Synthesis, structure, and reactivity of hydridobis(silylene)ruthenium(IV)–xantsil complexes (xantsil = (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl)) — A stabilized form of key intermediates in the catalytic oligomerization–deoligomerization of hydrosilanes[1]

Masaaki Okazaki, Jim Josephus Gabrillo Minglana, Nobukazu Yamahira, Hiromi Tobita, and Hiroshi Ogino

Abstract: Ru{κ^2(Si,Si)-xantsil}(CO)(η^6-$C_6H_5CH_3$) (**1**) was found to be a catalyst for oligomerization–deoligomerization of $HSiMe_2SiMe_3$ to give $H(SiMe_2)_nMe$ (n = 1–8 at 90 °C for 2 days). Treatment of **1** with $HSiMe_2SiMe_2OR$ (R = Me, t-Bu) led to quantitative formation of Ru{κ^3(O,Si,Si)-xantsil}(CO)(H){($SiMe_2$•••O(R)•••$SiMe_2$)} (R = Me (**2a**), t-Bu (**2b**)), which also worked as a catalyst for oligomerization–deoligomerization of $HSiMe_2SiMe_3$. Based on these experimental results, a mechanism involving silyl(silylene) intermediates was proposed for the oligomerization–deoligomerization of $HSiMe_2SiMe_3$. Complex **2a** reacted with MeOH in toluene-d_8 to give Ru{κ^2(Si,Si)-xantsil}(CO)(η^6-toluene-d_8) and $Me_2Si(OMe)_2$ with evolution of H_2. Under a CO atmosphere, **2a** was smoothly converted to its CO adduct Ru{κ^2(Si,Si)-xantsil}$(CO)_2$(H){($SiMe_2$•••O(Me)•••$SiMe_2$)} (**3**).

Key words: silylene complex, ruthenium, polysilane, dehydrogenative coupling, oligomerization.

Résumé : On a observé que le Ru{κ^2(Si,Si)-xantsil}(CO)(η^6-$C_6H_5CH_3$) (**1**) est un catalyseur pour l'oligomérisation–désoligomérisation du $HSiMe_2SiMe_3$ conduisant à la formation de $H(SiMe_2)_nMe$ (n = 1–8, à 90 °C pour deux jours). Le traitement du composé **1** avec du $HSiMe_2SiMe_2OR$ (R = Me, t-Bu) conduit à la formation quantitative du Ru{κ^3(O,Si,Si)-xantsil}(CO)(H){($SiMe_2$•••O(R)•••$SiMe_2$)} (R = Me (**2a**), t-Bu (**2b**)) qui peut aussi être utilisé comme catalyseur pour l'oligomérisation–désoligomérisation du $HSiMe_2SiMe_3$. Sur la base de ces résultats expérimentaux, on propose un mécanisme impliquant des intermédiaires silyl(silylènes) pour l'oligomérisation–désoligomérisation du $HSiMe_2SiMe_3$. Le complexe **2a** réagit avec le MeOH dans le toluène-d_8 pour donner du Ru{κ^2(Si,Si)-xantsil}(CO)(η^6-toluène-d_8) et du $Me_2Si(OMe)_2$ avec évolution de H_2. Sous atmosphère de CO, le composé **2a** est facilement transformé en un adduit avec du CO, Ru{κ^2(Si,Si)-xantsil}$(CO)_2$(H){($SiMe_2$•••O(R)•••$SiMe_2$)} (**3**).

Mots clés : complexe de silylène, ruthénium, polysilane, couplage déshydrogénant, oligomérisation.

[Traduit par la Rédaction]

Introduction

The chemistry of transition-metal silyl complexes is a continuously growing field and an area of active research over the past few decades (1). They have been found as key intermediates in the metal-mediated catalytic transformation reactions of organosilicon compounds (1, 2). However, studies on silyl complexes have mostly focused on the reactivity of the metal–silicon bonds which participate in the catalytic pathways (3) and only little attention has been paid to the possibility of silyl groups as ancillary ligands. Taking account of its strongly electron-releasing ability and exceptionally high trans influence (4), the silyl groups could work as an excellent ancillary ligand that generates an electron-rich and coordinatively unsaturated metal center (5, 6). Usual metal–silicon bonds are, however, highly reactive, and the

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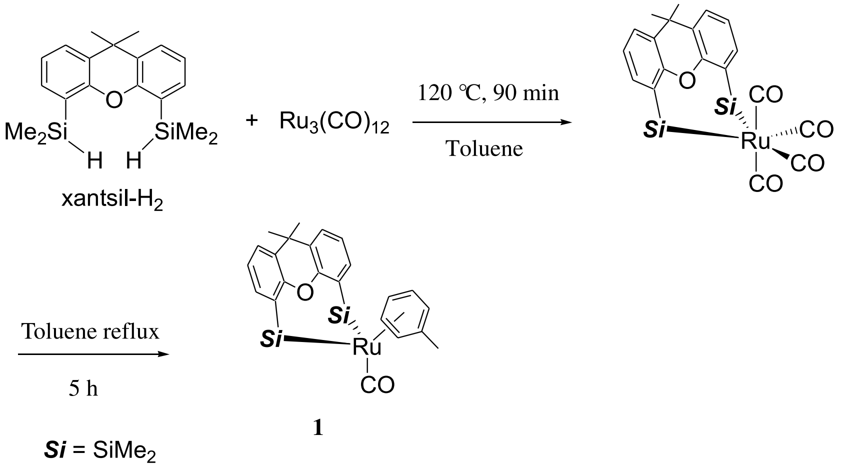
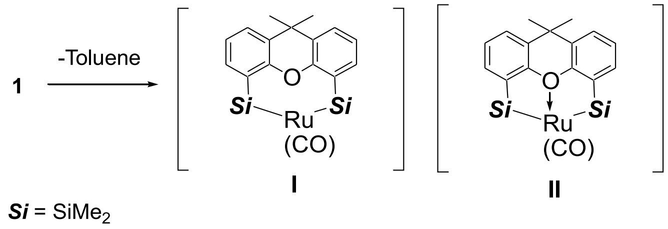
Scheme 1.



