# **ORGANOMETALLICS**

# Intramolecular C–H Bond Activation in Bridged Dicyclopentadienyl Dimethyl Dinuclear Complexes

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**S** Supporting Information

**ABSTRACT:** Photolysis of the doubly bridged dicyclopentadienyl dimethyl dinuclear complexes  $[(\eta^{5}-C_{5}H_{2}R)_{2}(SiMe_{2})_{2}]$ - $M_{2}(CO)_{4}Me_{2}$  (M = Ru, R = H (2a), <sup>f</sup>Bu (2b); M = Fe, R = H (2c)) in benzene yields the corresponding methylene-bridged complexes  $[(\eta^{5}-C_{5}H_{2}R)_{2}(SiMe_{2})_{2}]M_{2}(CO)_{2}(\mu$ -CO) $(\mu$ -CH<sub>2</sub>) (3a-c) and the M-M-bonded complexes  $[(\eta^{5}-C_{5}H_{2}R)_{2}(SiMe_{2})_{2}]M_{2}(CO)_{4}$  (1a-c). Irradiation of the analogous diethyl complex  $[(\eta^{5}-C_{5}H_{2}R)_{2}(SiMe_{2})_{2}]Ru_{2}(CO)_{4}Et_{2}$ (4) affords only 1a. Unlike the case for the doubly bridged complexes, photolysis of the singly bridged dicyclopentadienyl dimethyl diruthenium complexes  $[(\eta^{5}-C_{5}H_{4})_{2}(EMe_{2})]$ -



 $\operatorname{Ru}_2(\operatorname{CO})_4\operatorname{Me}_2(E = C (\mathbf{5a}); E = \operatorname{Si} (\mathbf{5b}))$  in benzene yields the corresponding "twisted" ruthenium methyl complexes with a cyclopentadienyl-Ru  $\sigma$  bond  $(\eta^5, \eta^5: \eta^1-C_5\operatorname{H}_4(\operatorname{EMe}_2)C_5\operatorname{H}_3)[\operatorname{Ru}(\operatorname{CO})_2][\operatorname{Ru}(\operatorname{CO})_2\operatorname{Me}]$  (**6a,b**) and the similar phenyl complexes  $(\eta^5, \eta^5: \eta^1-C_5\operatorname{H}_4(\operatorname{EMe}_2)C_5\operatorname{H}_3)[\operatorname{Ru}(\operatorname{CO})_2\operatorname{Ph}]$  (**7a,b**), from reaction with the benzene solvent. Plausible mechanisms for the formation of the different types of products are proposed involving intramolecular C-H bond activation. The molecular structures of **2a,c**, **3a,c**, **4**, **5a**, **6a**, and **7b**, determined by X-ray diffraction, are also presented.

# INTRODUCTION

Although "classic" transition-metal methyl complexes CpM- $(CO)_2$ Me (M = Fe, Ru) (type A in Chart 1) were synthesized half a century  $ago_1^{1,2}$  their catalytic applications to the activation of relatively inert bonds in organic molecules were discovered only in recent years, especially for the iron complex.<sup>3</sup> Nakazawa's group<sup>4</sup> and Pannell's group<sup>5</sup> reported a series of studies of organic reactions catalyzed by CpFe(CO)<sub>2</sub>Me, like the dehydrocoupling dimerization of  $R_n EH_{4-n}$  (E = Si, Ge, Sn; n = 2, 3), which mostly involve the activation of an E–H bond by the 16e species CpFe(CO)Me generated by the photoirradiation of the iron complex  $CpFe(CO)_2Me$ . To the best of our knowledge, no similar organic reaction catalyzed by the ruthenium analogue has been reported except a C-H bond activation reaction of benzene with Cp\*Ru(CO)<sub>2</sub>Me reported by Moss et al.<sup>6</sup> We considered that bridged dicyclopentadienyl dinuclear methyl analogues in which the bridging ligand locks the two reactive metal centers in close proximity may promote C-H activation. However, this type of chemistry has never been reported. Herein, we report our findings on the photochemical reactivity of a family of bridged dicyclopentadienyl dinuclear dimethyl complexes (types B and C in Chart 1).

# RESULTS AND DISCUSSION

Syntheses of  $[(\eta^5-C_5H_2R)_2(SiMe_2)_2]M_2(CO)_4Me_2$  (2a-c). Complexes 2a-c were prepared from the reaction of  $[((\eta^5-C_5H_2R)_2(SiMe_2)_2]M_2(CO)_4Me_2)$ 

 $(C_5H_2R)_2(SiMe_2)_2)M_2(CO)_4]^{2-}\cdot 2Na^+$  (synthesized from the corresponding M-M bond complexes 1a-c with an excess of Na-Hg alloy) with iodomethane in 38-52% yield (Scheme 1); they were isolated as colorless (2a,b) or yellow (2c) air-stable crystals. Their IR spectra (KBr film) indicate the expected three strong  $\nu(CO)$  absorptions in the range 2020–1936 cm<sup>-1</sup>. In the <sup>1</sup>H NMR spectra of **2a,c**, the cyclopentadienyl hydrogens occur as a doublet (5.33 ppm for 2a, 4.90 ppm for 2c) and a triplet (5.42 ppm for 2a, 4.95 ppm for 2c), consistent with an  $AB_2$  spin system. For **2b**, the spectrum shows a singlet (5.38) ppm) for the four equal cyclopentadienyl hydrogens. X-ray structural determinations of 2a,c (Figures 1 and 2) show their structures to be very similar to each other, both of which have a perfect crystallographic mirror plane passing through two metal atoms and the centroids of the two cyclopentadienyl rings. The metal atoms exhibit a three-legged piano-stool geometry. The configurations of the  $(\eta^5$ -C<sub>5</sub>H<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub>)<sub>2</sub> ligand are almost flat in 2a,c, which is reflected in the fold angles between the two cyclopentadienyl rings (170.6° in 2a, 170.2° in 2c). As expected, the M-M nonbonding distances (5.317 Å in 2a, 5.292 Å in 2c) are long. The structural features of 2a,c are very close to those of the diiodo complex  $[(\eta^5-C_5H_3)_2(SiMe_2)_2]$ - $Ru_2(CO)_4I_2$  reported by Angelici's group.

