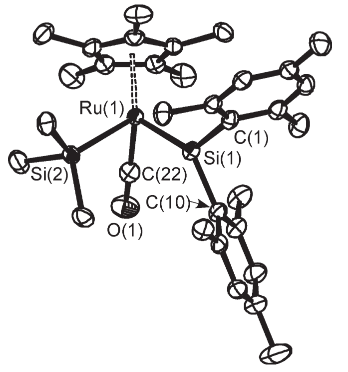


Figure 1. ORTEP drawing of **2** (50% thermal probability ellipsoids). Selected bond lengths (Å) and angles (deg): Ru(1)−Si(1) 2.2335(7), Ru(1)−Si(2) 2.4224(7), Ru(1)−C(22) 1.835(3), Si(1)−Ru(1)−Si(2) 93.85(2), C(1)−Si(1)−C(10) 105.43(12), C(1)−Si(1)−Ru(1) 125.76(8), Ru(1)−Si(1)−C(10) 127.89(9).

silyl ligand. The remaining spectroscopic data are also consistent with the structure of **2**.[10]

As shown in Figure 1, X-ray crystallographic studies[11] revealed that, except for the lengths of the M−Si bonds, the structural features of **2** were comparable to those of **1**. The Ru(1)−Si(1) bond length of 2.2335(7) Å was within the range of reported values for Ru=Si double bond lengths (2.22−2.34 Å),[12] while the Ru(1)−Si(2) bond length of 2.4224(7) Å was typical for a Ru−Si single bond. The difference between the M−Si bond lengths of **2** and **1**[4a] of about 0.08 Å corresponds almost exactly to the difference (0.09 Å) between the atomic radii of Ru (1.33 Å) and Fe (1.24 Å). In contrast to the Fe=Si bond of **1**, the longer Ru=Si bond of **2** allows for increased exposure to attacks by external molecules arising in its unique properties, as shown below.

As shown in Figure 2, the variable-temperature ^{1}H NMR spectroscopy (300 MHz) was employed to examine the fluxional behavior of **2**. At 298 K, the mesityl groups exhibited dissimilar signals for its four *o*-Me, four *m*-H, and two *p*-Me groups. At higher temperatures, the coalescence of each set of the *o*-Me, *p*-Me, and *m*-H signals into single signals verified the rotations of, within the NMR time scale, (1) the silylene unit around the Ru=Si double bond and (2) the two mesityl groups around the Si−C(mesityl) single bond.

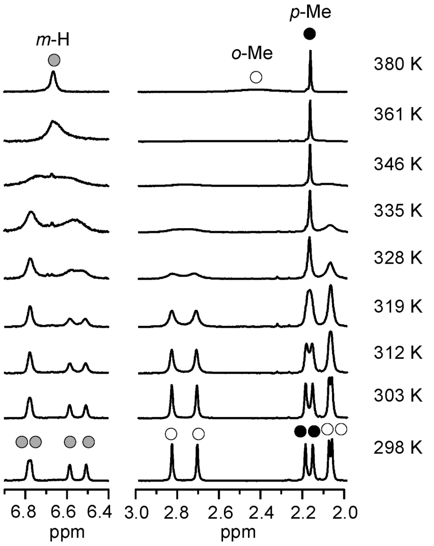
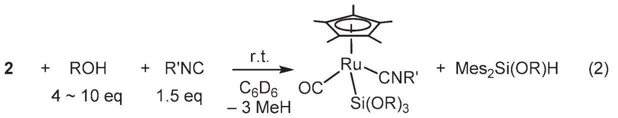


Figure 2. Variable-temperature ^{1}H NMR spectra of **2** in nonane-d_{20}.

Line-shape analysis of the *p*-Me signals in the variable-temperature ^{1}H NMR spectra of **2**[10] allowed for the determination of activation parameters for the Ru=Si bond rotation ($\Delta H^{\ddagger} = 64(3)$ kJ mol^{-1}, $\Delta S^{\ddagger} = -18(9)$ J K^{-1} mol^{-1}, and $\Delta G^{\ddagger}_{298} = 69(5)$ kJ mol^{-1}).[13] The negative value for $\Delta S^{\ddagger}$ implies that the transition state is more sterically congested than the ground state. Compared to the corresponding calculated activation barriers for (OC)$_5$Cr=SiH(OH) (0.46 kJ mol^{-1})[14a] and (OC)$_5$Mo=SiH$_2$ (1.5 kJ mol^{-1}),[14b] the significantly higher value of $\Delta H^{\ddagger}$ for **2** indicates the involvement of, besides the π-bonding energy for the Ru=Si bond, the energy required to overcome the steric repulsion between the mesityl groups and ligands on the ruthenium center. Several related complexes such as [Cp*(Me$_3$P)$_2$Ru=SiMe$_2$]$^+$,[15a] Cp*(dmpe)Mo=SiEt$_2$ (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$),[15b] and Cp*(Me$_3$Si)(OC)$_2$M=SiMes$_2$ (M = W,[3a] Mo[3b]) have also exhibited fast rotation around the M=Si bonds, within the NMR time scale, at room temperature, according to their NMR spectra; unfortunately, detailed analysis have yet to be reported. Furthermore, related kinetic studies for donor-stabilized bis(silylene) complexes have indicated that the M=Si bond rotation and the Si←O dative bond cleavage cannot be separated.[16]

Remarkably, the reaction of **2** with MeOH at room temperature, in the presence of isonitrile, ^{t}BuNC, or XylNC (Xyl = 2,6-dimethylphenyl), affords the trimethoxysilyl complex Cp*Ru(CO)(CNR′)[Si(OMe)$_3$] (**3a**: R′ = ^{t}Bu, **4a**: R′ = Xyl), together with Mes$_2$Si(OMe)H (**5a**) (eq 2). For these reactions, the isonitrile was added to trap the ruthenium species generated during the reaction. Similar results were also obtained with the use of EtOH instead of MeOH.



