

Heterolytic Cleavage of Dihydrogen Promoted by Sulfido-Bridged Tungsten–Ruthenium Dinuclear Complexes

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Abstract: A series of sulfido-bridged tungsten–ruthenium dinuclear complexes $\text{Cp}^*\text{W}(\mu\text{-S})_3\text{RuX}(\text{PPh}_3)_2$ (**4a**; X = Cl, **4b**; X = H), $\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{RuX}(\text{PPh}_3)_2$ (**5a**; X = Cl, **5b**; X = H), and $\text{Cp}^*\text{W}(\text{NPh})(\mu\text{-S})_2\text{RuX}(\text{PPh}_3)_2$ (**6a**; X = Cl, **6b**; X = H) have been synthesized by the reactions of $(\text{PPh}_4)[\text{Cp}^*\text{W}(\text{S})_3]$ (**1**), $(\text{PPh}_4)[\text{Cp}^*\text{W}(\text{O})(\text{S})_2]$ (**2**), and $(\text{PPh}_4)[\text{Cp}^*\text{W}(\text{NPh})(\text{S})_2]$ (**3**), with $\text{RuClX}(\text{PPh}_3)_3$ (X = Cl, H). The heterolytic cleavage of H_2 was found to proceed at room temperature upon treating **5a** and **6a** with $\text{NaBAR}^{\text{F}}_4$ ($\text{Ar}^{\text{F}} = 3, 5\text{-C}_6\text{H}_3\text{-}(\text{CF}_3)_2$) under atmospheric pressure of H_2 , which gave rise to $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2](\text{BAR}^{\text{F}}_4)$ (**7a**) and $[\text{Cp}^*\text{W}(\text{NHPH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2](\text{BAR}^{\text{F}}_4)$ (**8**), respectively. When $\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{Ru}(\text{PPh}_3)_2\text{H}$ (**5b**) was treated with a Brønsted acid, $[\text{H}(\text{OEt}_2)_2](\text{BAR}^{\text{F}}_4)$ or HOTf, protonation occurred exclusively at the terminal oxide to give $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2](\text{X})$ (**7a**; X = BAR^{F}_4 , **7b**; X = OTf), while the hydride remained intact. The analogous reaction of $\text{Cp}^*\text{W}(\mu\text{-S})_3\text{Ru}(\text{PPh}_3)_2\text{H}$ (**4b**) led to immediate evolution of H_2 . Selective deprotonation of the hydroxyl group of **7a** or **7b** was induced by NEt_3 and **4b**, generating $\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{Ru}(\text{PPh}_3)_2\text{H}$ (**5b**). Evolution of H_2 was also observed for the reactions of **7a** or **7b** with CH_3CN to give $[\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{Ru}(\text{CH}_3\text{CN})(\text{PPh}_3)_2](\text{X})$ (**11a**; X = BAR^{F}_4 , **11b**; X = OTf). We examined the H/D exchange reactions of **4b**, **5b**, and **7a** with D_2 and CH_3OD , and found that facile H/D scrambling over the W–OH and Ru–H sites occurred for **7a**. Based on these experimental results, the mechanism of the heterolytic H_2 activation and the reverse H_2 evolution reactions are discussed.

Introduction

Activation of molecular hydrogen is one of the fundamentally important reactions in organometallic chemistry,¹ and homolytic cleavage of the H–H bond to give two hydrides can be achieved via oxidative addition reactions on electron-rich transition metals. However, the splitting of dihydrogen into a hydride and a proton is less common. Heterolytic H–H cleavage has been found to occur on mononuclear complexes in two ways; (1) deprotonation of η^2 -coordinated H_2 with external or internal bases,^{2–4} and (2) addition of H_2 to M–E bonds (E = N, O, S) to generate M–H and E–H bonds.⁵ For instance, the acidic dihydrogen in $[\text{Cp}^*\text{Re}(\text{CO})(\text{NO})(\text{H}_2)]^+$ can be deprotonated by diethyl ether,^{3b} and the ruthenium complex with a tethered