rich chemistry of transition-metal silyl complexes is derived from this reactivity (1). In most cases, the silyl ligands are lost from the metals as a result of reductive elimination, migratory insertion, nucleophilic substitution, and so on. To avoid this drawback of silyl ligands, we designed a new type of bis(silyl) bidentate ligand “xantsil” (7). Thermolysis of $Ru_3(CO)_{12}$ and 4,5-bis(dimethylsilyl)-9,9-dimethylxanthene (xantsil-H_2) at 120 °C afforded Ru{κ^2(*Si*,*Si*)-xantsil}$(CO)_4$ in which three carbonyl ligands can be further replaced with a η^6-toluene ligand on reflux in toluene to give Ru{κ^2(*Si*,*Si*)-xantsil}(CO)(η^6-$C_6H_5CH_3$) (**1**) (Scheme 1). Complex **1** undergoes an extremely facile exchange of the toluene ligand for a free arene, indicating that **1** can formally become a source of either 12- or 14-electron, coordinatively unsaturated species (**I** or **II**), depending on the coordination mode of the xantsil ligand (Scheme 2). We report here the catalytic performance of **1** toward oligomerization–deoligomerization of $HSiMe_2SiMe_3$ to give $H(SiMe_2)_nMe$ (n = 1–8). We also describe the isolation and reactivity of the stabilized form of a silyl(silylene) complex, which can be considered as a key intermediate in the catalytic reaction. A part of this work has been communicated previously (7*b*).

Scheme 2.



Experimental section

General methods

Infrared spectra were obtained on a Horiba FT-730 spectrometer. NMR spectra were recorded on Bruker ARX-300 and AVANCE-300 instruments. Mass spectra were obtained on JEOL-HX110 and Hitachi M-2500S instruments operating in the EI mode. All reactions were performed under a dry nitrogen atmosphere using deoxygenated solvents dried with appropriate reagents. The organosilicon compounds *p*-Tol_2SiH_2 (8), $HSiMe_2SiMe_3$ (9), and $HSiMe_2SiMe_2OR$ (R = Me (10), *t*-Bu (11)) were synthesized according to published procedures. The complex **1** was synthesized by a procedure we previously reported (7*a*).

Reaction of 1 with *p*-Tol_2SiH_2

A Pyrex NMR tube (5 mm o.d.) was charged with **1** (5.0 mg, 0.00916 mmol) and was then attached to a vacuum line. *p*-Tol_2SiH_2 (19.5 mg, 0.00916 mmol) and chloroform-*d* (0.4 mL) were trap-to-trap transferred into it. The NMR tube was flame-sealed and the reaction was monitored by ^1H NMR spectroscopy. The sample was heated at 60 °C for 3 h and a red solution was obtained. The ^1H NMR spectral data showed that **1** was completely consumed and free toluene and xantsil-H_2 were formed as the major products. Unidentified signals can also be observed but their signals are of low intensities.

Oligomerization–deoligomerization of $HSiMe_2SiMe_3$ in the presence of 1

(a) NMR scale monitoring of the reaction

A Pyrex NMR tube (5 mm o.d.) was charged with **1** (13.4 mg, 0.0246 mmol) and was then attached to a vacuum line. $HSiMe_2SiMe_3$ (65.0 mg, 0.492 mmol) and dichloromethane-d_2 (800 μL) were trap-to-trap transferred into it. The NMR tube was flame-sealed and the reaction was monitored by ^1H NMR spectroscopy. At room temperature, the solution turned yellow in color and several signals corresponding to oligomerization–deoligomerization products $H(SiMe_2)_nMe$ appeared. No further changes were observed after 40 h at room temperature.

(b) GC and GC–MS monitoring of the reaction with a catalytic amount of 1

$HSiMe_2SiMe_3$ (65.0 mg, 0.49 mmol), *n*-decane (10.0 μL as an internal standard), and **1** (270 μg, 0.1 mol%) were placed in a 5 mL flask and the solution was stirred at room temperature for 2 days. The reaction was monitored by gas chromatography. Formation of $H(SiMe_2)_nMe$ in the molar ratio of 81 (n = 1) : 56 (n = 2) : 11 (n = 3) : 3 (n = 4) : 1 (n = 5) was observed based on the peak areas of the gas chromatogram. The products were confirmed by GC–MS.

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When the same reaction was performed at 90 °C for 2 days, formation of products with *n* of up to 8 were observed in the molar ratio of 346 (*n* = 1) : 96 (*n* = 2) : 83 (*n* = 3) : 64 (*n* = 4) : 35 (*n* = 5) : 13 (*n* = 6) : 4 (*n* = 7) : 1 (*n* = 8). These silicon-containing products were not isolated.

Synthesis of Ru{κ^3(*O,Si,Si*)-xantsil}(CO)(H){(SiMe$_2$•••O(Me)•••SiMe$_2$)} (2a)

$HSiMe_2SiMe_2OMe$ (81.0 mg, 0.546 mmol) was added to a solution of **1** (150 mg, 0.275 mmol) in CH_2Cl_2 (2.0 mL). After 90 min of stirring at room temperature, volatiles were removed under reduced pressure to give a pale yellow solid. Washing the solid with hexane three times afforded a colorless solid that was characterized as Ru{κ^3(*O,Si,Si*)-xantsil}(CO)(H){(SiMe$_2$•••O(Me)•••SiMe$_2$)} (**2a**). Yield: 160 mg, 98%. MS (EI, 70 eV) *m/z*: 602 (M^+, 72), 512 (M^+ – HMe_2SiOMe, 79), 480 (100). Anal. calcd. for $C_{25}H_{40}RuO_3Si_4$: C 49.88, H 6.70; found: C 49.79, H 6.67.

Synthesis of Ru{κ^3(*O,Si,Si*)-xantsil}(CO)(H){(SiMe$_2$•••O(*t*-Bu)•••SiMe$_2$)} (2b)

$HSiMe_2SiMe_2O$-*t*-Bu (35.0 mg, 0.184 mmol) was added to a solution of **1** (50.0 mg, 0.0916 mmol) in CH_2Cl_2 (1.0 mL). After 90 min of stirring at room temperature, the reaction mixture was treated similarly as described for the synthesis of **2a** to afford **2b** as a colorless solid. Yield: 50.0 mg, 84%. MS (EI, 70 eV) *m/z*: 587 (M^+ – *t*-Bu, 26), 513 (M^+ – *t*-Bu-$SiMe_2O$, 41), 325 (100). Anal. calcd. for $C_{28}H_{46}RuO_3Si_4$: C 52.21, H 7.20; found: C 51.71, H 7.16.

