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# Extremely Facile Arene Exchange on a Ruthenium(II) Complex Having a Novel Bis(silyl) Chelate Ligand (9,9-Dimethylxanthene-4,5-diyl)bis(dimethylsilyl) (Xantsil)

Hiromi Tobita,*,†,‡ Kenji Hasegawa,† Jim Josephus Gabrillo Minglana,†
Lung-Shiang Luh,§ Masaaki Okazaki,† and Hiroshi Ogino*,†

*Department of Chemistry, Graduate School of Science, Tohoku University,
Sendai 980-8578, Japan, and Coordination Chemistry Laboratories, Institute for Molecular
Science, Myodaiji, Okazaki 444-8585, Japan*

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*Summary: Thermolysis of $Ru_3(CO)_{12}$ in the presence of 4,5-bis(dimethylsilyl)-9,9-dimethylxanthene (xantsil$H_2$) (**1**) at 120 °C afforded cis-$Ru(CO)_4$(xantsil) [**2**; xantsil = (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl)] as a main product. Isolated **2** reacted with toluene on reflux to give cis-Ru(CO)(xantsil)($\eta^6$-$C_6H_5CH_3$) (**3**). The $\eta^6$-toluene ligand of **3** was cleanly replaced with $\eta^6$-benzene at room temperature by simply dissolving **3** in benzene.*

Studies on the chemical reactions of silyl transition metal complexes mostly focused on the reactivities of the Si−metal bonds and only little attention was paid to the ability of silyl ligands as supporting ligands.[1] Taking account of its strongly electron-releasing ability[2] and exceptionally high trans influence,[3] the silyl ligand could also work as an excellent supporting ligand, which might result in a new type of electron-rich metal center. However, because of the relatively high reactivity of the Si−metal bond, there were only few cases where a simple silyl ligand remains intact.[4] Chelate formation often stabilizes the complex, and a series of (phosphinoalkyl)silyl ligands were demonstrated to work as supporting ligands and enable reactivity studies on their complexes.[5] In contrast, reactions of complexes with bis(silyl) chelate ligands were scarcely investigated perhaps because they are less stable.[6] Recently, van Leeuwen et al. developed several diphosphine ligands having xanthene-like backbones and demonstrated their excellent effect on metal-catalyzed reactions based on their rigidity and large bite angle.[7] We applied this rigid backbone, aiming at stabilizing bis(silyl) chelate complexes. In this paper, we report the synthesis of some ruthenium(II) complexes containing a new rigid bis(silyl) chelate ligand, “xantsil”, and the extremely facilitated arene exchange at the Ru(II) center perhaps induced by the strong electron-releasing effect of the two *cis*-silyl groups in xantsil.

The precursor of the title chelate ligand xantsil$H_2$ (**1**) was prepared as colorless crystals in 89% yield by

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† Tohoku University.

‡ Institute of Molecular Science.

§ Present address: Institute of Chemistry, Academia Sinica, Taipei, 11529 Taiwan, ROC.

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(8) When 1 molar equiv of $Ru_3(CO)_{12}$ against **1** was used, **1** disappeared within 10 min and the yield of **2** estimated from the $^1H$ NMR spectrum was 71%. However, it was difficult to remove $Ru_3(CO)_{12}$ and an unidentified red crystalline byproduct from crude **2** by flash chromatography and recrystallization without losing a large amount of **2**.

(9) Crystal data for **2**: monoclinic, space group, $P2_1/n$, $a = 12.372(5)$ Å, $b = 10.10(1)$ Å, $c = 19.524(5)$ Å, $\beta = 93.20(3)°$, $V = 2436(2)$ Å$^3$, $Z = 4$. Data collection: Mo K$\alpha$, 20 °C, $2\theta = 3-55°$, 3112 independent reflections having $|I_o| > 3\sigma(I_o)$. Final $R = 0.042$, $R_w = 0.070$. Crystal data for **3**: monoclinic, space group, $P2_1/n$, $a = 9.565(8)$ Å, $b = 14.535(9)$ Å, $c = 18.479(6)$ Å, $\beta = 92.26(4)°$, $V = 2567(2)$ Å$^3$, $Z = 4$. Data collection: Mo K$\alpha$, 20 °C, $2\theta = 3-55°$, 3672 independent reflections having $|I_o| > 3\sigma(I_o)$. Final $R = 0.038$, $R_w = 0.065$. The structure was solved by the direct method (SIR92) and refined by full-matrix least-squares using the crystal structure analysis package teXsan on a Silicon Graphics Indy computer. Positions of non-hydrogen atoms were refined anisotropically.