R = Me	R′ = ^{t}Bu	**3a** 88%	**5a** 80%
R = Et	R′ = ^{t}Bu	**3b** 99%	**5b** 94%
R = Me	R′ = Xyl	**4a** 65%	**5a** 88%
R = Et	R′ = Xyl	**4b** 87%	**5b** 87%

Attempts to purify **3** and **4** were unsuccessful, either by chromatography (facile decomposition on silica gel and

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[10] For the details, see Supporting Information.

[11] Crystal data (150 K) for **2**: C$_{32}$H$_{46}$OSi$_2$Ru; fw 603.94; monoclinic; $P2_1/c$; $a = 10.5565(3)$ Å, $b = 18.7387(7)$ Å, $c = 15.7809(6)$ Å, $\beta = 95.1401(13)°$, $V = 3109.2(2)$ Å^3, density (calcd) 1.290 Mg/m^3, $Z = 4$. Final *R* indices $R = 0.0420$, $R_w = 0.1004$ for all data, 6879 unique reflections. Crystallographic Information has been deposited with the Cambridge Crystallographic Data Centre: CCDC 698346 (**2**).

[12] Based on a survey of the Cambridge Structural Database, CSD verison 5.29 (November 2007).

[13] Rotation barrier for the two mesityl groups around the Si−C (mesityl) single bond could be derived from the analysis of the *o*-Me or *m*-H signals. However, unfortunately, sufficient line-shape analysis was not possible for the *o*-Me signals, because four *o*-Me signals coalesced around 361 K, but, above this temperature, the very broad signal did not become sharp enough for the analysis even at 380 K, which was the upper limit of temperature due to the boiling point of the solvent. For the *m*-H signals, we were not able to get good visual line fitting. It seems that the long-range couplings between the *m*-protons in the mesityl groups affect the line width, and we could not estimate it exactly, even though we tested various coupling constants.

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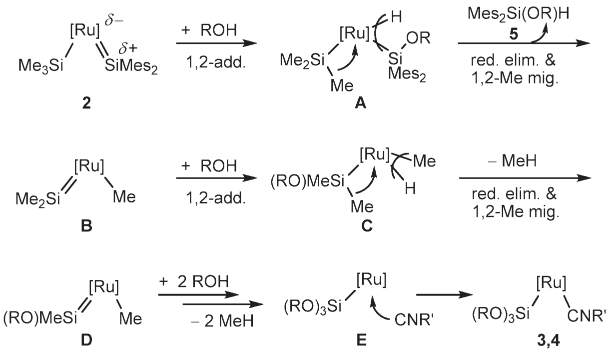
Scheme 1. Possible Mechanism for the Reaction of 2 with Alcohol



[Ru] = Cp*Ru(CO) R = Me, Et; R' = ^{t}Bu, Xyl

alumina) or by recrystallization (similar solubilities between **3** or **4** and **5**).[10] Nevertheless, existence of the $Si(OR)_3$ group, instead of the $SiMe_3$ group, was unambiguously confirmed using ^1H NMR and mass spectra of **3** and **4**.[10] The ^1H NMR spectrum of **4a** exhibited, in addition to the signals for Cp* and Xyl groups, a singlet at 3.65 ppm with an intensity of 9H that was assignable to the $Si(OMe)_3$ group. For reference, the ^1H NMR spectrum of $Cp^*Ru(CO)(CNXyl)SiMe_3$[10] exhibits a signal at 0.66 ppm for its $SiMe_3$ group. The molecular ion peak of **4a** appeared at $m/z = 517$, which is consistent with a structure that bears a $Si(OMe)_3$ group. The formation of **3** and **4** indicates that every Si−C bond on the $SiMe_3$ ligand was cleaved and functionalized at room temperature. In contrast, the Fe analogue of **2** simply produced $Cp^*Fe(CO)(CN^tBu)SiMe_3$ and **5a**.[10]

A possible mechanism for the substitution of the Me groups on the silyl ligand in **2** is shown in Scheme 1. Initially, 1,2-addition of the alcohol to the Ru═Si double bond affords **A**. Reductive elimination of $Mes_2Si(OR)H$ (**5**), followed by the 1,2-Me migration, gives methyl(silylene) complex **B**. Subsequently, addition of an alcohol to **B**, reductive elimination of methane, and 1,2-Me migration occur to produce **D**. The process from **B** to **D** repeats twice to give **E**. Finally, the coordination of isonitrile affords **3** or **4**. It is important to note that, for this reaction, partially alkoxylated products were not observed. Moreover, in a separate experiment, $Cp^*Ru(CO)(CNXyl)(SiMe_3)$, which could act as an intermediate for the reaction, was found to be unreactive toward excess methanol, even at 80 °C.[10] These results indicate that isonitrile does not coordinate to the metal center until the end of the multistep conversion of **A** to **E**.

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Supporting Information Available: Experimental details (PDF) and X-ray crystallographic data of **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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