N-donor group, $[(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{NMe}_2)\text{Ru}(\text{dppm})](\text{BF}_4)$, activates H_2 (60 atm) to afford $[(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{NHMe}_2)\text{RuH}(\text{dppm})](\text{BF}_4)$, presumably via coordination of H_2 at Ru and the subsequent intramolecular deprotonation.^{4c} Dihydrogen is reversibly added to the Ti=S bond of a titanocene sulfido complex $\text{Cp}^*_2\text{TiS}(\text{py})$, generating $\text{Cp}^*_2\text{Ti}(\text{H})(\text{SH})$.^{5b,c} Some S-bridged dinuclear complexes are also capable of promoting heterolytic H_2 cleavage.⁶ An early example is a cationic Rh_2 complex $[\{\text{Rh}(\text{triphos})\}_2(\mu\text{-S})_2]^{2+}$ (triphos = tris(diphenylphosphinomethyl) ethane), which is converted to $[\{\text{RhH}(\text{triphos})\}_2(\mu\text{-SH})_2]^{2+}$ by

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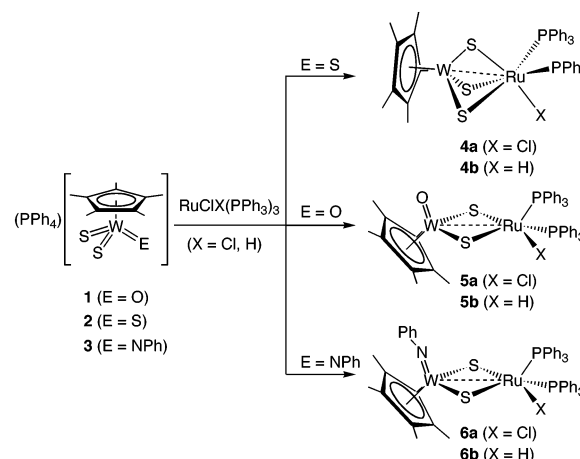
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the reaction with H_2 .^{6b} Later, a neutral Ir_2 complex $[\text{Ir}(\text{PPh}_3)_2]_2(\mu\text{-S})_2$ was shown to react with two equiv of H_2 , via homolytic and subsequent heterolytic pathways, and to eventually produce $[\text{IrH}(\text{PPh}_3)_2]_2(\mu\text{-H})(\mu\text{-S})(\mu\text{-SH})$.^{6c} More recently, the reaction of $[\text{Cp}_2\text{W}(\mu\text{-S})_2\text{Ir}(\text{PPh}_3)_2]^+$ with H_2 (10 atm) was reported to give three products, one of which was characterized as $[\text{Cp}_2\text{W}(\mu\text{-SH})_2\text{Ir}(\text{H})_2(\text{PPh}_3)_2]^+$ based on the ^{31}P NMR spectra.^{6d}

The heterolytic cleavage of H_2 has also been regarded as a key step in the metalloenzymatic reactions of hydrogenases, the active sites of which consist of the sulfur-bridged Fe/Fe and Fe/Ni dinuclear centers.⁷ To provide a clue to understand the reversible processes of biological H_2 activation, it is desirable to propose model reactions of the heterolytic H_2 activation on dinuclear metal centers,⁸ in addition to build the structural models of the active sites.⁹ Soluble transition metal sulfido clusters are attractive candidates for the investigation of the mechanism of H_2 activation. However, the construction of appropriate sulfur-bridged dinuclear systems which are reactive toward molecular hydrogen remains difficult, since dinucleation reactions often give rise to less reactive products. One of the effective ways to link two different metal centers by sulfur atoms is to use transition metal sulfido complexes as precursors. We have previously synthesized a series of tungsten thio complexes such as $(\text{PPh}_4)[\text{Cp}^*\text{W}(\text{S})_3]$ (**1**), $(\text{PPh}_4)[\text{Cp}^*\text{W}(\text{O})(\text{S})_2]$ (**2**), and $(\text{PPh}_4)[\text{Cp}^*\text{W}(\text{O})(\text{S})(\text{Se})]$,¹⁰ and have demonstrated that they were convenient entries into the construction of various heterometallic sulfido clusters with Fe, Cu, Pd, Ag, and Au.¹¹