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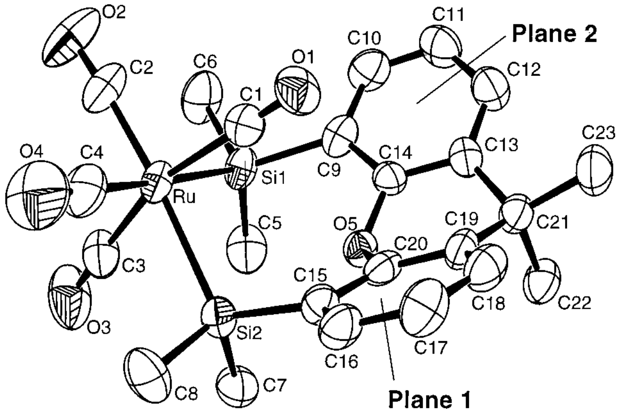
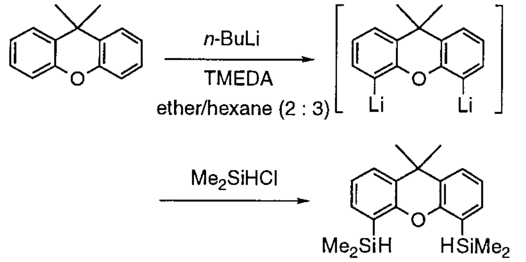


**Figure 1.** ORTEP view of **2**. Selected bond distances (Å) and angles (deg): Ru–Si1, 2.562(2); Ru–Si2, 2.564(2); Ru–C1, 1.963(6); Ru–C2, 1.968(7); Ru–C3, 1.910(6); Ru–C4, 1.966(7); Si1–Ru–Si2, 95.26(6); C1–Ru–C3, 162.8(2); Ru–C1–O1, 179.6(5).

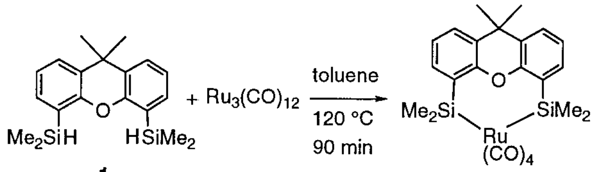
selective dilithiation at the 4,5-positions of 9,9-dimethylxanthene[7a] with 2 equiv of *n*-BuLi/TMEDA followed by reaction with chlorodimethylsilane (eq 1).



(1)

**1**

Heating a solution of **1** and 0.4 molar equiv of $Ru_3(CO)_{12}$ in toluene to 120 °C for 90 min provided *cis*-$Ru(CO)_4$(xantsil) (**2**) as a main product, which was isolated as colorless crystals in 35% yield (eq 2).[8]



(2)

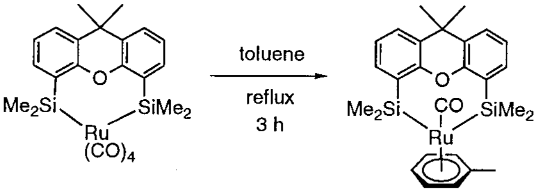
**1** **2**

The structure of **2** was unambiguously determined by the X-ray crystal structure analysis (Figure 1).[9] The two mutually cis silyl groups and four carbonyl ligands adopt a distorted octahedral arrangement around the ruthenium atom. The Si–Ru–Si angle (95.26(6)°) is slightly widened from 90° by formation of the eight-membered chelate ring. The dimethylxanthene moiety is strongly bent, and the dihedral angle between the least-squares planes of two aromatic rings in xantsil (planes 1 and 2) is 43.26°. This bending is attributed to the flexibility of the xanthene ring system and may be caused not only by the relatively narrow Si–Ru–Si angle but also by the steric repulsion between the dimethylxanthene moiety and a carbonyl ligand with C1 and O1: The interatomic distance between C1 and O5 (3.176(7) Å) is comparable to the sum of the van der Waals radii of carbon and oxygen atoms (3.1 Å).

