Interconversion among μ-Silylene, μ-Silyl, and μ-Silane Diruthenium Complexes in the Presence of Dihydrosilane

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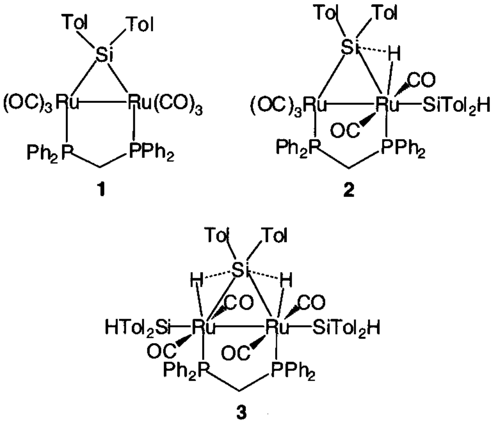
Received November 13, 2001

Summary: Irradiation of a toluene solution of $[Ru_2(CO)_6(\mu\text{-dppm})(\mu\text{-SiTol}_2)]$ (**1**) *in the presence of an excess of* Tol_2SiH_2 *produced a μ-silyl complex,* $[Ru_2(CO)_5(SiTol_2H)(\mu\text{-dppm})(\mu\text{-}\eta^2\text{-HSiTol}_2)]$ (**2**), *which was further converted to a μ-silane complex,* $[\{Ru(CO)_2(SiTol_2H)\}_2(\mu\text{-dppm})(\mu\text{-}\eta^2{:}\eta^2\text{-H}_2SiTol_2)]$ (**3**), *quantitatively. Complex* **3** *released* Tol_2SiH_2 *in the presence of CO to regenerate* **2**, *which finally reverted to* **1** *under thermal conditions. The X-ray crystal structures of* **1** *and* **3** *were determined.*

Complexes containing an agostic M−H−Si interaction (three-center−two-electron bond) have been of great interest in synthetic, structural, and theoretical organometallic chemistry.[1] These complexes have attracted much attention because of their importance not only as possible key intermediates in catalytic reactions such as hydrosilylation[2] and dehydrogenative polymerization of silanes[3] but also as models for intermediate complexes in C−H bond activation.[4] Although a large number of such complexes have been reported, dinuclear μ-silane complexes with two M−H−Si interactions are quite rare.[5−7] Graham and co-workers first suggested the existence of a μ-silane ligand in the dirhenium complex $Re_2(CO)_8(\mu\text{-}\eta^2{:}\eta^2\text{-H}_2SiPh_2)$ 30 years ago.[5a] Among the known μ-silane complexes, only two dinuclear complexes, $[Cp^*MX]_2(\mu\text{-}\eta^2{:}\eta^2\text{-H}_2Si^tBu_2)$ (M = Ru and X = CO,[7a] M = Fe and X = μ-H;[7b] $Cp^* = \eta^5\text{-}C_5Me_5$) were fully characterized by X-ray crystallography and spectroscopic techniques. We report here the synthesis of new μ-silyl (**2**, $Ru_2(CO)_5(SiTol_2H)(\mu\text{-dppm})(\mu\text{-}\eta^2\text{-HSiTol}_2)$; Chart 1) and μ-silane complexes (**3**, $\{Ru(CO)_2(SiTol_2H)\}_2(\mu\text{-dppm})(\mu\text{-}\eta^2{:}\eta^2\text{-H}_2SiTol_2)$) by the reaction of $[Ru_2(CO)_6(\mu\text{-dppm})(\mu\text{-SiTol}_2)]$ (**1**) with Tol_2SiH_2 under UV irradiation. The present results constitute the first convincing transformation of a μ-silylene complex to the corresponding μ-silyl and μ-silane complexes without apparent destruction of the μ-silylene−diruthenium ring skeleton. In the presence of an excess of carbon monoxide, the μ-silane complex **3** reverted thermally to **2** and then to **1**.