Oligomerization–deoligomerization of $HSiMe_2SiMe_3$ in the presence of 2a

A Pyrex tube (7 mm o.d.) was charged with **2a** (10 mg, 0.017 mmol), $HSiMe_2SiMe_3$ (44 mg, 0.33 mmol), and decane (10 μL) and was connected to the vacuum line. The tube was flame-sealed under vacuum and placed in the oil bath at 90 °C. After heating for 2 days, the tube was unsealed in the glovebox. Formation of $H(SiMe_2)_nMe$ with the molar ratio of 12 (*n* = 1) : 6 (*n* = 2) : 5 (*n* = 3) : 5 (*n* = 4) : 4 (*n* = 5) : 2 (*n* = 6) : 3 (*n* = 7) : 1 (*n* = 8) was observed based on the peak areas of the gas chromatogram. These organosilicon compounds were not isolated.

Reaction of 2a with MeOH in toluene-d_8

A Pyrex NMR tube (5 mm o.d.) was charged with **2a** (5.0 mg, 0.0083 mmol) and was then attached to a vacuum line. Toluene-d_8 (0.4 mL) and MeOH (6.7 mL, 0.17 mmol) were trap-to-trap transferred into it. The NMR tube was flame-sealed and the reaction was monitored by ^1H and ^{29}Si NMR spectroscopy. Within 1 h at room temperature, the signals of **2a** were cleanly replaced by those of Ru{κ^2(*Si,Si*)-xantsil}(CO)(η^6-toluene-d_8) (**1**-d_8) and $Me_2Si(OMe)_2$. NMR spectroscopic data of **1** were used to identify **1**-d_8 while an authentic sample matched the NMR and GC data for $Me_2Si(OMe)_2$. A singlet signal corresponding to H_2 was observed at δ 4.51. In this experiment, the products were not isolated.

Reaction of 2a with CO

A Schlenk tube was charged with **2a** (75 mg, 0.13 mmol) and toluene (12 mL). The solution was degassed by freeze–pump–thaw cycles and filled with CO introduced from a balloon. The procedure was repeated five times. After stirring the solution at room temperature for 16 h, volatiles were removed in vacuo. The yellow residue was washed with hexane to afford Ru{κ^2(*Si,Si*)-xantsil}(CO)$_2${(SiMe$_2$•••O(Me)•••SiMe$_2$)} (**3**) as a white solid. Yield: 67 mg, 85%. IR (KBr pellet, cm^{-1}): 1954 (ν (CO_{asym})). MS (FAB) *m/z*: 630 (M^+, 17), 602 (M^+ – CO, 24), 512 (M^+ – CO – $SiMe_2OMe$, 64). ^1H NMR (300 MHz, C_6D_6) δ: –3.81 (s, 1H, RuH), 0.40 (s, 12H, SiMe), 1.05 (s, 12H, SiMe), 1.51 (s, 6H, CMe_2), 2.33 (s, 3H, OMe), 7.16 (t, ^3J = 7.4 Hz, 2H, Ar), 7.29 (dd, ^3J = 7.4 Hz, ^4J = 1.6 Hz, 2H, Ar), 7.56 (dd, ^3J = 7.4 Hz, ^4J = 1.6 Hz, 2H, Ar). ^{13}C NMR (75.5 MHz, C_6D_6) δ: 6.3, 9.8 (SiMe), 27.3 (C*Me*$_2$), 36.3 (*C*Me$_2$), 51.4 (OMe), 123.4, 124.9, 131.0, 133.2, 134.6, 160.1 (Ar), 202.2 (CO). ^{29}Si NMR (C_6D_6) δ: –8.7 (xantsil), 97.3 (silylene). Anal. calcd. for $C_{26}H_{40}RuO_4Si_4$: C 49.57, H 6.40; found: C 49.04, H 5.98.

X-ray crystal structure determination of 2b and 3

Intensity data for X-ray crystal structure analysis were collected at 150 K on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite-monochromated Mo Kα radiation. A total of 44 images, corresponding to 220.0° oscillation angles, were collected with two different goniometer settings. Exposure time was 0.30 min for **2b** and 2.00 min for **3** per degree. Readout was performed in the 0.100 mm pixel mode. Numerical absorption corrections were applied on each crystal shape. The structures were solved by Patterson methods (PATTY) and refined by the least-squares technique. All non-hydrogen atoms were located and refined anisotropically. An atomic coordinate of a hydrogen atom connected to Ru in **3** was determined by the difference Fourier synthesis and refined isotropically. Other hydrogen atoms were placed at their geometrically calculated positions. Data reduction and refinement were performed using teXsan software packages. Crystallographic data of **2b** and **3** are listed in Table 1.[6]

Results and discussion

Reaction of 1 with dihydrosilane

It has been reported that transition-metal complexes mediate the dehydrogenative coupling of polyhydrosilanes and (or) redistribution of substituents on silicon atoms (2). The activity of Ru{κ^2(*Si,Si*)-xantsil}(CO)(η^6-toluene) (**1**) toward this reaction was first investigated. When a solution of **1** and excess *p*-Tol_2SiH_2 in $CDCl_3$ was heated at 60 °C for 3 h, a red solution containing xantsil-H_2 and toluene as the major

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[6] Supplementary data may be purchased from the Directory of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC 210554 (**2b**) and 210555 (**3**) contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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Table 1. Crystallographic data of **2b** and **3**.