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Scheme 1





Figure 1. Thermal ellipsoid drawing of  $[(\eta^{5}-C_{5}H_{3})_{2}(SiMe_{2})_{2}]$ -Ru<sub>2</sub>(CO)<sub>4</sub>Me<sub>2</sub> (2a) showing the labeling scheme and 30% probability ellipsoids. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)--Ru(2) 5.317(9), Ru(1)-C(4A) 2.082(13), Ru(1)-C(4') 1.895(13), Ru(1)-C(5) 1.870(5), Ru(1)-Cp(centroid) 1.914, Ru(2)-Cp(centroid) 1.920;  $\angle C(4')$ -Ru(1)-C(5) 90.1(8),  $\angle C(4')$ -Ru(1)-C(4A) 88.3(4),  $\angle C(4A)$ -Ru(1)-C(5) 84.8(7),  $\angle Cp(centroid)$ -Ru(1)-Ru(2)-Cp(centroid) 0,  $\angle Cp$ -Cp fold angle 170.6.

**Photolysis of 2a–c.** It has been reported that irradiation of Cp\*Ru(CO)<sub>2</sub>Me in benzene yields Cp\*Ru(CO)<sub>2</sub>Ph via C–H bond activation.<sup>6</sup> With **2a–c** in hand, our initial objective was to focus on a double C–H bond activation of benzene. Surprisingly, UV irradiation of a solution of **2a–c** in benzene under an N<sub>2</sub> or Ar atmosphere results in formation of the corresponding bridging methylene complexes  $[(\eta^{5}-C_{5}H_{2}R)_{2}(SiMe_{2})_{2}]M_{2}(CO)_{2}(\mu-CO)(\mu-CH_{2})$  (**3a–c**, 11–43% yield) and the M–M-bonded complexes  $[(\eta^{5}-C_{5}H_{2}R)_{2}(SiMe_{2})_{2}]M_{2}(CO)_{4}$  (**1a–c**, 21–37% yield) (Scheme 1), both of which do not involve C–H bond activation of benzene. Obviously, the photochemical behaviors of **2a–c** and Cp\*Ru(CO)<sub>2</sub>Me toward benzene were different. The photo-



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Figure 2. Thermal ellipsoid drawing of  $[(\eta^5-C_5H_3)_2(SiMe_2)_2]$ -Fe<sub>2</sub>(CO)<sub>4</sub>Me<sub>2</sub> (2c) showing the labeling scheme and 30% probability ellipsoids. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)--Fe(2) 5.292(11), Fe(1)-C(4A) 1.999(14), Fe(1)-C(4') 1.803(12), Fe(1)-C(5) 1.759(5), Fe(1)-Cp(centroid) 1.729, Fe(2)-Cp(centroid) 1.733;  $\angle C(4')$ -Fe(1)-C(5) 90.8(10),  $\angle C(4')$ -Fe(1)-C(4A) 89.7(4),  $\angle C(4A)$ -Fe(1)-C(5) 86.1(8),  $\angle Cp$ (centroid)-Fe(1)-Fe(2)-Cp(centroid) 0,  $\angle Cp$ -Cp fold angle 170.2.

reaction of 2a was also carried out in toluene and provided the same products (3a and 1a) as those in benzene, which indicates that the different aromatic solvents have no effect on the reaction. Thermal treatment of 2a in refluxing toluene for 24 h gave none of these products, which shows that UV irradiation is necessary for this reaction.

Complexes **3a,b** were isolated as yellow crystals, while **3c** was obtained as brown crystals. In the <sup>1</sup>H NMR spectra of **3a**–c, the most notable and characteristic chemical shifts are two doublets at low field which are assigned to the bridging methylene protons (8.77, 6.64 ppm in **3a**, 8.67, 6.56 ppm in **3b**, 10.05, 6.68 ppm in **3c**). In the IR spectra (KBr film) of **3a**–c,  $\nu$ (CO) absorptions in the ranges 1980–1936 and 1769–1796 cm<sup>-1</sup> indicate the presence of both terminal and bridging



Figure 3. Thermal ellipsoid drawing of  $[(\eta^{5}-C_{5}H_{3})_{2}(SiMe_{2})_{2}]$ -Ru<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -CO)( $\mu$ -CH<sub>2</sub>) (3a) showing the labeling scheme and 30% probability ellipsoids. Hydrogens are partially omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)–Ru(1A) 2.6557(5), Ru(1)–C(8) 1.854(3), Ru(1)–C(9) 1.99(2), Ru(1)–C(10A) 2.14(2), C(9)–O(2) 1.17(2), Ru(1)–Cp(centroid) 1.923;  $\angle$ Ru(1A)–Ru(1)–C(9) 48.1(7),  $\angle$ Ru(1A)–Ru(1)–C(10A) 52.1(6),  $\angle$ C(9)–Ru(1)–C(10A) 89.2(8),  $\angle$ Ru(1)–C(10A)–Ru(1A) 76.4(8),  $\angle$ C(8)–Ru(1)–Ru(1A)–C(8A) 1.8,  $\angle$ Cp(centroid)–Ru(1)–Ru(2)–Cp(centroid) 2.2,  $\angle$ Cp-Cp fold angle 119.3.

of which show approximate  $C_{2\nu}$  symmetry with the  $C_2$  axis passing through the midpoints of the M-M bonds and the Si(1) and Si(1A) atoms. The metal atoms are bridged symmetrically by a carbonyl and a methylene ligand, and each metal atom also carries a terminal carbonyl. The two terminal carbonyls are highly eclipsed, which is evident in the very small  $\angle C(8) - M(1) - M(1A) - C(8A)$  torsion angle (1.8° in 3a,  $0.8^{\circ}$  in 3c). The M–M bond distances (2.6557(5) Å in 3a, 2.4898(5) Å in 3c) are slightly shorter than those found for their respective nonbridged parents  $(\eta^5-C_5H_5)_2M_2(\mu-CO)(\mu-CO)$  $CH_2)(CO)_2$  (M = Ru, 2.707(1) Å; M = Fe, 2.5196(6) Å).<sup>8,9</sup> The presence of the bridging carbonyl and methylene in 3a leads to a distinctly shortened Ru-Ru bond distance, in comparison to that found in the all terminal carbonyl analogue 1a (2.8180(3) Å).<sup>7</sup> The short Ru-Ru distance causes severe bending of the doubly bridged  $(\eta^5 - C_5 H_3)_2 (SiMe_2)_2$  ligand, which is evident in a smaller  $\angle$ Cp-Cp fold angle (119.3°).