Chart 1



Complexes **1** and **2** were prepared by the reaction of $Ru_3(CO)_{10}(\mu\text{-dppm})$[8] with Tol_2SiH_2 (5 equiv) at 40 °C (Scheme 1). These complexes were isolated after their separation by flash chromatography (on silica gel, eluant 2/1 toluene/hexane) in 46% and 24% yields, respectively, and characterized by spectroscopy[9,10] and X-ray crystallography.[11,12] Although **1** and **2** structurally resemble each other except for a ligand on the Ru−Ru axis, **1** did not react with Tol_2SiH_2 up to ca. 60 °C, indicating that **2** was formed without the intermediacy of **1** during the reaction; at higher temperatures, a complex mixture containing **2** and unidentified products was obtained.

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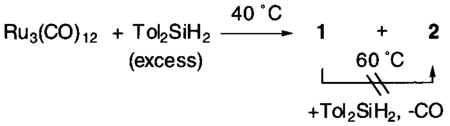
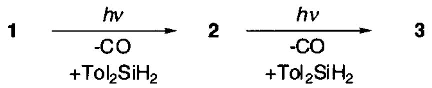
10.1021/om0109814 CCC: $22.00

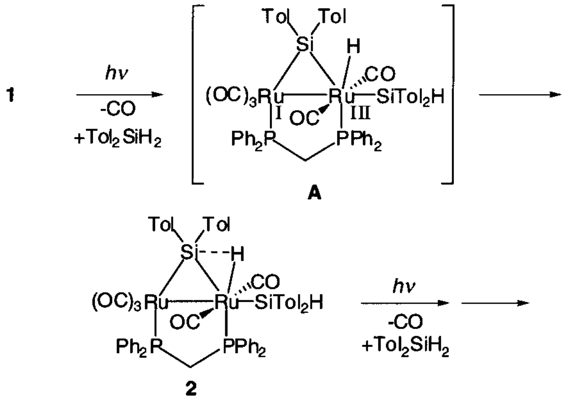
Scheme 1



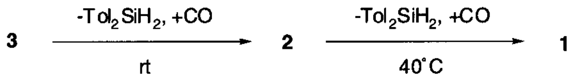
Scheme 2



Scheme 3



Scheme 4



Interestingly, irradiation of a toluene solution of **1** in the presence of an excess of Tol_2SiH_2 using a 450 W high-pressure mercury arc lamp ($\lambda > 300$ nm) in a sealed Pyrex tube at ca. 5 °C afforded a 1:1 mixture of two products, **2** and the μ-silane complex **3**. Removal of gaseous CO from the reaction mixture and then additional irradiation led to quantitative formation of **3**, which was isolated in 67% yield by recrystallization (Scheme 2). Complex **3** was characterized by spectroscopy[13] and by X-ray crystallography.[14,15]

Monitoring the photoreaction of **1** with Tol_2SiH_2 by ^1H NMR spectroscopy showed clearly the stepwise transformation of **1** to **2** and then to **3** without formation of any other stable intermediates. As shown in Scheme 3, the reaction is reasonably well understood in terms of the photochemical dissociation of a CO ligand from **1** followed by the oxidative addition of Tol_2SiH_2 to form intermediate **A**, which rearranges to **2** to balance the formal oxidation states of the two Ru atoms. Repeating a similar process from **2** leads to the formation of μ-silane complex **3**.[16] It is interesting to note that the Ru−H hydrides in **2** and **3** have an agostic Si- - -H interaction with a μ-silylene silicon but not with a side-bound silyl silicon. The present results provide a novel process to form agostic Si- - -H(M) bonds, in which the agostic hydrides are provided by external hydrosilanes. In this relation, Tessier et al. have suggested the μ-silyl complex $Fe_2(CO)_5(SiPh_2H)(\mu\text{-}\eta^2\text{-}HSiPh_2)$ might be formed by the thermal reaction of Ph_2SiH_2 with the postulated complex $Fe_2(CO)_8(\mu\text{-}SiPh_2)$.[17] Suzuki et al. have demonstrated that H_2 reacts with $[Cp^*Ru(\mu\text{-}SiPh_2)(\mu\text{-}H)]_2$ under high pressure to produce $[Cp^*Ru(\mu\text{-}\eta^2\text{-}HSiPh_2)]_2(\mu\text{-}H)(H)$, which regenerates the μ-$SiPh_2$ complex when it is heated.[18]