Scheme 1



Aiming to obtain reactive dinuclear sulfido complexes, the half-sandwich thio complexes of tungsten were combined with appropriate ruthenium complexes. Having both electron-rich and electron-deficient metal centers linked by sulfur atoms within a molecule, the W–Ru complexes might be anticipated to promote a new type of H_2 activation. Thus, $(\text{PPh}_4)[\text{Cp}^*\text{W}(\text{S})_3]$ (**1**), $(\text{PPh}_4)[\text{Cp}^*\text{W}(\text{O})(\text{S})_2]$ (**2**), and $(\text{PPh}_4)[\text{Cp}^*\text{W}(\text{NPh})(\text{S})_2]$ (**3**) were used as building blocks and reacted with $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{RuCl}(\text{H})(\text{PPh}_3)_3$. Here we report a series of S-bridged W–Ru dinuclear complexes obtained therefrom, and a thorough investigation of their reactivity toward H_2 and protons. To assess the mechanism of H_2 activation by the W–Ru complexes, H/D exchange reactions were also carried out with the hydrogenated products, and their deprotonation and H_2 dissociation reactions were examined.

Results and Discussion

Synthesis of S-Bridged W–Ru Complexes. A series of W–Ru dinuclear complexes were synthesized in high yield from the reactions of half-sandwich dithio- and trithio-complexes of W(VI) with phosphine/chloride complexes of Ru(II). The reactions of the tungsten trithio complex $(\text{PPh}_4)[\text{Cp}^*\text{W}(\text{S})_3]$ (**1**) with 1 equiv of $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{RuCl}(\text{H})(\text{PPh}_3)_3$ ¹² in CH_3CN at room temperature yielded the W–Ru complexes with three bridging sulfides, $\text{Cp}^*\text{W}(\mu\text{-S})_3\text{RuX}(\text{PPh}_3)_2$ (**4a**; X = Cl, **4b**; X = H), in 77% and 83% yields, respectively. The crystals obtained from a CH_2Cl_2 /hexane solution of **4a** and those from a toluene/hexane solution of **4b** were subjected to X-ray structure analysis. These compounds are moderately sensitive toward oxygen and moisture, and the combustion analysis and the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are in accord with the formulation. The two phosphine ligands at Ru are equivalent in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for both **4a** and **4b**. In the case of **4b**, a triplet signal at $\delta = -10.30$ in the ^1H NMR spectrum and the IR ν -(Ru–H) band at 1930 cm^{-1} suggest the existence of a Ru–H bond. Thus during the reactions of $(\text{PPh}_4)[\text{Cp}^*\text{W}(\text{S})_3]$ (**1**) with $\text{RuCl}(\text{X})(\text{PPh}_3)_3$ (X = Cl, H), one phosphine ligand is liberated along with the formation of PPh_4Cl , while one chloride ligand or one hydride ligand remains intact at the Ru center.

The reaction of $(\text{PPh}_4)[\text{Cp}^*\text{W}(\text{O})(\text{S})_2]$ (**2**) with $\text{RuClX}(\text{PPh}_3)_3$ (X = Cl, H) followed by a standard workup afforded the

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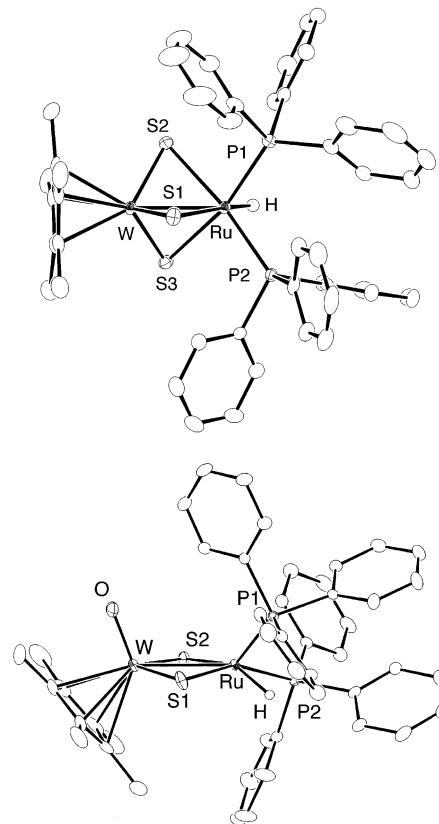
Table 1. Selected Bond Distances (Å) and Angles (deg) for $\text{Cp}^*\text{W}(\mu\text{-S})_3\text{RuX}(\text{PPh}_3)_2$ (X = Cl (**4a**), H (**4b**)) and $\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{RuX}(\text{PPh}_3)_2$ (X = Cl (**5a**), H (**5b**))