In contrast to the method (Scheme 1) used to prepare the methylene-bridged 3a-c, the nonbridged and singly bridged dicyclopentadienyl ruthenium analogues are synthesized by the reactions of the corresponding dinuclear tetracarbonyl complexes with LiBHEt<sub>3</sub> in aromatic solvents<sup>10-12</sup> or in a rare case from the thermolysis of diruthenium carbonyl complexes  $(\eta^5-C_5H_4R)_2Ru_2(\mu-CO)_2(CO)_2$  with di- or trihy-



Figure 4. Thermal ellipsoid drawing of  $[(\eta^{5}-C_{5}H_{3})_{2}(SiMe_{2})_{2}]$ -Fe<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -CO)( $\mu$ -CH<sub>2</sub>) (3c) showing the labeling scheme and 30% probability ellipsoids. Hydrogens are partially omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)–Fe(1A) 2.4898(5), Fe(1)–C(8) 1.743(2), Fe(1)–C(9) 1.84(3), Fe(1)– C(10A) 2.04(3), C(9)–O(2) 1.19(3), Fe(1)–Cp(centroid) 1.757;  $\angle$ Fe(1A)–Fe(1)–C(9) 48.4(9),  $\angle$ Fe(1A)–Fe(1)–C(10A) 53.4(8),  $\angle$ C(9)–Fe(1)–C(10A) 92.1(12),  $\angle$ Fe(1)–C(10A)–Fe(1A) 74.5(9),  $\angle$ C(8)–Fe(1)–Fe(1A)–C(8A) 0.8,  $\angle$ Cp(centroid)–Fe(1)–Fe(2)– Cp(centroid) 1.0,  $\angle$ Cp-Cp fold angle 110.9.

drosilanes  $H_nSiR'_{4-n}$  (n = 2, 3) for 1 week.<sup>13</sup> This paper reports for the first time that compounds 3a-c with bridging carbonyl and methylene ligands can be synthesized directly by the photolysis of the corresponding dimethyl dinuclear complexes in aromatic solvents. In order to gain insight into the reaction mechanism, a labeling experiment was carried out in order to investigate the source of the bridging CH<sub>2</sub> moieties. Photolysis of  $2a \cdot d_6$  (synthesized from  $[((\eta^5 \cdot C_5H_3)_2(SiMe_2)_2)$ -Ru<sub>2</sub>(CO)<sub>4</sub>]<sup>2-</sup>·2Na<sup>+</sup> with CD<sub>3</sub>I) in benzene afforded 1a and the bridging CD<sub>2</sub> complex  $[(\eta^5 \cdot C_5H_3)_2(SiMe_2)_2]Ru_2(CO)_2(\mu$ -CO)( $\mu$ -CD<sub>2</sub>) ( $3a \cdot d_2$ ) (Scheme 2), which is evident in the presence of the same peaks as for 3a in the <sup>1</sup>H NMR spectrum, except for the two peaks at low field assigned to methylene protons. This experiment confirms that the  $\mu$ -CH<sub>2</sub> moiety in 2acomes from methyl groups attached to ruthenium. In addition, to examine whether this reaction takes place via an intra-

Scheme 2



molecular or intermolecular pathway, we carried out the photolysis of  $2a \cdot d_6$  and 2c in  $C_6D_6$ , which was followed by <sup>1</sup>H NMR. Only the corresponding  $3a \cdot d_2$  and 3c were observed, and no crossover products 3a and  $3c \cdot d_2$  were detected. This indicated that the photolysis of 2a - c in  $C_6H_6$  proceeds via an intramolecular rather than an intermolecular pathway.

On the basis of our results and those in previous related reports,<sup>14,15</sup> a plausible mechanism for the formation of **3a** is tentatively proposed in Scheme 3. First, a CO is lost from **2a** 





under UV radiation to give a 16e unsaturated ruthenium species (A); this is followed by oxidative addition of a C–H bond on methyl group attached to the other ruthenium atom to form **B**. In the next step, elimination of CH<sub>4</sub> from **B** results in intermediate **C**. Finally, a terminal CO ligand in **C** moves into a bridging position to give the final product **3a**. When photolysis of **2a** in C<sub>6</sub>D<sub>6</sub> was followed by <sup>1</sup>H NMR, the presence of a singlet at  $\delta$  0.16 ppm corresponding to CH<sub>4</sub> further supported the above mechanism. We also attempted to use CCl<sub>4</sub> to trap intermediate **B** by a halogen–hydrogen exchange reaction; unfortunately, we did not succeed in isolating the corresponding chloride.

The mechanism for the formation of **1a** seems more straightforward (Scheme 4): UV irradiation causes homolysis of the Ru–CH<sub>3</sub> bond in **2a**, the resulting intramolecular diruthenium radicals form a Ru–Ru bond to give the final product **1a**, and two methyl radicals combine to generate ethane or react with free CO released in the formation of **3a** to afford acetone. Similarly, following the photolysis of **2a** in  $C_6D_6$ , the <sup>1</sup>H NMR spectrum exhibits two distinct singlets at  $\delta$ 

Scheme 4



1.55 and 0.80 ppm corresponding to acetone and ethane protons, which further supports the above mechanism.

On the basis of the mechanism proposed above, it seems that the ratio of the two products **3a** and **1a** depends on the competition between two processes: loss of CO and homolysis of the Ru–CH<sub>3</sub> bond in **2a**. To test this hypothesis, another control experiment was carried out. Before irradiation, carbon monoxide was bubbled into a benzene solution of **2a** for 5 min. Photolysis of this solution afforded only **1a**; no **3c** was observed by TLC monitoring and column chromatography (eq 1). On the basis of experimental evidence, we suggest that the added carbon monoxide inhibits the loss of CO step which gives the bridging methylene product **3a** via intramolecular C–H bond activation. However, another possibility could not be ruled out: that the reaction of the methyl radicals with CO is faster, which facilitates the process of homolysis of the Ru–CH<sub>3</sub> bond.

$$2a \xrightarrow{C_6H_6 h\nu}_{CO(1 \text{ atm})} 1a$$
(1)

Photolysis of  $[(\eta^5-C_5H_3)_2(SiMe_2)_2]Ru_2(CO)_4Et_2$  (4). The diethyl analogues of 2a-c, which were synthesized by a method similar to that in Scheme 1, show spectroscopic (NMR, IR) characteristics similar to those of 2a. The molecular structure of 4, determined by X-ray single-crystal diffraction (Figure 5),