When a benzene solution of **3** was allowed to stand at room temperature in the presence of an excess of CO, complex **2** was regenerated cleanly with loss of Tol_2SiH_2. Upon further heating at 40 °C for 2 days, complete reversion of **2** to **1** resulted (Scheme 4). Easier release of Tol_2SiH_2 from **3** rather than from **2** may suggest that the terminal silyl group instead of the bridging silylene is eliminated during the conversion of **3** to **2** and that of **2** to **1**; the reactivity difference between **3** and **2** is in accord with the trans effect of a silyl group being stronger than that of the CO group.[16]

The crystal structures of **1** and **3** determined by X-ray crystallography are shown in Figures 1 and 2 with selected bond lengths and angles. In **3**, ditolylsilane bridges two ruthenium atoms almost symmetrically. The bridging hydrides are observed at 1.58(9) and 1.61(9) Å from Ru1 and Ru2, respectively, and at 1.86(9) and 1.88(12) Å from Si2 and Si3, respectively. These Si−H distances are much longer than the covalent Si−H bond distances of 1.56(9) and 1.57(10) Å in the terminal silyl groups in **3** but within the corresponding distances for other reported compounds with apparent M−H−Si interactions.[1] There is no interaction between the agostic hydrogens and the silyl silicon atoms in **3**, as evidenced by the long distances between these atoms

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(9) **1** (yellow crystals): Anal. Calcd for $C_{45}H_{36}O_6P_2Ru_2Si$: C, 56.01; H, 3.76. Found: C, 56.35; H, 4.01. For spectral data, see the supporting information.

(10) **2** (yellow crystals): Anal. Calcd for $C_{58}H_{52}O_5P_2Ru_2Si_2$: C, 60.61; H, 4.56. Found: C, 60.21; H, 4.95. For spectral data, see the supporting information.

(11) X-ray analysis of **1**: $C_{45}H_{36}O_6P_2Ru_2Si$; fw 964.95; yellow prism; monoclinic; space group $P2_1/n$ (No. 14); $a = 10.842(3)$ Å, $b = 18.947(5)$ Å, $c = 20.201(2)$ Å, $b = 90.59(3)°$, $V = 6468.6(3)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.545$ g/cm^3; μ(Mo Kα) = 8.82 cm^{-1}. The reflection intensities were collected on a Rigaku/AFC-5R four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å) at 150 K. The structure was solved by direct methods, using SIR 92,[12] and refined by full-matrix least squares on F^2. A total of 10 018 reflections were measured, and of these, 7087 reflections ($I > 3.0\sigma(I)$) were used in the refinement: $R = 0.034$, $R_w = 0.072$.

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(13) **3** (yellow crystals): Anal. Calcd for $C_{71}H_{68}O_4P_2Ru_2Si_3$: C, 63.94; H, 5.14. Found: C, 63.51; H, 5.24. For spectral data, see the supporting information.

(14) X-ray analysis of **3**: $C_{71}H_{68}O_4P_2Ru_2Si_3$; fw 1333.66; yellow prism; monoclinic; space group $P2_1/c$ (No. 14); $a = 12.4237(2)$ Å, $b = 27.4560(9)$ Å, $c = 21.6781(6)$ Å, $\beta = 118.9812(2)°$, $V = 6468.6(3)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.369$ g/cm^3; μ(Mo Kα) = 6.20 cm^{-1}. The reflection intensities were collected on a Rigaku/MSC CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å) at 150 K. The structure was solved by direct methods, using MULTAN 88,[15] and refined by full-matrix least squares on F^2. A total of 26 327 reflections were measured, and of these, 10 248 reflections ($I > 4.0\sigma(I)$) were used in the refinement: $R = 0.037$, $R_w = 0.076$.