4a		4b		5a		5b	
W–Ru	2.6188(2)	W–Ru	2.6106(3)	W–Ru	2.8511(4)	W–Ru	2.8492(4)
W–S1	2.2302(7)	W–S1	2.2226(8)	W–O	1.746(4)	W–O	1.730(4)
W–S2	2.2159(7)	W–S2	2.2253(7)	W–S1	2.261(1)	W–S1	2.264(1)
W–S3	2.2314(7)	W–S3	2.2367(9)	W–S2	2.250(1)	W–S2	2.276(1)
Ru–S1	2.4079(7)	Ru–S1	2.5387(8)	Ru–S1	2.320(1)	Ru–S1	2.329(1)
Ru–S2	2.4981(8)	Ru–S2	2.4719(8)	Ru–S2	2.230(1)	Ru–S2	2.331(1)
Ru–S3	2.5056(7)	Ru–S3	2.4931(8)	Ru–Cl	2.428(1)	Ru–H	1.62(5)
Ru–Cl	2.4192(7)	Ru–H	1.56(3)	W–S1–Ru	76.96(4)	W–S1–Ru	76.67(4)
W–S1–Ru	68.63(2)	W–S1–Ru	66.11(2)	W–S2–Ru	76.98(4)	W–S2–Ru	76.39(3)
W–S2–Ru	67.19(2)	W–S2–Ru	67.29(2)				
W–S3–Ru	66.83(2)	W–S3–Ru	66.75(2)				

analytically pure W–Ru bis(μ -sulfido) complexes $\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{RuX}(\text{PPh}_3)_2$ (**5a**; X = Cl, **5b**; X = H) in 82% and 86% yields, respectively. In these dinuclear complexes, the oxo ligand does not bridge the two metal centers, as suggested by the characteristic $\nu(\text{W}=\text{O})$ bands at 895 cm^{-1} (**5a**) and 901 cm^{-1} (**5b**) in the IR spectra.¹³ The X-ray quality crystals were grown by layering hexane onto a CH_2Cl_2 solution of **5a** or onto a toluene solution of **5b**. Again, one phosphine ligand was removed from Ru during the reactions, and coordination of a chloride or a hydride ligand at Ru was retained. In a similar manner, the W–Ru complexes having a $\text{W}=\text{NPh}$ moiety, $\text{Cp}^*\text{W}(\text{NPh})(\mu\text{-S})_2\text{RuX}(\text{PPh}_3)_2$ (**6a**; X = Cl, **6b**; X = H) were synthesized using $(\text{PPh}_4)[\text{Cp}^*\text{W}(\text{NPh})(\text{S})_2]$ (**3**),¹² which were characterized by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, IR, and by FAB-mass for **6a**. Their NMR spectra resemble those of the corresponding W–Ru complexes having a terminal oxo group, **5a** and **5b**. The IR spectra are featured by the bands at 1336 cm^{-1} (**6a**) and 1346 cm^{-1} (**6b**) which are assignable to the $\text{W}=\text{NPh}$ stretching vibrations.¹⁴

There appear two doublets in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the chloride complexes, **5a** and **6a**, at room temperature, indicating that the two phosphine ligands are chemically nonequivalent. This observation is consistent with the solid-state structure of **5a** as will be shown below. On the other hand, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the hydride congeners, **5b** and **6b**, show a single peak at room temperature. However, the phosphorus signal for **5b** was found to be significantly broadened with lowering the temperature, and to split into two broad peaks at $-85\text{ }^\circ\text{C}$. Thus the site exchange of the two phosphine ligands occurs more readily for the hydride complexes.

