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Nonphotochemical Synthesis and Structure of the First Donor-Stabilized [Bis(silylene)]ruthenium Complex

Hiromi Tobita,* Hiroaki Wada, Keiji Ueno, and Hiroshi Ogino*

Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980, Japan

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Summary: The first donor-stabilized [bis(silylene)]ruthenium compex, $Cp(Ph_3P)Ru(SiMe_2{-}{-}{-}O(Me){-}{-}{-}SiMe_2)$, has been synthesized by the thermal reaction of $CpRu(PPh_3)_2Me$ with $HMe_2SiSiMe_2OMe$. The X-ray crystal structure analysis of this complex revealed its distorted-piano-stool structure, containing a $RuSi_2O$ four-membered chelate ring with two short Ru–Si bonds and two long Si–O bonds.

Transition-metal complexes containing unsaturated silicon centers are considered to play important roles in many metal-promoted transformations of silicon compounds.[1] Since 1987, the synthesis of silylene complexes ($R_2Si{=}ML_n$) has been achieved by a number of different approaches,[1–6] and after several fruitful years, Tilley et al.[7] and West et al.[8] recently succeeded in the syntheses and crystal structure analyses of three different types of donor-free silylene complexes containing sp^2-hybridized silicon centers.

Alkoxy-bridged bis(silylene) transition-metal complexes occupy a unique position in the field of donor-stabilized silylene complexes. These have been prepared by the photolysis of (alkoxydisilanyl)carbonyliron[6a–e] and -manganese[6f] complexes and can be regarded as internally donor stabilized silyl–silylene complexes. Donor-free (silylsilylene)iron complexes are assumed to be the key intermediates of deoligomerization accompanied by alkyl and aryl scrambling,[9] and skeletal redistribution,[10] of oligosilanyliron complexes. The key step in the synthesis of alkoxy-bridged bis(silylene) complexes is [1,2]-migration of the terminal silyl group from the disilanyl group to a coordinatively unsaturated metal center.[6] This simple reaction is potentially widely applicable to many different transition-metal analogues. However, use of the photodissociation of CO to generate a coordinatively unsaturated metal center seriously restricts the applicability of this route, because quite a few carbonyl complexes, such as $CpRu(CO)_2SiMe_2SiMe_3$ and $(OC)_5ReSiMe_2SiMe_3$,[11] have been reported to be resistant to CO expulsion under the usual photolytic conditions. We report here that the coordinatively unsaturated (disilanyl)metal intermediate can also be generated by thermal reaction of $CpRu(PPh_3)_2$-Me with $HMe_2SiSiMe_2OMe$, directly forming the first ruthenium bis(silylene) complex via [1,2]-silyl migration.[12]

It is well-known that $CpRu(PPh_3)_2X$ (X = Cl, Me, etc.) readily dissociates one of its bulky triphenylphosphine ligands under mild heating to generate the reactive 16-electron intermediate $CpRu(PPh_3)X$.[13] Thus, as a preliminary experiment, we examined the thermal reaction of $CpRu(PPh_3)_2Me$ (**1**)[14] with dimethyl-*p*-tolylsilane to estimate the reactivity of the coordinatively unsaturated intermediate from **1** toward oxidative addition of hydrosilanes. The reaction proceeded smoothly at 90 °C in

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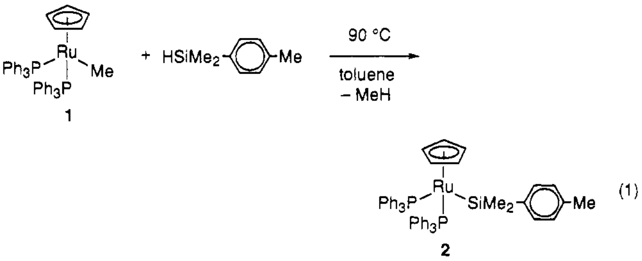
toluene to give $CpRu(PPh_3)_2SiMe_2(p\text{-}Tol)$ (**2**)[15] in 64% yield (eq 1). All spectroscopic and elemental analysis data