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(16) When a mixture of **1** and an excess of $(p\text{-}t\text{-}BuC_6H_4)_2SiH_2$ in benzene-d_6 was irradiated at 5 °C, the stepwise formation of $Ru_2(CO)_5[Si(p\text{-}t\text{-}BuC_6H_4)_2H](\mu\text{-dppm})(\mu\text{-}\eta^2\text{-}HSiTol_2)$ (**2a**) and $\{Ru(CO)_2[Si(p\text{-}t\text{-}BuC_6H_4)_2H]\}_2(\mu\text{-dppm})(\mu\text{-}\eta^2{:}\eta^2\text{-}H_2SiTol_2)$ (**3a**) was observed by NMR spectroscopy. However, thermal reaction of **3a** in the presence of CO gave several products. These results suggest that the bridging silylene is intact during these transformations at low temperatures, while at high temperatures, scrambling occurs between the bridging silylene and side-bound silyl groups. For experimental details, see the Supporting Information.

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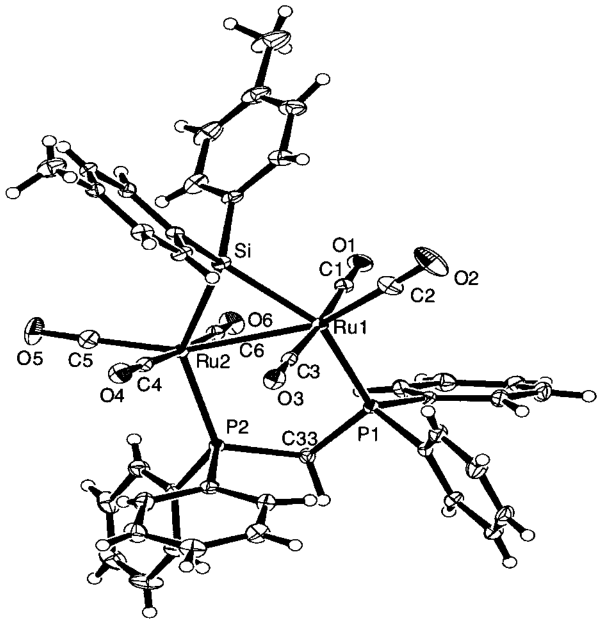

Figure 1. ORTEP drawing of **1**. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Ru−Ru, 2.9072(8); Ru1−Si1, 2.425(2); Ru2−Si2, 2.427(2); Ru1−P1, 2.390(2); Ru2−P2, 2.394(2); Ru2−Ru1−Si3, 53.21(5); Ru1−Si−Ru2, 73.64(6).

(>2.5 Å). The Ru−Ru distance of 3.0248(7) Å in **3** is near the longer limit of the reported Ru−Ru single-bond distances[19] and longer than those in μ-silylene complex **1** (2.9072(8) Å) and the known μ-silane diruthenium complex $[\mathrm{Cp^*Ru(CO)}]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{H_2Si^tBu_2})$ (2.9637(8) Å).[7a] The lengthening of the Ru−Ru bond is ascribed to the strong trans influence of the terminal silyl groups which occupy positions trans to the Ru−Ru bond. No significant differences are found among Ru−Si distances in **1** and **3**, despite the difference of the bonding nature; all the Ru−Si distances were between 2.408 and 2.432 Å.

The IR spectrum (KBr) of **3** showed broad peaks at 1863 $\mathrm{cm^{-1}}$ and 1817 $\mathrm{cm^{-1}}$ assigned to Ru−H−Si stretching bands, which was confirmed by comparison of the spectra of **3** and the deuterated complex $\{\mathrm{Ru(CO)_2(SiTol_2D)}\}_2(\mu\text{-dppm})(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{D_2SiTol_2})$ (**3**-d_4).[20] For **2**, a broad peak at 1790 $\mathrm{cm^{-1}}$ is assignable to the Ru−H−Si stretching bands.[7]