Compound	**2b**	**3**
Formula	$C_{28}H_{46}O_3RuSi_4$	$C_{26}H_{40}O_4RuSi_4$
Formula weight	644.08	630.01
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$ (No. 4)	$P2_1/n$ (No. 14)
a (Å)	18.216(3)	10.1538(5)
b (Å)	9.634(1)	17.1435(8)
c (Å)	19.327(2)	18.0994(8)
β (°)	109.647(6)	93.999(3)
V (Å^3)	3194.2(7)	3142.9(2)
Z	4	4
$D_{\text{calcd.}}$ (g cm^{-3})	1.339	1.331
D_{observed} (g cm^{-3})	Not measured	Not measured
μ (Mo Kα) (cm^{-1})	6.67	6.79
Crystal size (mm)	0.10 × 0.10 × 0.10	0.20 × 0.20 × 0.10
Radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
Monochromator	Graphite	Graphite
T (°C)	–123	–123
2θ Range (°)	2.2–55.0	3.3–55.0
No. of reflections measured	23 418	25 522
No. of unique data	7668 (R_{int} = 0.066)	7157 (R_{int} = 0.052)
No. of parameters refined	650	320
R^a	0.114	0.061
$R_w{}^b$	0.216	0.117
$R1^c$	0.075	0.034
No. of reflections to calc R1	6219	6061
Goodness-of-fit indicator^d	1.40	1.01
Largest shift (esd, final cycle)	0.091	0.003
Max / min resid electron dens (eÅ^{-3})	0.93 / –1.01	0.47 / –0.55

[a] $R = \Sigma\,(F_o{}^2 - F_c{}^2) / \Sigma\,F_o{}^2$
[b] $R_w = [\Sigma\,w(F_o{}^2 - F_c{}^2)^2 / \Sigma\,w(F_o{}^2)^2]^{1/2}$, $w = [\sigma_c{}^2(F_o{}^2) + (p(\mathrm{Max}(F_o{}^2, 0) + 2F_c{}^2)/3)^2]^{-1}$, where p = 0.1130 (2*b*) and 0.0920 (3).
[c] $R1 = \Sigma\,||F_o| - |F_c|| / \Sigma\,|F_o|$ for $I > 2.0\sigma(I)$.
[d] $[\Sigma\,w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{variables}})]^{1/2}$.

products was obtained (eq. [1]). The ^{1}H NMR spectrum showed the signals for xantsil-H_2, toluene, and other less-intense signals of the unidentified by-products, which did not provide any sign of dehydrogenative coupling or redistribution reaction of the dihydrosilane.

[1]

$$\mathbf{1} + p\text{-}\mathrm{Tol_2SiH_2} \xrightarrow{60\ ^\circ\mathrm{C,\ 3\ h}} \text{xantsil-}\mathrm{H_2} + \mathrm{C_6H_5CH_3} + \text{etc.}$$

Reaction of 1 with hydrodisilane

A CD_2Cl_2 solution of $HSiMe_2SiMe_3$ was treated with a catalytic amount of **1** (5.0 mol%) and the reaction was monitored by ^{1}H NMR spectroscopy. Oligomerization and deoligomerization occurred to give $H(SiMe_2)_nMe$ (n = 1–5). Identification of the oligosilanes was carried out by comparison of spectroscopic data with authentic samples (9, 12).[7] The reaction was performed using 0.1 mol% of **1** and was monitored by GC and GC–MS spectroscopy. The oligomerization–deoligomerization reactions proceeded at room temperature, and after 2 days, $H(SiMe_2)_nMe$ (n = 1–5) was formed in the molar ratio of 81 (n = 1) : 56 (n = 2) : 11 (n = 3) : 3 (n = 4) : 1 (n = 5) (eq. [2]). A similar reaction performed at 90 °C provided $H(SiMe_2)_nMe$ (n = 1–8) in the molar ratio of 346 (n = 1) : 96 (n = 2) : 83 (n = 3) : 64 (n = 4) : 35 (n = 5) : 13 (n = 6) : 4 (n = 7) : 1 (n = 8). The products were also confirmed by ^{1}H NMR spectral data.

[2]

$$\mathrm{HSiMe_2SiMe_3} \xrightarrow{0.1\ \text{mol \% of}\ \mathbf{1}} \mathrm{H(SiMe_2)}_n\mathrm{Me}$$

n = 1-5 (r.t., 2 days)
n = 1-8 (90 °C, 2 days)

A plausible mechanism for the ruthenium-mediated oligomerization–deoligomerization of $HSiMe_2(SiMe_2)_nMe$ is given in Scheme 3. The catalytic reaction proceeds via repeated oxidative addition of Si-H, 1,2-silyl migration, and reductive elimination processes. Initial oxidative addition of

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[7] ^{1}H NMR data for $H(SiMe_2)_nMe$ (300 MHz, $CDCl_3$) δ n = 3: 0.06 (s, 9H, $SiMe_3$), 0.09 (s, 6H, $SiMe_2$), 0.12 (d, J = 4.5 Hz, 6H, Si*Me*$_2$H), 3.69 (septet, J = 4.5 Hz, 1H, SiH); n = 4: 0.07 (s, 9H, $SiMe_3$), 0.09 (s, 6H, $SiMe_2$), 0.12 (s, 6H, $SiMe_2$), 0.13 (d, J = 4.5 Hz, 3H, Si*Me*$_2$H), 3.72 (septet, J = 4.5 Hz, 1H, HSi); n = 5 (C_6D_6): 0.15 (s, 9H, $SiMe_3$), 0.20 (d, J = 4.5 Hz, 6H, Si*Me*$_2$H), 0.22 (s, 6H, $SiMe_2$), 0.23 (s, 6H, $SiMe_2$), 0.26 (s, 6H, $SiMe_2$), 4.11 (septet, J = 4.5 Hz, 1H, SiH); n = 6 (C_6D_6): 0.16 (s, 9H, $SiMe_3$), 0.20 (d, J = 4.5 Hz, 6H, Si*Me*$_2$H), 0.23 (s, 6H, $SiMe_2$), 0.25 (s, 6H, $SiMe_2$), 0.30 (s, 6H × 2, $SiMe_2$), 4.11 (septet, J= 4.5 Hz, 1H, SiH).

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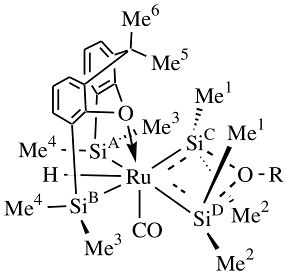
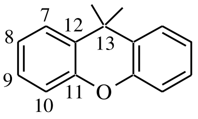
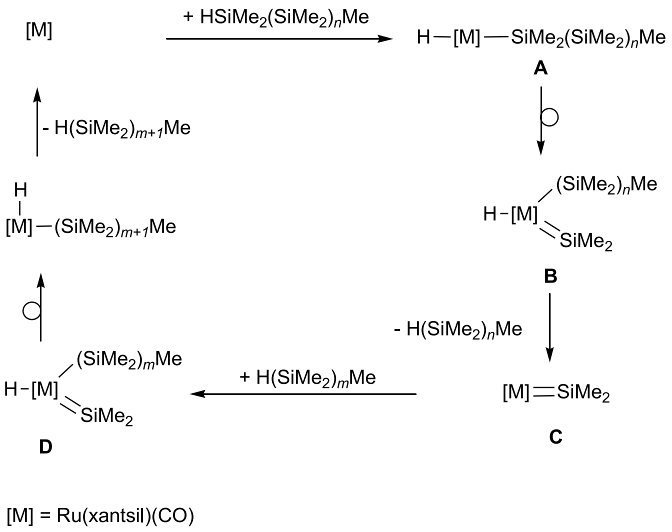
Table 2. NMR and IR spectroscopic data of **2a** and **2b**.