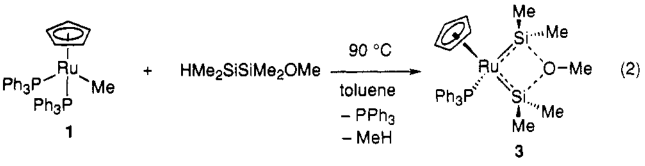


(1)

for **2** are consistent with its structure. A closely related reaction has been reported by Tilley et al. for $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2CH_2SiMe_3$, in which the Me_3SiCH_2 group is replaced by a silyl group on treatment with a hydrosilane.[3a,b]

By analogy with other known reactions involving addition of silane accompanied by the elimination of a small molecule,[1] the reaction of eq 1 can be viewed as proceeding through the following four steps: (1) thermal dissociation of PPh_3, (2) oxidative addition of $HSiMe_2(p\text{-}Tol)$ across the Si–H bond to give the 16e intermediate, (3) reductive elimination of methane, and (4) recoordination of PPh_3.[3a,b] Another possible mechanism involves the oxidative addition of $HSiMe_2(p\text{-}Tol)$ to the ortho-metalated 16e intermediate $Cp\{\eta^2\text{-}o\text{-}(Ph_2P)C_6H_4\}Ru$.[16]

We then examined the reaction of **1** with $HMe_2SiSiMe_2OMe$[17] under similar conditions: heating the mixture in toluene at 90 °C for 24 h followed by cooling it to −30 °C provided yellow crystals of the alkoxy-stabilized [bis(silylene)]ruthenium complex $Cp(Ph_3P)Ru(SiMe_2{-}{-}{-}O(Me){-}{-}{-}SiMe_2)$ (**3**)[19] in 56% yield (eq 2). Complex **3** is apparently



(2)

less air-sensitive than the analogous iron bis(silylene) complexes.

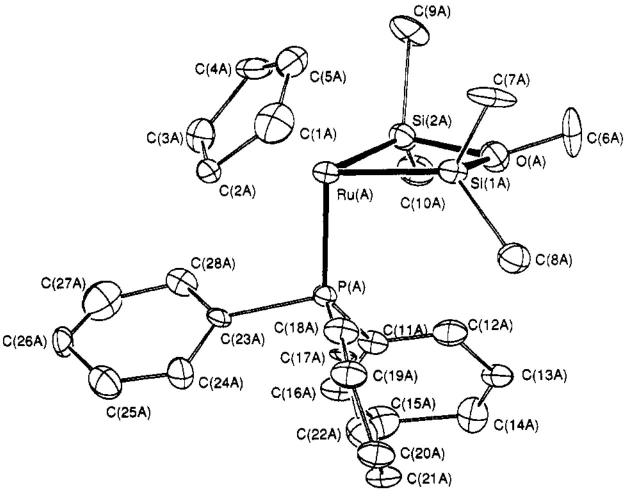


Figure 1. ORTEP diagram of $Cp(Ph_3P)Ru(SiMe_2{-}{-}{-}O(Me){-}{-}{-}SiMe_2)$ (**3**) (molecule A). Important interatomic distances (Å) and angles (deg): Ru(A)–Si(1A) = 2.333(5), Ru(A)–Si(2A) = 2.333(4), Si(1A)–O(A) = 1.790(10), Si(2A)–O(A) = 1.846(13), O(A)–C(6A) = 1.52(2), Ru(A)–P(A) = 2.224(3), Si(1A)···Si(2A) = 2.659(5), Ru(A)···O(A) = 3.142(12); Si(1A)–Ru(A)–Si(2A) = 69.5(2), Si(1A)–O(A)–Si(2A) = 94.0(6), Ru(A)–Si(1A)–O(A) = 98.4(3), Ru(A)–Si(2A)–O(A) = 96.8(4), Si(1A)–Ru(A)–P(A) = 94.43(14), Si(2A)–Ru(A)–P(A) = 95.37(12), Ru(A)–Si(1A)–C(7A) = 121.9(5), Ru(A)–Si(1A)–C(8A) = 127.5(5), C(7A)–Si(1A)–C(8A) = 99.6(6), Ru(A)–Si(2A)–C(9A) = 113.9(4), Ru(A)–Si(2A)–C(10A) = 135.0(4), C(9A)–Si(2A)–C(10A) = 100.8(6).