Structures of the W–Ru Dinuclear Complexes. The X-ray structure analyses were carried out for $\text{Cp}^*\text{W}(\mu\text{-S})_3\text{RuX}(\text{PPh}_3)_2$ (**4a**; X = Cl, **4b**; X = H) and $\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{RuX}(\text{PPh}_3)_2$ (**5a**; X = Cl, **5b**; X = H), and selected geometrical parameters are summarized in Table 1. Since their molecular structures are very similar to those of **4b** and **5b**, the perspective views of only the

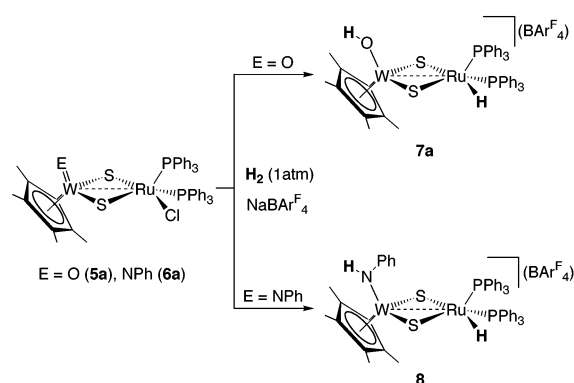
**Figure 1.** Molecular structures of $\text{Cp}^*\text{W}(\mu\text{-S})_3\text{RuH}(\text{PPh}_3)_2$ (**4b**) (top) and $\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2$ (**5b**) (bottom).

latter two hydride complexes are shown in Figure 1. The hydrides were located at reasonable positions in the last Fourier maps, and they are included in the drawings. For **4a** and **4b**, three sulfur atoms bridge the Cp^*W unit and Ru, and the slightly distorted octahedral geometry at Ru is completed by coordination of two phosphine ligands and a chloride (or a hydride). In the case of **5a** and **5b**, the two metal centers are linked by two sulfur atoms, and the Ru site assumes a square pyramidal geometry with one phosphine at the apical site. Consequently, the two phosphines are nonequivalent in the solid state, while those of **5b** are fluxional in solution on the $^{31}\text{P}\{^1\text{H}\}$ NMR time scale. The WS_2Ru rhomboids are slightly puckered, where the dihedral angles between the WS_2 and RuS_2 planes are 18.5° (**5a**) and 10.5° (**5b**). The apical phosphine coordination for the hydride complex **5b** tilts notably toward the less bulky hydride position. Thus the W–Ru–P1 angle of 120.0° for **5b** is large, compared with the corresponding angle of 100.7° for the

- (13) (a) Faller, J. W.; Ma, Y. *Organometallics* **1988**, *7*, 559. (b) Legzdins, P.; Phillips, E. C.; Rettig, S. J.; Sánchez, L.; Trotter, J.; Yee, V. C. *Organometallics* **1988**, *7*, 1877. (c) Faller, J. W.; Ma, Y. *Organometallics* **1989**, *8*, 609. (d) Gorzelli, M.; Bock, H.; Gang, L.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1991**, *412*, 95. (e) Rau, M. S.; Kretz, C. M.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3447. (f) Rau, M. S.; Kretz, C. M.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1994**, *13*, 1624. (g) Chakraborty, D.; Bhattacharjee, M.; Krätznert, Siefken, R.; Roesky, H. W.; Uson, I.; Schmidt, H.-G. *Organometallics*, **1999**, *18*, 106. (14) (a) Glassman, T. E.; Vale, M. G.; Schrock, R. R. *Organometallics* **1991**, *10*, 4046. (b) Legzdins, P.; Phillips, E. C.; Rettig, S. J.; Trotter, J.; Veltheer, J. E.; Yee, V. C. *Organometallics* **1992**, *11*, 3104.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2][\text{BAr}^{\text{F}}_4]$ (**7a**·2C₄H₁₀O) and $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2](\text{OTf})$ (**7b**)