Figure 5. Thermal ellipsoid drawing of  $[(\eta^{5}-C_{5}H_{3})_{2}(SiMe_{2})_{2}]$ -Ru<sub>2</sub>(CO)<sub>4</sub>Et<sub>2</sub> (4) showing the labeling scheme and 30% probability ellipsoids. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)---Ru(2) 4.788(5), Ru(1)-C(8) 1.867(2), Ru(1)-C(9) 1.864(2), Ru(1)-C(10) 2.164(2), C(10)-C(11) 1.514(4), Ru(1)-Cp(centroid) 1.925; ∠C(8)-Ru(1)-C(9) 88.96(9), ∠C(8)-Ru(1)-C(10) 86.56(9), ∠C(9)-Ru(1)-C(10) 86.4(1), ∠Ru(1)-C(10)-C(11) 113.8(2), ∠Cp(centroid)-Ru(1)-Ru(2)-Cp(centroid) 4.4, ∠Cp-Cp fold angle 172.0.

shows approximate  $C_{2\nu}$  symmetry with the  $C_2$  axis passing through the midpoints of the Ru(1), Ru(1A) atoms and Si(1), Si(1A) atoms. The Ru(1)---Ru(1A) nonbonding distance (4.788 Å) is much shorter than that (5.317 Å) in **2a**, which is attributed to coordination of two Ru(CO)<sub>2</sub>Et fragments on the concave surface of the slightly bent, doubly bridged ( $\eta^5$ - $C_5H_3$ )<sub>2</sub>(SiMe<sub>2</sub>)<sub>2</sub> ligand, in comparison to that on the convex surface in **2a**.

Similarly, a solution of **4** in  $C_6D_6$  was sealed in the NMR tube, which was photolyzed for 30 min. Unlike **2a**-c, the reaction gave clean **1a**, ethane (0.80 ppm), and ethylene (5.25

ppm) by following the reaction with the <sup>1</sup>H NMR spectra. Unfortunately, we did not see a peak for hydrogen (4.47 ppm) (Scheme 5). This indicates that  $\beta$ -hydride elimination



dominates the photoreaction chemistry rather than intramolecular C–H bond activation. The same products (ethane and ethylene) have been observed from the photolysis of the mononuclear iron analogue  $(\eta^5-C_5H_5)Fe(CO)_2Et.^{14}$ 

Photolysis of  $[(\eta^5-C_5H_4)_2(EMe_2)]Ru_2(CO)_4Me_2$  (5a, E = C; **5b**, **E=Si**). To examine the importance of the double bridge in the photochemistry of 2a-c (Scheme 1), we studied the reactions of the singly bridged dicyclopentadienyl dimethyl diruthenium compounds 5a,b, which were prepared by similar methods. The IR spectrum of 5a contains the expected strong  $\nu$ (CO) absorptions (2014, 1952 cm<sup>-1</sup>) for terminal carbonyls. In the <sup>1</sup>H NMR spectrum of **5a**, the cyclopentadienyl hydrogens occur as two sets of pseudotriplets (5.24 and 5.04 ppm), consistent with an AA'BB' spin system. The Ru-Me hydrogens occur as one singlet at 0.31 ppm. Since the spectroscopic data do not provide information on the relative orientation of both metal moieties, a single-crystal X-ray structural determination of 5a was carried out (Figure 6). The crystal structure of 5a shows a three-legged piano-stool geometry around each of two Ru atoms, which are linked by the singly bridging ligand  $(\eta^5 - C_5 H_4)_2(CMe_2)$ ; each Ru atom is also bonded to two carbonyls and one methyl group. The most remarkable feature of the molecular structure is that the two  $Ru(CO)_2Me$  fragments are coordinated in an exo disposition with respect to the Cp rings of the bridging ligand and are located in a mutually cis orientation. This structural feature is quite different from that of the dichloro complex [ $(\eta^5$ - $C_5H_3)_2(SiMe_2)]Ru_2(CO)_4Cl_2$  reported by Gimeno's group,<sup>12</sup> in which two metal fragments adopt a trans arrangement. Complex 5b, as reported by Gimeno, was synthesized by a

different method: namely, by the reaction of the corresponding diiodo compound with Li[CuMe<sub>2</sub>].<sup>12</sup>

With **5a,b** in hand, our original objective was to compare their photochemistry with that of the doubly bridged complexes **2a**-c, which resulted in intramolecular C–H bond activation (Scheme 1). Surprisingly, UV irradiation of solutions of **5a,b** in benzene under a N<sub>2</sub> atmosphere results in the formation of "twisted" ruthenium methyl complexes with a cyclopentadienyl–Ru  $\sigma$  bond,  $(\eta^5, \eta^5: \eta^1-C_5H_4(EMe_2)C_5H_3)[Ru(CO)_2][Ru (CO)_2Me]$  (**6a,b**) and the phenyl complexes  $(\eta^5, \eta^5: \eta^1-C_5H_4(EMe_2)C_5H_3)[Ru(CO)_2][Ru C_5H_4(EMe_2)C_5H_3)[Ru(CO)_2][Ru(CO)_2Ph]$  (**7a,b**) (Scheme 6), the latter product resulting from C–H bond activation of benzene. Obviously, the photochemical behavior of **5a,b** is very different than that of doubly bridged analogues **2a**-c.

Complexes 6a,b were isolated as air-stable colorless crystals. The IR spectra of **6a**,**b** indicate the expected four strong  $\nu$ (CO) absorptions in the range 2038-1924 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectra of 6a,b show seven sets of peaks for protons in the two different cyclopentadienyl rings, two singlets for the different CH<sub>3</sub> protons in the CMe<sub>2</sub> or SiMe<sub>2</sub> group, and one singlet for the Ru-CH<sub>3</sub> protons. An X-ray structural determination of 6a (Figure 7) shows an asymmetrical structure: the ruthenium atom in the  $Ru(CO)_2Me$  fragment is coordinated with a Cp ligand in an  $\eta^5$  mode, and the other ruthenium atom is coordinated with two Cp rings in an  $\eta^1$  and  $\eta^5$  manner. The Ru(1)-C(10) bond distance (2.079(4) Å) in **6a** is very close to those values in its analogues (2.08 Å in  $(\eta^5, \eta^5; \eta^1)$ - $C_5H_4CMe_2C_5H_3)[Ru(CO)_2][Ru(CO)_2H],^{16}$  2.054(3) Å in  $(\eta^5,\eta^5;\eta^1-C_5H_4CMe_2C_5H_3)[Ru(CO)_2][Ru(CO)_2Cl],^{17}$  and 2.070(5) Å (the mean value) in  $(\eta^5, \eta^5: \eta^1-C_5H_4CH_2C_5H_3)$ [Ru- $(CO)_2$  [Ru $(CO)_2$ Cl]<sup>18</sup>). The five-membered ring Ru(1)-C(1)-C(6)-C(9)-C(10) adopts an envelope form, in which C(6) lies 0.12 Å out of the plane defined by the other four atoms away from Ru(2).