The structure of **3** has been determined by an X-ray crystal structure analysis.[20] The crystal contains two independent molecules (A and B), but there is no essential structural difference between them. The structure of molecule A is shown in Figure 1. The complex adopts a distorted-piano-stool geometry. Of particular interest are the Ru–Si and Si---O(tricoordinate) distances. The Ru—Si distances (2.333(5) and 2.333(4) Å for molecule A; 2.348(5) and 2.290(4) Å for molecule B; average value 2.326 Å) are almost the same as that of Tilley's base-stabilized silylene-ruthenium complex $[(\eta^5\text{-}C_5Me_5)(Me_3P)_2RuSiPh_2(NCMe)]BPh_4{\cdot}CH_2Cl_2$ (2.328(2) Å)[3a,b] and are between that in Tilley's base-free silylene complex $(OC)_4OsSi(S\text{-}$

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[15] Preparation of **2**: To $CpRu(PPh_3)_2Me$ (**1**; 0.285 g, 0.407 mmol) in a Pyrex tube (10 mm o.d.) connected to a vacuum line was added $HSiMe_2(p\text{-}Tol)$ (65.3 mg, 0.435 mmol) and toluene (3.0 mL) by the trap-to-trap-transfer technique. The tube was sealed under vacuum, heated to 90 °C for 18 h, and then opened in a glovebox. After removal of the solvent under vacuum, recrystallization of the residual solid from toluene–pentane afforded $CpRu(PPh_3)_2SiMe_2(p\text{-}Tol)$ (**2**; 0.219 g, 0.261 mmol, 64%) as yellow-orange crystals. Spectral data for **2**: ^1H NMR (C_6D_6, 300 MHz) δ 0.67 (6H, s, SiMe), 2.32 (3H, s, $SiC_6H_4\textit{Me}$), 4.33 (5H, s, Cp), 6.97–7.64 (34H, m, PPh_3, $SiC_6\textit{H}_4Me$); ^{13}C NMR (C_6D_6, 75.5 MHz) δ 10.7 (SiMe), 21.5 ($SiC_6H_4\textit{Me}$), 85.3 (Cp), 127.1–153.6 (PPh_3, $Si\textit{C}_6H_4Me$); ^{29}Si NMR (DEPT 45°, C_6D_6, 59.3 MHz) δ 4.1 (t, $^2J_{Si-P}$ = 24.0 Hz); ^{31}P NMR (C_6D_6, 36.3 MHz) δ 52.9; IR (KBr pellet) 1479, 1431 (aromatic ring C–C stretch), 1084 (in-plane aromatic C–H bend), 798, 789, 741, 694 (out-of-plane aromatic C–H bend) cm^{-1}; MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe) *m/z* 840 (17, M^+), 825 (2.5 $M^+ - Me$), 749 (6.7, $M^+ - p$-Tol), 691 (49, $M^+ - SiMe_2(p\text{-}Tol)$), 578 (100, $M^+ - PPh_3$). Anal. Calcd for $C_{50}H_{48}P_2RuSi$: C, 71.48; H, 5.77. Found: C, 71.76, H, 6.04.

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[17] $HMe_2SiSiMe_2OMe$ was prepared from $HMe_2SiSiMe_2H$ by monochlorination of Si–H with $CuCl_2$/cat. CuI[18] followed by methoxylation with $MeOH/(H_2N)_2CO$ in 22% overall yield. Spectral data for $HMe_2SiSiMe_2OMe$: ^1H NMR (C_6D_6, 300 MHz) δ 0.13 (6H, d, $^3J_{H-H}$ = 4.6 Hz, Si(H)–*Me*), 0.21 (6H, s, Si(OMe)–*Me*), 3.27 (3H, s, Si-O*Me*), 3.94 (1H, sep, $^3J_{H-H}$ = 4.6 Hz, Si–H); ^{13}C NMR (C_6D_6, 75.5 MHz) δ −6.6 (Me), −0.7 (Me), 50.8 (OMe); ^{29}Si NMR (C_6D_6, 59.6 MHz) δ −44.2, 16.7; IR (neat) 1248 (Si–Me), 1088 (Si–OMe) cm^{-1}; exact mass calcd for $C_5H_{16}OSi_2$ 148.0740, found 148.0733.