	2a	**2b**
	^{1}H NMR (300 MHz, C_6D_6) δ	^{1}H NMR (300 MHz, CD_2Cl_2) δ
Ru-H	–1.75	–2.23
SiMe	–0.07(1), 0.67(2), 0.89(3), 1.01(4)	0.13(1), 0.59(3), 0.62(4), 0.88(2)
CMe_2	1.21(5), 1.43(6)	1.24(5), 1.75(6)
OR	2.52 (Me)	1.38 (*t*-Bu)
ArH	6.97–7.03 (m, 7,8), 7.48 (dd, *J* = 2.6, 6.1 Hz, 9)	7,12 (t, *J* = 7.4 Hz, 8), 7.23 (dd, *J* = 1.6, 7.4 Hz, 7), 7.48 (dd, *J* = 1.6, 7.4 Hz, 9)
	^{13}C{^{1}H} NMR (75.5 MHz, THF-d_8) δ	^{13}C{^{1}H} NMR (75.5 MHz, THF-d_8) δ
SiMe	3.4(1), 4.8(2), 7.7(3), 14.6(4)	6.2(1), 7.2(3), 10.0(4), 14.0(2)
CMe_2	23.2(5), 31.9(6), 36.4(13)	30.7(5), 30.9(6), 35.8(13)
OR	52.0 (Me)	22.6 (CMe_3), 92.3 (CMe_3)
Ar	124.4, 125.8, 131.4(7, 8, 9), 135.0, 136.4(10, 12), 162.5(11)	123.5, 124.9, 130.7 (7, 8, 9), 134.4, 136.0(10, 12), 161.9(11)
CO	204.3	204.2
	^{29}Si{^{1}H} NMR (59.6 MHz, C_6D_6) δ	^{29}Si{^{1}H} NMR (59.6 MHz, CD_2Cl_2) δ
Xantsil	14.6	15.4
Silyene	107.4	107.6
	IR (KBr), $\tilde{\nu}$/cm^{-1}	IR (KBr), $\tilde{\nu}$/cm^{-1}
ν (CO)	1929	1923





Scheme 3.



$HSiMe_2(SiMe_2)_nMe$ to a coordinatively unsaturated [Ru(xantsil)(CO)] species gives a hydrido(silyl)ruthenium(IV) intermediate **A**, which undergoes 1,2-silyl migration to form a hydrido(silyl)(silylene) intermediate **B**. Reductive elimination of Si-H gives $H(SiMe_2)_nMe$ and a coordinatively unsaturated silylene complex **C**, which in turn undergoes oxidative addition of $H(SiMe_2)_mMe$ to generate hydrido(silyl)(silylene) intermediate **D**. 1,2-Migration of the silyl ligand followed by Si-H reductive elimination regenerates the coordinatively unsaturated [Ru(xantsil)(CO)] species together with $H(SiMe_2)_{m+1}Me$. The 1,2-migration steps of the silyl groups are responsible not only for the cleavage of silicon–silicon bonds which leads to deoligomerization, but also for the formation of silicon–silicon bonds, which leads to oligomerization.

Transition-metal-mediated redistribution of hydropolysilanes have been reported for titanium (13), zirconium (13), and platinum (14). Complex **1** is the first ruthenium catalyst that is effective in the redistribution of hydropolysilanes.

Reaction of 1 with $HSiMe_2SiMe_2OMe$

The mechanism in Scheme 3 involves the silyl(silylene) complexes as key intermediates. This kind of complex having a metal–silicon double bond is highly reactive and difficult to isolate but can be internally stabilized by an alkoxy group (15). Thus, treatment of **1** with $HSiMe_2SiMe_2OR$ (R = Me, *t*-Bu) in CH_2Cl_2 resulted in the clean formation of Ru{κ^3(*O*,*Si*,*Si*)-xantsil}(CO)(H){$SiMe_2$•••O(R)•••$SiMe_2$} (**2a** (R = Me), **2b** (R = *t*-Bu)), which were isolated in 98% and 84% yields, respectively (eq. [3]). Spectroscopic data of **2a** and **2b** are summarized in Table 2. Spectroscopic features of **2a**

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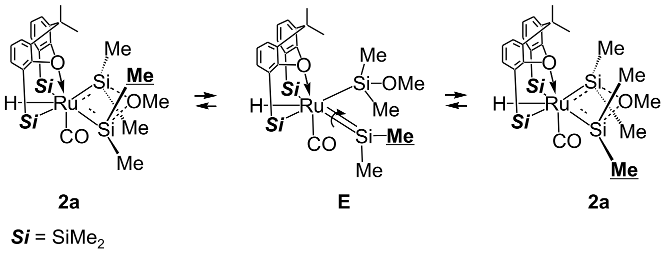
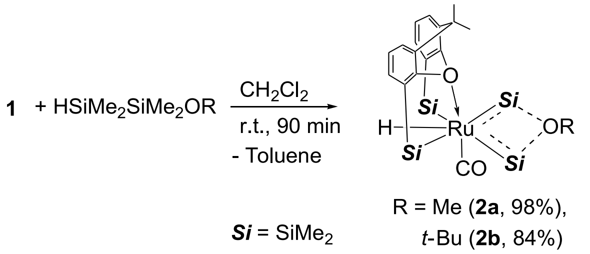
Scheme 4.