Complexes 7a,b were also isolated as air-stable colorless crystals, which show spectroscopic patterns similar to those for 6a,b, except that the phenyl group on ruthenium atom in 7a,b replaces the methyl group in 6a,b. The molecular structure of 7b (Figure 8) is also very similar to that of ruthenium methyl complex 6a. The Ru(1)–C(12) bond distance (2.080(7) Å) in 7b compares very well with data (2.079(4) Å) for 6a. The five-membered ring Ru(1)–C(1)–Si(1)–C(8)–C(12) adopts a stable envelope form, in which C(1) lies 0.21 Å out of the plane defined by the other four atoms away from Ru(2).



Figure 6. Thermal ellipsoid drawing of  $[(\eta^5-C_5H_4)_2(CMe_2)]Ru_2(CO)_4Me_2$  (5a) showing the labeling scheme and 30% probability ellipsoids. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)-C(9) 1.863(3), Ru(1)-C(10) 1.878(4), Ru(1)-C(11) 2.138(4), Ru(1)-Cp(centroid) 1.918, Ru(2)-C(17) 1.858(4), Ru(2)-C(18) 1.872(4), Ru(2)-C(19) 2.141(4), Ru(2)-Cp(centroid) 1.922;  $\angle C(4)-C(1)-C(12)$  105.7(2),  $\angle C(2)-C(1)-C(3)$  108.4(3),  $\angle Cp$ -Cp fold angle 95.1.





Figure 7. Thermal ellipsoid drawing of  $(\eta^5, \eta^5; \eta^1-C_5H_4CMe_2C_5H_3)$ -[Ru(CO)<sub>2</sub>][Ru(CO)<sub>2</sub>Me] (6a) showing the labeling scheme and 30% probability ellipsoids. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)–C(1) 2.249(4), Ru(1)–C(10) 2.079(4), Ru(1)–C(14) 1.885(4), Ru(1)–C(15) 1.871(5), Ru(1)–Cp(centroid) 1.900, Ru(2)–C(16) 1.863(8), Ru(2)–C(17) 1.862(5), Ru(2)–C(18) 2.154(6), Ru(2)–Cp(centroid) 1.923; ∠C(7)–C(6)–C(8) 108.8(4), ∠C(1)–C(6)–C(9) 106.4(3), ∠C(6)–C(9)–C(10) 122.3(3), ∠C(9)–C(10)–Ru(1) 116.4(3), ∠C(10)–Ru(1)–C(1) 78.3(2), ∠Ru(1)–C(1)–C(6) 115.9(3), ∠Cp-Cp fold angle 91.7.

A plausible pathway for the formation of 6a,b is proposed in Scheme 7. First, a CO dissociates from 6 under UV radiation to give a 16e unsaturated ruthenium species (D). This is followed by oxidative addition of an ortho C-H bond on the other cyclopentadienyl ring to form E; this is the key step which distinguishes the singly bridged dicyclopentadienyl dimethyl dinuclear complexes from the doubly bridged analogues. In the doubly bridged system, the unsaturated ruthenium center in intermediate A could not approach a C-H bond on the other cyclopentadienyl ring because of the rigid structure of the doubly bridged ligand; therefore, it activates an adjacent C-H bond on the methyl group attached to the other ruthenium atom. However, in the singly bridged system, due to free rotation around the E–C  $\sigma$  bond, the structure of intermediate D is more flexible, and the unsaturated ruthenium center can reach an ortho C-H bond on the other cyclopentadienyl ring, to form the stable five-membered-ring structure E. In the final step, elimination of CH<sub>4</sub> and recoordination of CO in E results in the final product **6a**,**b**.

We considered that complexes 7a,b are obtained from the C-H bond activation of benzene by 6a,b, since the complex

 $Cp*Ru(CO)_2Me$  has been described to activate the C–H bond of benzene by photolysis to give the similar Ru–phenyl complex  $Cp*Ru(CO)_2Ph.^6$  The photolysis of **6a** in benzene was carried out and indeed yielded the expected product **7a** (eq 2).

$$\mathbf{6a} \xrightarrow{\mathbf{C}_6\mathbf{H}_6, \ h\nu} \mathbf{7a} \tag{2}$$

# CONCLUSION

UV irradiation of bridged dicyclopentadienyl dimethyl dinuclear complexes in benzene affords different types of products which depend on whether there are one or two bridges. Photolysis of the doubly bridged dicyclopentadienyl dimethyl dinuclear complexes  $[(\eta^5 - C_5 H_2 R)_2 (SiMe_2)_2]$ - $M_2(CO)_4Me_2$  (2a-c) in benzene yields the corresponding bridging methylene complexes  $[(\eta^5-C_5H_2R)_2(SiMe_2)_2]-M_2(CO)_2(\mu-CO)(\mu-CH_2)$  (3a-c) and the M-M-bonded complexes  $[(\eta^5-C_5H_2R)_2(SiMe_2)_2]M_2(CO)_4$  (1a-c). However, photolysis of the singly bridged dicyclopentadienyl dimethyl diruthenium complexes  $[(\eta^5 - C_5 H_4)_2 (EMe_2)] Ru_2 (CO)_4 Me_2$  (E = C (5a); E = Si (5b)) in benzene yields the "twisted" ruthenium methyl complexes  $(\eta^5, \eta^5: \eta^1-C_5H_4(EMe_2)C_5H_3)$ [Ru- $(CO)_2$  [Ru(CO)<sub>2</sub>Me] (6a,b) and the phenyl complexes  $(\eta^5, \eta^5; \eta^1 - C_5 H_4(EMe_2)C_5 H_3)[Ru(CO)_2][Ru(CO)_2Ph]$ (7a,b). A labeling experiment confirms that the  $\mu$ -CH<sub>2</sub> moiety in 3a comes from the methyl group attached to the Ru atom. Excess carbon monoxide in solution inhibits the loss of CO to afford **3a.** Plausible mechanisms for the formation of different types of products are proposed to involve intramolecular activation of C-H bonds on different groups, which depend on the rigid structure of the doubly bridged complexes and the flexible structure of the singly bridged complexes. Photolysis of the diethyl analogue 4 only gives 1a via preferential  $\beta$ -hydride elimination. In summary, the bridged dimethyl dinuclear complexes show photochemical reactivity different from that of the mononuclear methylruthenium complex Cp\*Ru- $(CO)_2$ Me in aromatic solvents. Studies of catalytic applications of the bridged dicyclopentadienyl dimethyl dinuclear complexes in organic reactions are in progress.