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[19] Preparation of **3**: To $CpRu(PPh_3)_2Me$ (**1**; 3.10 g, 4.42 mmol) in a Pyrex tube (20 mm o.d.) connected to a vacuum line was added $HMe_2SiSiMe_2OMe$ (0.935 g, 6.32 mmol) and toluene (12 mL) by the trap-to-trap transfer technique. The tube was sealed under vacuum and heated at 90 °C for 24 h. As the reaction mixture was cooled to 5 °C and then to −32 °C, yellow crystals precipitated out. The tube was opened in a glovebox, and after the supernatant liquid was removed, the crystals were washed with hexane to give $Cp(Ph_3P)Ru(SiMe_2{-}{-}{-}O(Me){-}{-}{-}SiMe_2)$ (**3**; 1.42 g, 2.47 mmol, 56%) as yellow crystals. Spectral data for **3**: ^1H NMR (C_6D_6, 300 MHz) δ 0.10 (6H, s, SiMe), 0.50 (6H, s, SiMe), 2.82 (3H, s, OMe), 4.55 (5H, s, Cp), 7.03–7.67 (15H, m, PPh_3); ^{13}C NMR (C_6D_6, 50.3 MHz) δ 7.9 (d, $^3J_{C-P}$ = 2.5 Hz, SiMe), 10.4 (SiMe), 50.3 (OMe), 81.1 (Cp), 127.4–144.0 (PPh_3); ^{29}Si NMR (DEPT 45°, C_6D_6, 59.3 MHz) δ 108.7 (d, $^2J_{Si-P}$ = 25.0 Hz); ^{31}P NMR (C_6D_6, 36.3 MHz) δ 68.5; IR (toluene solution) 1238 (Si–Me), 1090 (Si–OMe) cm^{-1}; MS (EI, 70 eV) *m/z* 576 (100, M^+), 561 (3.5, $M^+ - Me$), 545 (5.7, $M^+ - OMe$), 530 (7.8, $M^+ - OMe - Me$), 487 (7.5, $M^+ - SiMe_2 - OMe$), 429 (2.6, $Cp(Ph_3P)Ru^+$), 314 (23, $M^+ - PPh_3$), 262 (62, PPh_3^+). Anal. Calcd for $C_{28}H_{35}OPRuSi_2$: C, 58.40; H, 6.14. Found: C, 58.05; H, 6.41.

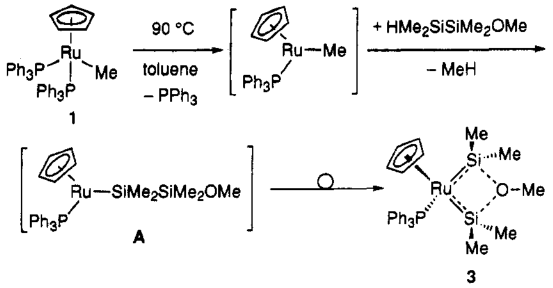
[20] Crystal data for **3**: formula $C_{28}H_{35}OPRuSi_2$, monoclinic, space group *Ia* (variant of No. 9), a = 18.811(12) Å, b = 15.250(2) Å, c = 19.191(3) Å, β = 98.70(2)°, V = 5442(5) Å^3, Z = 8, d_{calcd} = 1.41 g cm^{-3}. X-ray diffraction data were collected at 150 K on a Rigaku AFC-5R diffractometer with a rotating anode (45 k V, 200 mA) with graphite-monochromated Mo Kα radiation. Reflections (8093) with $3° < 2\theta < 50°$ were collected by the ω-scan technique. The structure was solved by direct methods (RANTAN-81) and refined with block-diagonal least squares using individual anisotropic thermal parameters for non-hydrogen atoms. The final R factor was 0.057 (R_W = 0.057) for 5297 reflections with $|F_o| > 3\sigma(F_o)$.