[3]



and **2b** are almost the same and, thus, all further discussions of spectroscopic data refer to **2a**. The $^{29}Si\{^1H\}$ NMR spectrum shows two singlet signals at δ 14.6 and 107.4, which are assigned to the xantsil silicon and silylene silicon atoms, respectively. The chemical shift of silylene moieties is characteristic of base-stabilized silylene complexes (1*c*). The ^1H NMR spectrum of **2a** shows a singlet at –1.75 ppm that can be assigned to Ru-H. Four singlet signals for the methyl groups on silicon atoms appear at –0.07 (6H), 0.67 (6H), 0.89 (6H), and 1.01 (6H), which are assigned to SiMe(1), SiMe(2), SiMe(3), and SiMe(4), respectively (see Table 2). The signals of the CMe_2 part on xantsil appear inequivalently at 1.21 (Me(5)) and 1.43 (Me(6)). These assignments are established by the combination of $^{29}Si–^1H$ COLOC and ^1H NOESY spectra. In the ^1H NOESY spectrum, a positive correlation peak is clearly observed between Ru-H and SiMe(4) resonances, indicating that the Ru-H hydrogen atom is located within the Si^A-Ru-Si^B angle.

The ^1H NOESY spectrum also shows a negative correlation peak between the signals of methyl groups on the silylene silicon atoms (Me(1) and Me(2)), implying the intramolecular exchange process of the methyl groups on the bis(silylene) ligand. The dynamic process probably involves the cleavage of a silicon–oxygen bond, followed by rotation of the resulting donor-free silylene moiety around the ruthenium–silicon double bond to exchange the methyl group environments (Scheme 4). This mechanism is essentially the same as those of the exchange of SiMe groups in $Cp(CO)_2W\{SiMe_2•••Do•••SiMe_2\}$ (Do = OMe, NEt_2) (16) and $Cp^*(Me_3P)Ru\{SiMe_2•••OR•••SiMe_2\}$ (R = Me, *t*-Bu) (11). The strongly electron-releasing xantsil ligand is expected to make the ruthenium center electron rich. Enhanced back donation from the metal *d*π orbital toward the Si-O σ* orbital weakens the Si—O bond and accelerates its cleavage to generate the base-free silyl(silylene) complex **E**. This intermediate **E** is also stabilized by the electron-rich ruthenium center through back donation from the metal *d*π orbital toward the empty *p* orbital of the silylene silicon atom.

The $^{13}C\{^1H\}$ NMR spectrum displays the expected resonances for **2a** that are consistent with the ^1H NMR spectral data. The IR spectrum shows a strong band at 1929 cm^{-1} attributable to the CO-stretching vibration mode. Elemental analysis and mass spectral data are in good agreement with the formula of **2a**.

Table 3. Selected bond lengths (Å) and angles (°) for **2b**.

	Molecule A	Molecule B
Bond lengths (Å)		
Ru—Si(1)	2.395(4)	2.407(4)
Ru—Si(2)	2.402(4)	2.394(4)
Ru—Si(3)	2.443(3)	2.439(3)
Ru—Si(4)	2.424(4)	2.425(3)
Ru—O(2)	2.289(8)	2.277(8)
Ru—C(5)	1.79(1)	1.80(1)
Si(1)—O(1)	1.813(9)	1.810(9)
Si(2)—O(1)	1.827(9)	1.844(9)
O(1)—C(1)	1.52(1)	1.51(1)
O(3)—C(5)	1.17(2)	1.18(2)
Bond angles (°)		
Si(1)-Ru-Si(2)	67.9(1)	68.0(1)
Si(1)-Ru-Si(3)	151.1(1)	152.6(1)
Si(1)-Ru-Si(4)	87.1(1)	83.4(1)
Si(1)-Ru-O(2)	93.8(2)	92.7(2)
Si(1)-Ru-C(5)	89.0(5)	90.4(5)
Si(2)-Ru-Si(3)	84.2(1)	85.5(1)
Si(2)-Ru-Si(4)	154.3(1)	150.3(1)
Si(2)-Ru-O(2)	95.0(2)	92.4(2)
Si(2)-Ru-C(5)	89.6(5)	88.8(4)
Si(3)-Ru-Si(4)	119.4(1)	121.3(1)
Si(3)-Ru-O(2)	80.6(2)	81.1(2)
Si(3)-Ru-C(5)	98.8(5)	96.1(4)
Si(4)-Ru-O(2)	80.2(2)	80.6(2)
Si(4)-Ru-C(5)	96.0(5)	99.8(4)
O(2)-Ru-C(5)	175.2(6)	176.9(5)
Ru-Si(1)-O(1)	98.9(3)	98.9(3)
Ru-Si(2)-O(1)	98.2(3)	98.3(3)
Si(1)-O(1)-Si(2)	94.8(4)	94.6(4)
Si(1)-O(1)-C(1)	132.5(7)	132.9(8)
Si(2)-O(1)-C(1)	131.6(7)	131.8(8)
Ru-C(5)-O(3)	178(1)	177(1)

X-ray structure analysis of 2b

The structure of **2b** was unequivocally determined by the X-ray diffraction study. The crystal contains two independent molecules **A** and **B**, but there is no essential difference between them. The selected bond lengths and angles for **2b** are listed in Table 3. All further discussions of structural details refer to molecule **A**. The ORTEP view of **A** is shown in Fig. 1. The Ru-H hydrogen atom could not be located crystallographically, but the ^1H NOESY spectrum clearly shows that it must be found inside the unusually widened Si(3A)-Ru(A)-Si(4A) angle (119.4(1)°). Thus, the molecule takes a distorted seven-coordinate pentagonal bipyramid geometry with the nearly planar arrangement of all four silicon atoms (mean deviation from the least square Si_4 plane: 0.0161 Å). The xanthene moiety is strongly bent (dihedral angle between the arene rings C(14A)-C(19A) and C(20A)-C(25A): 136.5°). The bond lengths of Ru-Si (bis(silylene)) (avg. 2.399 Å) are shorter than those of Ru-Si (xantsil) (avg.

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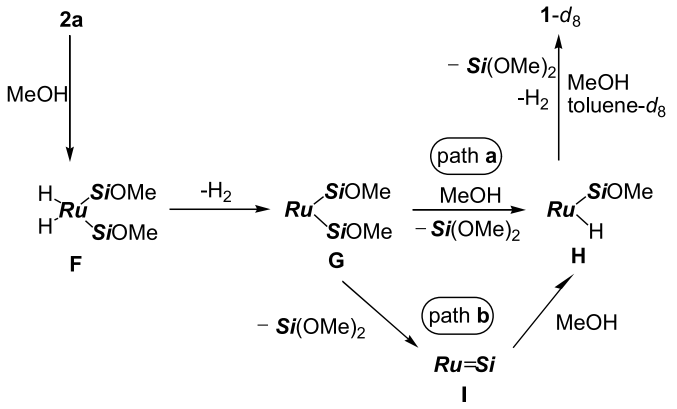
Scheme 5.