# EXPERIMENTAL SECTION

**General Considerations.** Schlenk and vacuum line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under nitrogen prior to use. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV400 instrument at room temperature with TMS as internal standard. IR spectra were recorded as KBr disks on a Nicolet 560 ESP FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. Photolyses were conducted with a 250 W high-pressure Hg lamp with the reaction vessel in an ice–water bath. The complexes  $[(\eta^5-C_5H_2R)_2(SiMe_2)_2]$ - $M_2(CO)_4$  (1a–c),<sup>19–21</sup>  $[(\eta^5-C_5H_4)_2(CMe_2)]Ru_2(CO)_4$ <sup>16</sup> and  $[(\eta^5-C_5H_4)_2(SiMe_2)]Ru_2(CO)_4$ <sup>17</sup> were prepared by literature methods.



**Figure 8.** Thermal ellipsoid drawing of  $(\eta^{5},\eta^{5}:\eta^{1}-C_{5}H_{4}SiMe_{2}C_{5}H_{3})[Ru(CO)_{2}][Ru(CO)_{2}Ph]$  (7b) showing the labeling scheme and 30% probability ellipsoids. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)–C(1) 2.236(7), Ru(1)–C(12) 2.080(7), Ru(1)–C(19) 1.894(9), Ru(1)–C(20) 1.87(1), Ru(1)–Cp(centroid) 1.892, Ru(2)–C(13) 2.095(8), Ru(2)–C(21) 1.853(9), Ru(2)–C(22) 1.871(9), Ru(2)–Cp(centroid) 1.923;  $\angle C(6)-Si(1)-C(7)$  110.6(5),  $\angle C(1)-Si(1)-C(8)$  98.6(4),  $\angle Si(1)-C(8)-C(12)$  119.7(6),  $\angle C(8)-C(12)-Ru(1)$  121.0(5),  $\angle C(12)-Ru(1)-C(1)$  84.2(3),  $\angle Ru(1)-C(1)-Si(1)$  115.5(3),  $\angle Cp$ -Cp fold angle 83.4.

Scheme 7



**Synthesis of**  $[(\eta^5-C_5H_3)_2(SiMe_2)_2]Ru_2(CO)_4Me_2$  (2a). A solution of 1a (100.0 mg, 0.18 mmol) in THF (40 mL) was added to Na/Hg (50 mg/2 mL) and THF (20 mL). After the mixture was stirred for 20 h at ambient temperature, the resulting solution was cannulated from the amalgam layer and added to a solution of iodomethane (57 mg, 0.40 mmol) in THF (20 mL). The resulting solution was stirred for 4 h; volatiles were removed under reduced pressure, and the residue was chromatographed on an alumina column. Elution with petroleum ether developed a colorless band. After vacuum removal of the solvents from the above eluate, the residue was recrystallized from *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> (1/1) at -10 °C to afford **2a** (48 mg, 46%) as colorless crystals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  5.42 (t, *J* = 2.4 Hz, 2H, C<sub>5</sub>H<sub>3</sub>), 0.34 (s, 6H, Si(CH<sub>3</sub>)), 0.32 (s, 6H, Si(CH<sub>3</sub>)). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>C<sub>6</sub>):  $\delta$  4.81 (t, *J* = 2.4 Hz, 2H, C<sub>5</sub>H<sub>3</sub>), 4.73 (d, *J* = 2.4 Hz, 4H, C<sub>5</sub>H<sub>3</sub>), 0.58 (s, 6H, Si(CH<sub>3</sub>)), 0.50 (s, 6H, Si(CH<sub>3</sub>)), 0.09 (s, 6H, Ru(CH<sub>3</sub>)). IR ( $\nu_{CO}$ )

KBr): 2020 (s), 1957 (s), 1941 (s) cm<sup>-1</sup>. Anal. Calcd for  $C_{20}H_{24}O_4Ru_2Si_2$ : C, 40.94; H, 4.12. Found: C, 40.73; H, 4.06.

**Synthesis of** [( $\eta^5$ -C<sub>5</sub>H<sub>2</sub><sup>t</sup>Bu)<sub>2</sub>(SiMe<sub>2</sub>)<sub>2</sub>]Ru<sub>2</sub>(CO)<sub>4</sub>Me<sub>2</sub> (2b). When 1b (100 mg, 0.15 mmol) was reacted with Na/Hg and then iodomethane (45 mg, 0.32 mmol) in THF, 2b (40 mg, 38%, colorless crystals) was obtained, using the same method as in the preparation of 2a. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 5.38 (s, 4H, C<sub>5</sub>H<sub>2</sub>), 1.23 (s, 18H, C(CH<sub>3</sub>)), 0.52 (s, 6H, Si(CH<sub>3</sub>)), 0.40 (s, 6H, Si(CH<sub>3</sub>)), 0.39 (s, 6H, Ru(CH<sub>3</sub>)). IR ( $\nu_{CO}$ ): 2013 (s), 1959 (s), 1936 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>28</sub>H<sub>40</sub>O<sub>4</sub>Ru<sub>2</sub>Si<sub>2</sub>: C, 48.12; H, 5.77. Found: C, 48.25; H, 5.61.

**Synthesis of**  $[(\eta^5-C_5H_3)_2(SiMe_2)_2]Fe_2(CO)_4Me_2$  (2c). When 1c (100 mg, 0.21 mmol) was reacted with Na/Hg and then iodomethane (64 mg, 0.45 mmol) in THF, 2c (55 mg, 52%, yellow crystals) was obtained, using the same method as in the preparation of 2a. <sup>1</sup>H NMR (400 MHz, CDCl\_3):  $\delta$  4.95 (t, 2H, C<sub>5</sub>H<sub>3</sub>), 4.90 (d, 4H, C<sub>5</sub>H<sub>3</sub>), 0.66 (s, 6H, Si(CH<sub>3</sub>)), 0.25 (s, 6H, Fe(CH<sub>3</sub>)), 0.21 (s, 6H, Si(CH<sub>3</sub>)). IR ( $\nu_{CO}$ ): 2009 (s), 1952 (s), 1937 (s)) cm<sup>-1</sup>. Anal. Calcd for C<sub>20</sub>H<sub>24</sub>Fe<sub>2</sub>O<sub>4</sub>Si<sub>2</sub>: C, 48.40; H, 4.87. Found: C, 48.57; H, 4.66.