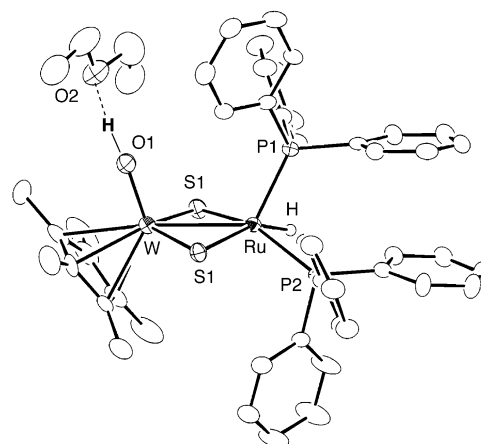
7a				7b			
W–Ru	2.8124(5)	Ru–H	1.56(6)	W–Ru	2.8306(4)	Ru–H	1.68(8)
W–O1	1.829(4)	O1–O2	2.580(7)	W–O1	1.858(4)	O1–O2	2.66(1)
W–S1	2.248(1)	W–S1–Ru	75.68(4)	W–S1	2.249(1)	W–S1–Ru	76.49(3)
W–S2	2.232(1)	W–S2–Ru	76.84(4)	W–S2	2.233(1)	W–S2–Ru	77.30(4)
Ru–S1	2.335(1)			Ru–S1	2.322(1)		
Ru–S2	2.291(1)			Ru–S2	2.299(1)		

Scheme 2

chloride congener **5a**. The W=O bond lengths of 1.746(4) and 1.730(4) Å are as expected for multiple bonding.¹⁴

The W–S distances of 2.2159(7) – 2.2367(9) for **4a** and **4b** are similar to those of $\text{Cp}^*\text{W}(\text{S})(\mu\text{-S})_2\text{FeCl}_2$ (W– μS ; av. 2.25 Å),¹⁵ and fall between the W–S (thiolate) single bond lengths of half-sandwich thiolate complexes of W(VI) (2.33–2.45 Å)^{10,16} and the W=S multiple bond lengths of $(\text{PPh}_4)[\text{Cp}^*\text{W}(\text{S})_3]$ (**1**) (av. 2.19 Å).^{10a} Thus, there appears to be partial W–S multiple bond character in the W–Ru dinuclear structures, and their oxidation states were assigned to be W(VI) and Ru(II). For **4b**, the Ru–S1 bond which is trans to the hydride ligand is 0.046–0.067 Å longer than the other two Ru–S bonds, which accounts for the strong trans influence of hydride.¹⁷ On the other hand, the Ru–S bonds of **5a** and **5b** are substantially short, while the W–S bonds are elongated, compared with those of the triply bridged structures of **4a** and **4b**. This may have something to do with the different coordination numbers of Ru, and the coordinatively unsaturated Ru centers of **5a** and **5b** could be stabilized by π -interactions with the bridging sulfides. The observed W–Ru distances indicate dative bonding between the electron rich Ru(II) center and the electron deficient W(VI) center, where the triply bridged W–Ru bonds of **4a** and **4b** are much shorter and the W–S–Ru angles are more acute.

Activation of H₂ by the W–Ru Complexes. Considering the coordinative unsaturation of Ru in $\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{RuX}(\text{PPh}_3)_2$ (**5a**; X = Cl, **5b**; X = H), their reactions with H₂ were examined. There was no sign of reaction upon heating a CH₂Cl₂ solution of **5a** or **5b** under 10 atm of H₂. However, when **5a** was treated in CH₂Cl₂ with NaBAr^F₄ (Ar^F = 3,5-(CF₃)₂C₆H₃)¹⁸ under 1 atm of H₂, we noticed a quick color change of the

**Figure 2.** Structure of the complex cation of $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2][\text{BAr}^{\text{F}}_4]\cdot 2\text{C}_4\text{H}_{10}\text{O}$ (**7a**·2C₄H₁₀O). The hydrogen atom bound to Ru was crystallographically located, whereas the hydroxyl hydrogen is added at an appropriate position in the figure in order to emphasize the hydrogen bonding with the ether molecule.

solution from dark green to purple. The reaction was complete within five minutes at room temperature, and $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2][\text{BAr}^{\text{F}}_4]$ (**7a**) was isolated as a purple powder in 84% yield. Thus in this reaction, H₂ splits into the hydridic center attached to Ru and the protic center at the oxo ligand, where the formal oxidation states of the metal atoms are unchanged. The imido analogue of **5a**, $\text{Cp}^*\text{W}(\text{NPh})(\mu\text{-S})_2\text{RuCl}(\text{PPh}_3)_2$ (**6a**), was also found to activate atmospheric H₂ under the presence of NaBAr^F₄, resulting in the formation of $[\text{Cp}^*\text{W}(\text{NHPh})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2][\text{BAr}^{\text{F}}_4]$ (**8**).