Ru = Ru(xantsil)(CO), ***Si*** = $SiMe_2$

2.434 Å), but significantly longer than those of the previously reported bis(silylene) ruthenium complexes (2.31–2.33 Å) (17). This lengthening could be due to the trans influence of silyl groups (4) and (or) to the weaker back donation from the highly oxidized Ru(IV) center to silicon. The distance of Ru-O(2A) is 2.289(8) Å, which clearly indicates that the oxygen atom of the xanthene moiety is coordinated to the ruthenium center to satisfy the 18-electron rule. Thus, xantsil in **2b** is working as a terdentate ligand.

Catalytic oligomerization–deoligomerization of $HSiMe_2SiMe_3$ in the presence of 2a

To get further convincing evidence in support of the existence of silyl(silylene) complexes in the catalytic reaction of eq. [2], we carried out the thermal reaction of $HSiMe_2SiMe_3$ in the presence of a catalytic amount of **2a**. Indeed, $HSiMe_2SiMe_3$ was converted to $H(SiMe_2)_nMe$ (n = 1–8) after 2 days at 90 °C with the molar ratios of 12 (n = 1) : 6 (n = 2) : 5 (n = 3) : 5 (n = 4) : 4 (n = 5) : 2 (n = 6) : 3 (n = 7) : 1 (n = 8). This result clearly showed that the bis(silylene) complex **2a** can be incorporated into the catalytic cycle in Scheme 3.

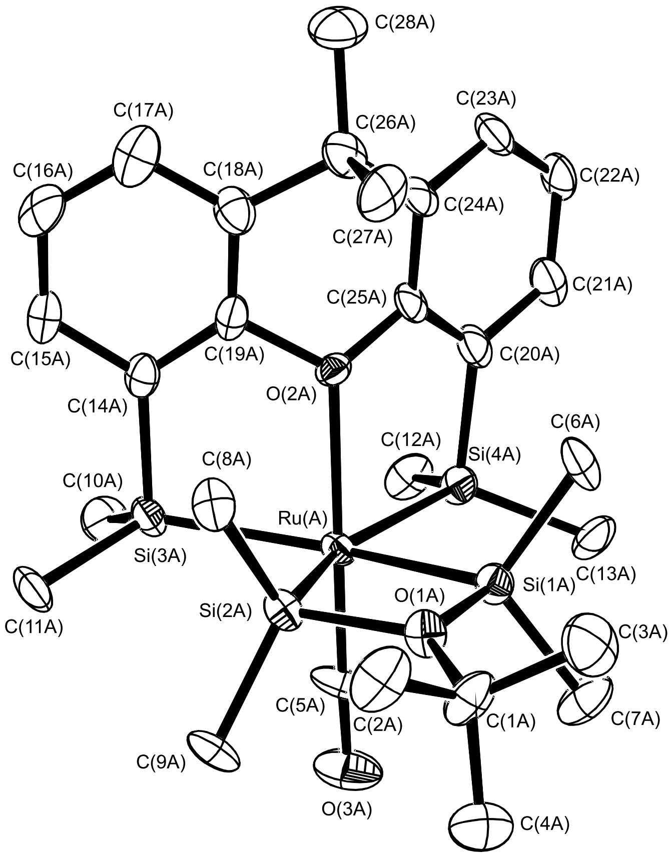
Reaction of 2a with MeOH

It has been reported that silylene complexes show high reactivity toward various nucleophiles such as alcohols (18). The reaction of **2a** with MeOH in toluene-d_8 was carried out and monitored by NMR spectroscopy. It proceeded cleanly to give Ru{κ^2(*Si*,*Si*)-xantsil}(CO)(η^6-toluene-d_8) (**1**-d_8) and $Me_2Si(OMe)_2$ with evolution of H_2 gas (eq. [4]). Spectroscopic data of **1** was used to identify **1**-d_8, while that of the authentic sample was used to identify $Me_2Si(OMe)_2$.

[4]
$$\mathbf{2a} + 3\,\mathrm{MeOH} \xrightarrow[\text{Toluene-}d_8]{\text{r.t.}} \mathbf{1}\text{-}d_8 + 2\mathrm{Me_2Si(OMe)_2} + 2\mathrm{H_2}$$

In a proposed mechanism for this reaction (Scheme 5), the highly polarized ruthenium–silylene bond is attacked by MeOH to give a hydrido(methoxysilyl)ruthenium intermediate **F**. Reductive elimination of dihydrogen gives bis(methoxysilyl) complex **G**. In path **a**, successive nucleophilic attacks of excess MeOH toward the silyl silicon atom, followed by reductive elimination of H_2, gives **1**-d_8 and two

Fig 1. An ORTEP drawing of **2b**.

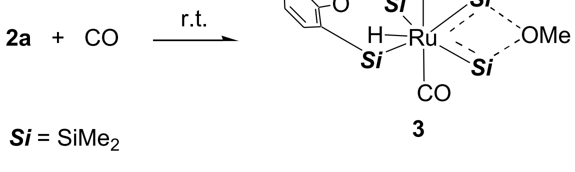


molecules of $Me_2Si(OMe)_2$ via intermediate formation of **H**. An intramolecular nucleophilic attack of the methoxy group in **G** must also be considered, which leads to the formation of the silylene complex intermediate **I** (path **b**). Nucleophilic attack of MeOH on a silylene silicon atom in **I** gives **H**, which is finally converted to **1**-d_8 through an intermolecular nucleophilic attack by MeOH.

Reaction of 2a with CO

When the reaction of **2a** with 1 atm (1 atm = 101.325 kPa) of CO was monitored by means of ^1H NMR spectroscopy at room temperature, quantitative formation of **3** was observed (eq. [5]). An analytically pure sample was obtained in 85% yield by washing the residue with hexane.