Photolysis of 2a in Benzene. A solution of 2a (20 mg, 0.03 mmol) in benzene (5 mL) was irradiated with UV light for 4 h. Solvent was pumped off from the resulting yellow solution, and the residue was chromatographed on an alumina column using petroleum ether/ $CH_2Cl_2$  (6/1) as eluent; a yellow band was eluted and collected. Then, another yellow band was eluted with petroleum ether-CH2Cl2 (4/1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> (1/1)at -10 °C. From the first fraction, 6 mg (32%) of yellow crystalline 1a was obtained. From the second fraction, 8 mg (43%) of yellow crystalline 3a was obtained. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.77 (d, J = 2.0 Hz, 1H,  $\mu$ -CH<sub>2</sub>), 6.64 (d, J = 2.0 Hz, 1H,  $\mu$ -CH<sub>2</sub>), 6.02 (t, 2H, C<sub>5</sub>H<sub>3</sub>), 5.65 (dd, 2H, C<sub>5</sub>H<sub>3</sub>), 5.61 (dd, 2H, C<sub>5</sub>H<sub>3</sub>), 0.76 (s, 3H, Si(CH<sub>3</sub>)), 0.61 (s, 3H, Si(CH<sub>3</sub>)), 0.49 (s, 3H, Si(CH<sub>3</sub>)), 0.48 (s, 3H, Si(CH<sub>3</sub>)). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  -3.01, -2.14, 3.07, 3.80 (Si(CH<sub>3</sub>)), 91.47, 92.79, 94.25, 107.24, 112.05 (Cp), 106.02 (µ-CH<sub>2</sub>), 202.28, 205.00 (CO). IR ( $\nu_{CO}$ ): 1976 (s), 1942 (s), 1781 (s) cm<sup>-</sup> Anal. Calcd for C<sub>18</sub>H<sub>20</sub>O<sub>3</sub>Ru<sub>2</sub>Si<sub>2</sub>: C, 39.84; H, 3.71. Found: C, 40.03; H. 7.62

**Photolysis of 2b in Benzene.** A solution of **2b** (20 mg, 0.03 mmol) in benzene (5 mL) was irradiated with UV light for 4 h. Using the same method as in the photolysis of **2a**, **1b** (4 mg, 21%, yellow

crystals) and **3b** (5 mg, 27%, yellow crystals) were obtained. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.67 (d, J = 2.0 Hz, 1H,  $\mu$ -CH<sub>2</sub>), 6.56 (d, J = 2.0 Hz, 1H,  $\mu$ -CH<sub>2</sub>), 5.49 (d, J = 1.2 Hz, 2H, C<sub>5</sub>H<sub>2</sub>), 5.46 (d, J = 1.2 Hz, 2H, C<sub>3</sub>H<sub>2</sub>), 1.33 (s, 18H, C(CH<sub>3</sub>)), 0.72 (s, 3H, Si(CH<sub>3</sub>)), 0.56 (s, 3H, Si(CH<sub>3</sub>)), 0.46 (s, 3H, Si(CH<sub>3</sub>)), 0.45 (s, 3H, Si(CH<sub>3</sub>)). IR ( $\nu$ <sub>CO</sub>): 1980 (s), 1962 (s), 1937 (s), 1796 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>26</sub>H<sub>36</sub>O<sub>3</sub>Ru<sub>2</sub>Si<sub>2</sub>: C, 47.69; H, 5.54. Found: C, 47.55; H, 5.62.

**Photolysis of 2c in Benzene.** A solution of **2c** (20 mg, 0.04 mmol) in benzene (5 mL) was irradiated with UV light for 8 h. Using the same method as in the photolysis of **2a**, **1c** (7 mg, 37%, dark green crystals) and **3c** (2 mg, 11%, red crystals) were obtained. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.05 (m, 1H, μ-CH<sub>2</sub>), 6.68 (m, 1H, μ-CH<sub>2</sub>), 5.68 (m, 2H, C<sub>5</sub>H<sub>3</sub>), 5.63 (m, 2H, C<sub>5</sub>H<sub>3</sub>), 5.32 (m, 2H, C<sub>5</sub>H<sub>3</sub>), 0.40 (s, 12H, Si(CH<sub>3</sub>)). IR ( $\nu_{CO}$ ): 1968 (s), 1936 (s), 1769 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>18</sub>H<sub>20</sub>Fe<sub>2</sub>O<sub>3</sub>Si<sub>2</sub>: C, 47.81; H, 4.46. Found: C, 47.95; H, 4.62.

Photolysis of 2a and CO in Benzene. A solution of 2a (20 mg, 0.03 mmol) in benzene (5 mL) was bubbled with CO for 5 min and then photolyzed with UV light for 2 h. Using the same method as in the photolysis of 2a, only 1a (10 mg, 53%, yellow crystals) was obtained.

**Synthesis of** [( $\eta^5$ -C<sub>5</sub>H<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub>)<sub>2</sub>]Ru<sub>2</sub>(CO)<sub>4</sub>Et<sub>2</sub> (4). When 1a (100 mg, 0.15 mmol) was reacted with Na/Hg and then iodoethane (50 mg, 0.32 mmol) in THF, 2b (72 mg, 65%, colorless crystals) was obtained, using the same method as in the preparation of 2a. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  5.38 (t, J = 2.4 Hz, 2H, C<sub>5</sub>H<sub>3</sub>), 5.32 (d, J = 2.4 Hz, 4H, C<sub>5</sub>H<sub>3</sub>), 1.76 (q, J = 7.6 Hz, 4H, CH<sub>2</sub>CH<sub>3</sub>), 1.35 (t, J = 7.6 Hz, 6H, CH<sub>2</sub>CH<sub>3</sub>), 0.54 (s, 6H, Si(CH<sub>3</sub>)), 0.31 (s, 6H, Si(CH<sub>3</sub>)). IR ( $\nu_{CO}$ ): 2020 (s), 1999 (s), 1960 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>28</sub>O<sub>4</sub>Ru<sub>2</sub>Si<sub>2</sub>: C, 42.98; H, 4.59. Found: C, 42.71; H, 4.37.

**Photolysis of 4 in Benzene.** A solution of 4 (20 mg, 0.03 mmol) in benzene (5 mL) was photolyzed with UV light for 4 h. Using the same method as in the photolysis of 2a, only 1a (12 mg, 66%, yellow crystals) was obtained.