The most characteristic feature of the structure of **2** is the extremely long Ru–Si bonds. The bond lengths of Ru–Si1 (2.562(2) Å) and Ru–Si2 (2.564(2) Å) represent the longest such bonds reported in the Cambridge Data Base, where the lengths of Ru–Si single bonds range from 2.338 to 2.507 Å. This lengthening can be attributed to the special steric requirement of xantsil ligand: Rigid xantsil ligand fixes two methyl groups, C5 and C7, at an extremely short interatomic distance (3.49(1) Å) compared to the sum of the van der Waals radii of two methyl groups (4.0 Å). The steric repulsion between them forces the other two methyl groups, C6 and C8, to move toward the carbonyl ligands C2O2 and C4O4. The observed interatomic distances for C2···C6 and C4···C8 are 3.09(1) and 3.11(1) Å, respectively. As a result of the repulsion between these atoms, the Ru–Si bonds are significantly stretched.

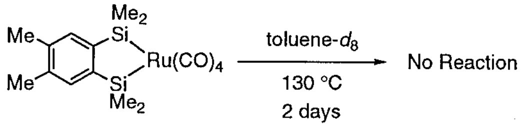
The variable-temperature NMR study on the $CD_2Cl_2$ solution of **2** clearly indicates the existence of fluxional behavior. At 210 K, each of the Si–Me and 9-Me groups on xantsil shows two signals, which is consistent with the X-ray crystal structure. On warming, each of them coalesces and finally becomes a sharp singlet at room temperature. From the data for the exchange of 9-Me groups [$\Delta\nu$ (at 210 K) = 139 Hz, $T_c$ = 240 K], the barrier at 240 K was calculated by the coalescence point method to be $\Delta G^{\ddagger}_{240}$ = 47 kJ mol$^{-1}$. A likely process is the inversion of the puckered chelate ring.

To estimate the effect of xantsil on displacement of CO ligands, **2** was heated in boiling toluene for 3 h. It resulted in replacement of three CO ligands by a $\eta^6$-toluene ligand to afford **3** in 95% yield (eq 3). In comparison with the analogous replacement reaction of $Ru(CO)_4(SiCl_3)_2$ with benzene which occurs at 80 °C,[10] **2** requires more forced conditions, probably because xantsil is more electron-releasing than $SiCl_3$ and, therefore, strengthens the Ru–CO bonds by stronger back-donation.[11] On the other hand, complex **4**,[12] which is electronically closely similar to **2**, did not undergo an analogous replacement of COs at all in toluene-$d_8$ at 130 °C for 2 days (eq 4). This result implies that the steric effect of the eight-membered chelate ring in **2**, perhaps



(3)

**2** **3**



(4)

**4**

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(10) $Ru(CO)_4(SiCl_3)_2$ is known to undergo cis–trans isomerization at 80 °C (trans:cis = 65:35 at 84.6 °C in Decalin), and the cis form is suggested to react with benzene: Pomeroy, R. K.; Graham, W. A. G. *Can. J. Chem.* **1975**, *53*, 2985.

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(12) Complex **4** was prepared by applying Fink's procedure described in the following paper: Fink, W. *Helv. Chim. Acta* **1976**, *59*, 606.