[5]

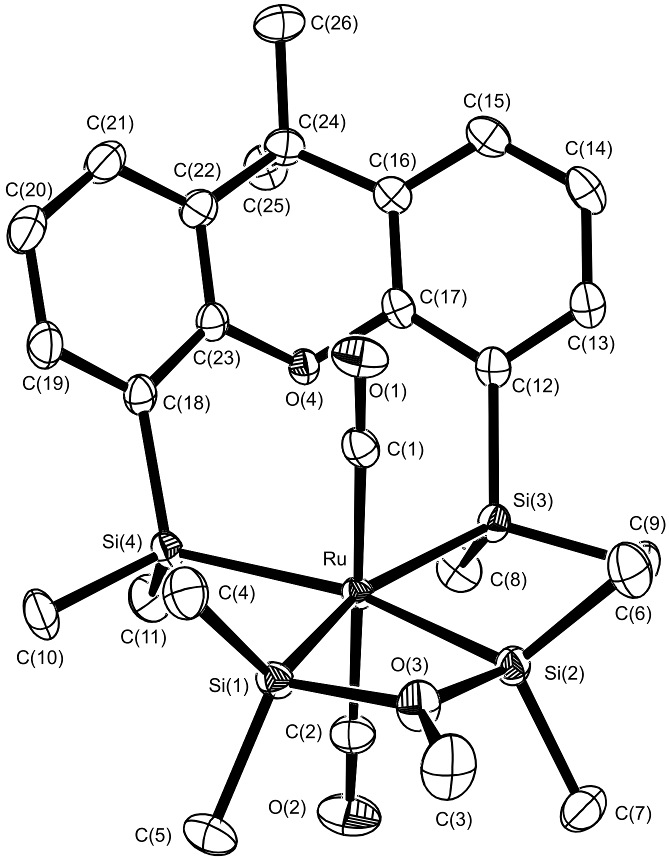


3

Si = $SiMe_2$

The X-ray diffraction study of **3** was performed using a colorless crystal obtained by cooling a toluene–hexane solution at –30 °C. The structure of **3** is depicted in Fig. 2. The selected interatomic distances and bond angles for **3** are listed in Table 4. The distance of Ru-O(4) is 3.581(2) Å, indicating the cleavage of the Ru—O bond in **2a**. One CO molecule is coordinated to the resulting vacant site of the ru-

Fig 2. An ORTEP drawing of **3**.



thenium center. The hydrogen atom of the Ru—H bond was located inside the widened Si(3)-Ru-Si(4) angle (109.37(2)°) by the difference Fourier synthesis and refined isotropically. Thus, complex **3** also takes a distorted seven-coordinate pentagonal bipyramid geometry with the nearly planar arrangement of all four silicon atoms and one hydrogen atom. The bond lengths of Ru—Si (silylene) (avg. 2.41 Å) and Ru—Si (xantsil) (avg. 2.50 Å) are similar to the values of **2b**.

In the ^{1}H NMR spectrum, the CMe_2 portion and the Si-Me groups on xantsil, as well as the Si-Me groups on the bis(silylene) ligand each appear as one singlet signal at δ 1.51 (CMe_2, 6H)), 0.40 (SiMe, 12H), and 1.05 ppm (SiMe, 12H), although the assignment of Si-Me groups is not clear. If complex **3** maintains the crystal structure illustrated in Fig. 2 in solution without any dynamic behavior, six singlet signals should appear. However, this is not the case even at 210 K. A likely process is the rapid inversion of the puckered chelate ring of xantsil. This dynamic behavior of **3** is in sharp contrast with Ru{κ^2(*Si*,*Si*)-xantsil}$(CO)_4$. In this complex, each of the CMe_2 and $SiMe_2$ groups on xantsil shows two signals at 210 K. On warming, each of them coalesces and finally becomes a sharp singlet at room temperature (7*a*). Other spectroscopic features of **3** resemble those of **2**.

Conclusions

Over the past few decades, silyl(silylene) complexes have been proposed as intermediates in the stoichiometric and catalytic metal-mediated transformation reactions of organosilicon compounds (2, 3*b*). The results described here provide further evidence for the participation of silyl(silylene) complexes in the catalytic cycles of the metal-mediated oligomerization–deoligomerization of hydrodisilanes.

Table 4. Selected interatomic distances (Å) and bond angles (°) for **3.**

Interatomic distances (Å)	
Ru—Si(1)	2.4108(6)
Ru—Si(2)	2.4191(7)
Ru—Si(3)	2.4970(6)
Ru—Si(4)	2.4970(7)
Ru—C(1)	1.917(2)
Ru—C(2)	1.918(3)
Ru-H(1)	1.59(4)
Si(1)—O(3)	1.802(2)
Si(2)—O(3)	1.800(2)
O(1)—C(1)	1.141(3)
O(2)—C(2)	1.142(3)
Ru•••O(4)	3.581(2)
Bond angles (°)	
Si(1)-Ru-Si(2)	69.73(2)
Si(1)-Ru-Si(3)	160.34(2)
Si(1)-Ru-C(1)	87.81(7)
Si(1)-Ru-C(2)	91.13(8)
Si(2)-Ru-Si(3)	90.74(2)
Si(2)-Ru-Si(4)	159.89(3)
Si(2)-Ru-C(1)	90.01(7)
Si(3)-Ru-Si(4)	109.37(2)
Si(3)-Ru-C(1)	90.05(7)
Si(3)-Ru-C(2)	91.07(8)
Si(4)-Ru-C(1)	89.66(7)
Si(4)-Ru-C(2)	89.99(9)
C(1)-Ru-C(2)	178.9(1)
Si(1)-Ru-H(1)	145(1)
Si(2)-Ru-H(1)	145(1)
Si(3)-Ru-H(1)	54(1)
Si(4)-Ru-H(1)	55(1)
C(1)-Ru-H(1)	88(1)
C(2)-Ru-H(1)	92(1)
Ru-Si(1)-O(3)	94.71(6)
Ru-Si(2)-O(3)	94.50(6)
Si(1)-O(3)-Si(2)	100.09(9)

Reactivity of **2a** toward CO indicates that complex **2a** is labile and generates a *coordinatively unsaturated silylene complex* via dissociation of the xantsil oxygen atom under mild conditions. A number of metal-mediated stoichiometric and catalytic transformations of organosilicon compounds appear to involve coordinatively unsaturated silylene complexes (1, 2, 3, 19). Although synthesis and reactivity of silylene complexes have been reported, only scattered reports on coordinatively unsaturated ones are available (19). Complex **3** would be an ideal candidate for examining the reactivity of coordinatively unsaturated silylene complexes.

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