**Synthesis of**  $[(\eta^5-C_5H_4)_2(CMe_2)]Ru_2(CO)_4Me_2$  (5a). When the complex  $[(\eta^5-C_5H_4)_2(CMe_2)]Ru_2(CO)_4$  (200 mg, 0.41 mmol) was reacted with Na/Hg and then iodomethane (120 mg, 0.85 mmol) in THF, 5a (110 mg, 52%, white wax solid) was obtained, using the same method as in the preparation of 2a. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  5.24 (t, J = 2.4 Hz, 4H, Cp-H), 5.04 (t, J = 2.4 Hz, 4H, Cp-H), 1.49 (s, 6H, C(CH<sub>3</sub>)), 0.31 (s, 6H, Ru(CH<sub>3</sub>)). IR ( $\nu_{CO}$ ): 2014 (s), 1952 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>19</sub>H<sub>20</sub>O<sub>4</sub>Ru<sub>2</sub>: C, 44.35; H, 3.92. Found: C, 44.54; H, 4.15.

Synthesis of  $[(\eta^5-C_5H_4)_2(SiMe_2)]Ru_2(CO)_4Me_2$  (5b). When the complex  $[(\eta^5-C_5H_4)_2(SiMe_2)]Ru_2(CO)_4$  (200 mg, 0.40 mmol) was reacted with Na/Hg and then iodomethane (120 mg, 0.85 mmol) in THF, 5b (125 mg, 59%, white solid) was obtained, using the same method as in the preparation of 2a.

Photolysis of 5a in Benzene. A solution of 5a (50 mg, 0.10 mmol) in benzene (10 mL) was photolyzed with UV light for 3 h. Using the same method as in the photolysis of 2a, 6a (27 mg, 56%, colorless crystals) and 7a (6 mg, 11%, colorless solid) were obtained. Data for **6a** are as follows. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  5.67 (m, 1H, Cp-H), 5.57 (m, 1H, Cp-H), 5.38 (m, 1H, Cp-H), 5.26 (m, 1H, Cp-H), 5.04 (m, 1H, Cp-H), 4.78 (m, 1H, Cp-H), 4.68 (m, 1H, Cp-H), 1.50 (s, 3H, C(CH<sub>3</sub>)), 1.47 (s, 3H, C(CH<sub>3</sub>)), 0.26 (s, 3H, Ru(CH<sub>3</sub>)). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 5.00 (dd, 1H, Cp-H), 4.73 (m, 1H, Cp-H), 4.70 (m, 1H, Cp-H), 4.49 (dd, 1H, Cp-H), 4.43 (m, 1H, Cp-H), 4.39 (t, 1H, Cp-H), 4.32 (dd, 1H, Cp-H), 1.18 (s, 3H,  $C(CH_3)$ ), 0.93 (s, 3H,  $C(CH_3)$ ), 0.67 (s, 3H,  $Ru(CH_3)$ ). IR ( $\nu_{CO}$ ): 2038 (s), 1990 (s), 1974 (s), 1924 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>18</sub>H<sub>16</sub>O<sub>4</sub>Ru<sub>2</sub>: C, 43.37; H, 3.24. Found: C, 43.43; H, 3.07. Data for 7a are as follows. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.46 (m, 2H, Ph-H), 6.94 (m, 3H, Ph-H), 5.73 (m, 1H, Cp-H), 5.60 (m, 1H, Cp-H), 5.39 (m, 1H, Cp-H), 5.28 (m, 1H, Cp-H), 5.21 (m, 1H, Cp-H), 4.81 (m, 1H, Cp-H), 4.75 (m, 1H, Cp-H), 1.52 (s, 3H, C(CH<sub>3</sub>)), 1.48 (s, 3H,  $C(CH_3)$ ). IR ( $\nu_{CO}$ ): 2023 (s), 1998 (s), 1972 (s), 1941 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>23</sub>H<sub>18</sub>O<sub>4</sub>Ru<sub>2</sub>: C, 49.28; H, 3.24. Found: C, 49.37; H, 3.011.

**Photolysis of 5b in Benzene.** A solution of **5b** (50 mg, 0.09 mmol) in benzene (10 mL) was photolyzed with UV light for 0.5 h.

Using the same method as in the photolysis of **2a**, **6b** (21 mg, 43%, colorless crystals) and **7b** (5 mg, 9%, colorless crystals) were obtained. Data for **6b** are as follows. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  5.72 (m, 1H, Cp-H), 5.55 (m, 1H, Cp-H), 5.42 (m, 1H, Cp-H), 5.20 (m, 1H, Cp-H), 5.15 (m, 1H, Cp-H), 4.96 (m, 1H, Cp-H), 0.50 (s, 3H, Si(CH<sub>3</sub>)), 0.42 (s, 3H, Si(CH<sub>3</sub>)), 0.25 (s, 3H, Ru(CH<sub>3</sub>)). IR ( $\nu_{CO}$ ): 2037 (s), 1993 (s), 1973 (s), 1929 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>17</sub>H<sub>16</sub>O<sub>4</sub>Ru<sub>2</sub>Si: C,39.68; H, 3.13. Found: C, 39.73; H, 3.09. Data for 7b are as follows. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.45 (m, 2H, Ph-H), 6.93 (m, 3H, Ph-H), 5.80 (m, 1H, Cp-H), 5.60 (m, 1H, Cp-H), 5.41 (m, 3H, Cp-H), 5.16 (m, 1H, Cp-H), 4.99 (m, 1H, Cp-H), 0.52 (s, 3H, Si(CH<sub>3</sub>)), 0.42 (s, 3H, Si(CH<sub>3</sub>)). IR ( $\nu_{CO}$ ): 2026 (s), 2001 (s), 1970 (s), 1945 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>18</sub>O<sub>4</sub>Ru<sub>2</sub>Si: C, 45.83; H, 3.15. Found: C, 45.65; H, 3.23.

Photolysis of 6a in Benzene. A solution of 6a (20 mg, 0.04 mmol) in benzene (5 mL) was photolyzed with UV light for 4 h. Using the same method as in the photolysis of 2a, 7a (7 mg, 31%, colorless solid) was obtained.

**Crystallographic Studies.** Single crystals of complexes **2a,c**, **3a,c**, **4**, **5a**, **6a**, and **7b** suitable for X-ray diffraction were obtained by crystallization from *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> (1/1). Data collection was performed on a Bruker SMART 1000 diffractometer, using graphitemonochromated Mo K $\alpha$  radiation ( $\omega$ -2 $\theta$  scans,  $\lambda$  = 0.71073 Å). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by fullmatrix least squares. All calculations were using the SHELXTL-97 program system. The crystal data and summary of X-ray data collection are presented in Tables 1 and 2 in the Supporting Information.

## ASSOCIATED CONTENT

#### Supporting Information

Crystallographic data tables and CIF files giving crystallographic details for complexes 2a,c, 3a,c, 4, 5a, 6a, and 7b. This material is available free of charge via the Internet at http:// pubs.acs.org.

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# Notes

The authors declare no competing financial interest.

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