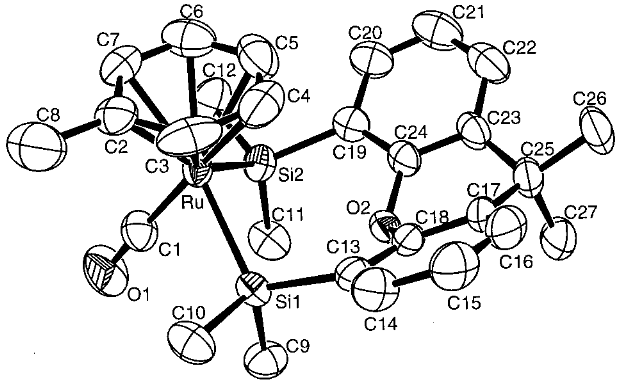
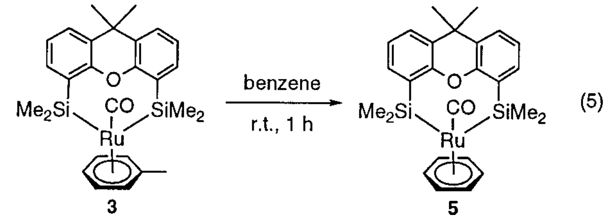


**Figure 2.** ORTEP view of **3**. Selected bond distances (Å) and angles (deg): Ru−Si1, 2.421(1); Ru−Si2, 2.421(2); Ru−C1, 1.818(5); Ru−C2, 2.328(5); Ru−C3, 2.288(5); Ru−C4, 2.288(5); Ru−C5, 2.320(6); Ru−C6, 2.332(6); Ru−C7, 2.312(5); Si1−Ru−Si2, 94.83(6)°; Ru−C1−O1, 177.8(5).

by stabilization of a five-coordinate intermediate with a wider Si−Ru−Si angle, or the existence of a possibly coordinative oxygen atom in a xanthene ring may play an important role in facilitating the displacement of CO ligands. A xanthene-based diphosphine ligand has been reported to work as a tridentate ligand toward palladium.[7e]

The coordinated toluene shows its $^1$H NMR signals of aromatic protons at $\delta$ 3.79 (1H, t), 4.54 (2H, t), and 4.87 (2H, d) ppm. Only an IR band assigned to $\nu_{CO}$ appears at 1913 cm$^{-1}$. The molecular structure of **3** is shown in Figure 2.[9] While the Si−Ru−Si angle (94.83(6)°) and the dihedral angle between the least-squares planes of two aromatic rings in xantsil (45.77°) are similar to the values of **2**, the Ru−Si bonds exhibit remarkable shortening from those of **2**. The average Ru−Si bond length for **3** (2.421 Å) is well in the normal range of Ru−Si single bonds (vide supra). This is apparently due to the much smaller steric repulsion of the xantsil ligand toward the $\eta^6$-toluene ligand in **3** compared to that toward a combination of three facial CO ligands in **2**.

An interesting reaction of complex **3** is the extremely facile exchange of the $\eta^6$-toluene ligand for a free arene: When the crystals of **3** were dissolved in $C_6D_6$, the NMR signals of **3** weakened gradually and disappeared after about 1 h at room temperature. The reaction of **3** with $C_6H_6$ at room temperature afforded the benzene complex **5** in 100% yield (eq 5).[13] The $^1$H NMR spectrum of **5** closely resembles that of **3** except for the region of coordinated arene ring protons, where **5** shows a singlet at $\delta$ 4.49 ppm for $\eta^6$-benzene.



(5)

The arene exchange has been mechanistically investigated for the complexes of group 6[14,15] and group 9[14,16] elements and ruthenium.[14,17] Several possible mechanisms have been proposed, although none of them appear to be conclusive. The arene exchange that occurs at room temperature is rare.[16,18] Complex **3** represents the first example of a ruthenium complex that undergoes the arene exchange at room temperature, probably due to the coordination of the oxygen atom in xantsil in the intermediate and/or the trans effect of the strongly electron-releasing xantsil ligand which labilizes $\sigma$- and $\pi$-basic aromatic ligands. This also implies that **3** and **5** may be useful as precursors which supply a new electron-rich, coordinatively unsaturated fragment "Ru(CO)(xantsil)" at room temperature. Taking these advantages of **3** and **5**, the arene exchange mechanism and the reactivity of these complexes with various small molecules are now under investigation.

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**Supporting Information Available:** Experimental details and spectroscopic data for compounds **1**−**3** and **5** and crystallographic data for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] We also tentatively observed the clean exchange of $\eta^6$-toluene ligand in **3** for *p*-xylene, mesitylene, anisole, and 4,4′-bitolyl ligands.

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