p-Tol)[Ru(η^5-C_5Me_5)(PMe_3)$_2$] (2.286(2) Å)[7a] and those in the usual silyl complexes (2.34–2.51 Å).[1] The Si---O(tricoordinate) distances (1.790(10) and 1.846(13) Å for molecule A; 1.855(10) and 1.849(13) Å for molecule B; average value 1.835 Å) are significantly longer than the usual Si–O single bonds (typically 1.63 Å)[21] and are even longer than those for the iron and manganese analogues (η^5-C_5Me_5)(OC)Fe($SiMe_2$---O(Me)---$SiMe_2$) (1.793(9) and 1.799(8) Å)[6a,b] and $(OC)_4$Mn($SiMe_2$---O(Me)---$SiMe_2$) (1.784(5) and 1.795(4) Å).[6f] These bond lengths strongly support the structure of **3** with partial double-bond character for the Ru–Si bonds and partial dative-bond character for the Si---O bonds.

The Ru–Si–O–Si four-membered ring is slightly bent to let O(tricoordinate) be closer to the PPh_3 ligand (dihedral angle between the Si(1)–Ru–Si(2) and Si(1)–O–Si(2) planes: 11.7° for molecule A and 8.5° for molecule B). This is probably due to the bulky triphenylphosphine ligand, which wedges itself between the two methyl groups containing C(8A) and C(10A) to widen the angle between the axes of the C(8A)–Si(1A) and C(10A)–Si(2A) bonds. Two methyl groups on each silicon atom are bent away from the ruthenium center to render the geometry at the silicon nearly planar (the sum of the bond angles at each silicon, i.e. C–Si–C and two Ru–Si–C's, is 349.9° (average), as in other alkoxy-stabilized bis(silylene) complexes.[6a,b,f]

The ^{29}Si NMR chemical shift of 108.7 ppm is shifted significantly downfield from those for usual silylruthenium complexes such as **2** (4.06 ppm) and (η^5-C_5Me_5)Ru(H)(PMe_3)($SiPh_2Cl$)$_2$ (57.8 ppm),[3b] and the downfield shift is comparable with those for typical alkoxy-bridged bis(silylene) complexes, e.g. (η^5-C_5Me_5)(OC)Fe($SiMe_2$---O(Me)---$SiMe_2$) (125.2 ppm)[6a,b] and $(OC)_4$Mn($SiMe_2$---O(Me)---$SiMe_2$) (115.4 ppm).[6f] The $^2J_{Si-P}$ coupling constant for **3** (25.0 Hz) is similar to that for **2** (24.0 Hz). The upfield shift of the ^{1}H NMR signal for methoxy protons (2.82 ppm) is typical of methoxy-bridged bis(silylene) complexes.[6]

Scheme 1



The formation of **3** can be explained by the mechanism shown in Scheme 1. A series of reactions involving expulsion of PPh_3 from **1**, oxidative addition of $HMe_2SiSiMe_2OMe$ across the Si–H bond to the coordinatively unsaturated ruthenium center, and evolution of methane gives the intermediate **A**. A local structure in **A**, a methoxydisilanyl group bound to a coordinatively unsaturated metal center, also exists in the key intermediate of the photoreaction of (alkoxydisilanyl)carbonylmetal complexes.[6] Therefore, **A** undergoes the same type of reaction, i.e. [1,2]-silyl migration and cyclization, to give **3**. The present study clearly demonstrates for the first time that the [1,2]-silyl migration step does not require photoirradiation.

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Supplementary Material Available: Listings of crystal data, atomic coordinates, thermal parameters, interatomic distances, and bond angles and a diagram showing molecule B for **3** and a figure giving ^{1}H NMR spectrum for $HMe_2SiSiMe_2OMe$ (15 pages). Ordering information is given on any current masthead page.

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