The existence of the agostic Ru−H−Si interaction in **2** and **3** in solution was clearly demonstrated by NMR spectroscopy. The ^{1}H resonances due to the Ru−H hydrogens in **2** and **3** appeared at −8.87 (d, $^2J_{\mathrm{HP}} = 34.2$ Hz) and −8.84 ppm (m, $^2J_{\mathrm{HP}} = 31.0$ Hz),[13] respectively, with satellites due to a ^{29}Si nucleus ($J_{\mathrm{SiH}} = 36.0$ and 24.4 Hz, respectively). The J_{SiH} values are in the range of those for known complexes having agostic M−H−Si interactions (20−136 Hz)[1,4d,21] but close to the lower end of the range; the interaction may be comparable to that in a μ-silyl complex, $\mathrm{Fe_2(CO)_5(SiPh_2H)}(\mu\text{-}\eta^2\text{-}\mathrm{HSiPh_2})$ ($J_{\mathrm{SiH}} = 48.3$ Hz).[17] Remarkably, the J_{SiP} value between the bridging ^{29}Si and ^{31}P nuclei for **3** (13.1 Hz) is less than half of that for **1** (35.5 Hz); two J_{SiP} values (9.3 and 48.3 Hz) were observed for **2**. The smaller J_{SiP} values would also be a good indication of the Ru−H−Si bonding. Furthermore, the ^{29}Si resonances for the bridging silicon nuclei for **2** and **3** (**2**; 150.4 ppm, **3**; 154.8 ppm) are shifted to the higher field compared to that of μ-silylene complex **1** (172.6 ppm). The high-field shift of the bridging ^{29}Si resonances can be taken as another indication of the significant agostic Ru−H−Si interaction in **2** and **3**.[7]

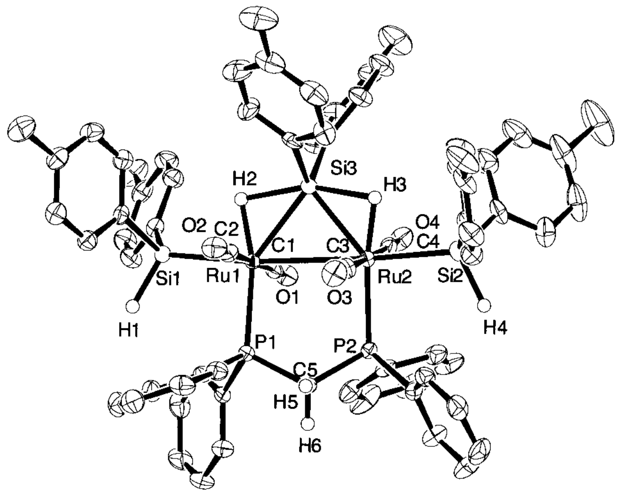

Figure 2. ORTEP drawing of **3**. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Ru1−Ru2, 3.0248(7); Ru1−Si1, 2.422(2); Ru2−Si2, 2.427(2); Ru1−Si3, 2.432(2); Ru2−Si3, 2.408(2); Ru1−H2, 1.58(9); Ru2−H3, 1.61(9); Si3−H2, 1.86(9); Si3−H3, 1.88(12); Ru2−Ru1−Si3, 50.97(5); Ru1−Ru2−Si3, 51.67(4); Ru1−Si3−Ru2, 77.36(6).

Although significant agostic interaction in **2** and **3** is evidenced both in the solid state and in solution, the interaction may be rather weak, as suggested by the rather small J_{SiH} values of ca. 30 Hz. To elucidate the whole bonding nature in **1**−**3**, DFT calculations of their model complexes are now in progress.

Acknowledgment. This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan (Grant-in-Aids for Scientific Research (B) No. 11440185 (M. K.)).

Supporting Information Available: Tables giving details of the X-ray structure determination, atomic coordinates, and bond lengths and angles, figures giving thermal ellipsoid plots for **1** and **3**, IR spectra of **3** and **3**-d_4, ^{1}H NMR spectra of **2**, **3**, and **3**-d_4, and text giving experimental details for the preparation of **1**−**3** and **3**-d_4. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0109814

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[20] For spectral data of **3**-d_4 (yellow crystals), see the supporting information.

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