Complexes **7a** and **8** were characterized spectroscopically, and the structure of **7a** was determined by crystallographic analysis. Their ¹H NMR spectra show resonances for W–OH and Ru–H at δ 9.07 and –3.37 for **7a**, and at δ 5.69 and δ –3.98 for **8**. Disappearance of the characteristic $\nu(\text{W}=\text{O})$ band and appearance of a $\nu(\text{Ru–H})$ band at 2019 cm^{–1} and a $\nu(\text{O–H})$ band at 3453 cm^{–1} in the IR spectrum of **7a** also agree with the formation of the W–OH and Ru–H moieties. As in the case of **5b**, two phosphines in **7a** and **8** are equivalent in the ³¹P{¹H} NMR spectra at room temperature, due to a facile site exchange at Ru.

Single crystals of $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2][\text{BAr}^{\text{F}}_4]$ (**7a**) suitable for X-ray diffraction study were obtained from an ether solution at –78 °C. The complex was crystallized with ether molecules as solvent of crystallization, and there was no short contact between the complex cation and the BAr^F₄ anion. Each ether molecule is situated in the neighborhood of the hydroxyl group of the complex cation, with O–O separation of 2.58 Å, indicating the WOH–O(ether) hydrogen bonding. The cation of **7a** with the hydrogen-bonded ether is shown in Figure 2, and the selected geometrical parameters are listed in Table 2.

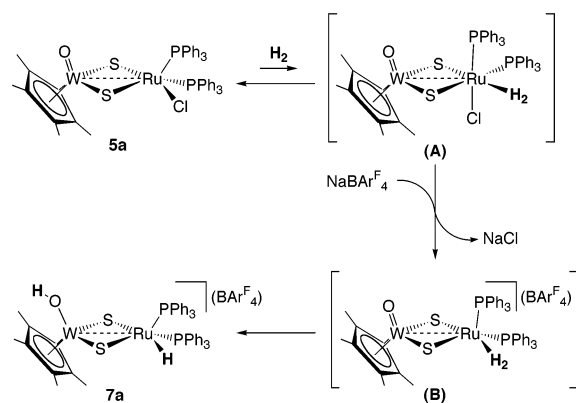
(15) Kawaguchi, H.; Tatsumi, K., unpublished result.

(16) (a) O'Regan, M. B.; Liu, A. H.; Finch, W. C.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 4331. (b) Brunet, N.; Legzdins, P.; Trotter, J.; Yee, V. C. *Acta Crystallogr. Sect. C*, **1995**, *51*, 193. (c) Cao, R.; Tatsumi, K. *Inorg. Chem.* **2002**, *41*, 4102.

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Scheme 3



The dinuclear core geometry is very similar to those of $\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2$ (**5b**), except for the W–O distance. The W–O bond length of 1.829(4) Å is substantially longer than the W=O distance of 1.746(4) Å in **5a**, which confirms that the oxygen atom attached to W is no longer a terminal oxo ligand but a hydroxyl group. It may be worth noting that the W–S bond lengths of **7a** are slightly shorter by 0.030 Å (av.) than those of **5a**. The shortening of the W–S bonds reflects the lesser extent of π donation to W from the hydroxy ligand than that from oxo ligand, thereby allowing stronger π donation from the bridging sulfides.

Intriguingly, neither $\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{RuCl}(\text{PPh}_3)_2$ (**5a**) nor $\text{Cp}^*\text{W}(\text{NPh})(\mu\text{-S})_2\text{RuCl}(\text{PPh}_3)_2$ (**6a**) reacts with NaBARF_4 alone under N_2 . As was mentioned earlier, **5a** (and **6a**) does not react with H_2 in the absence of NaBARF_4 , even under 10 atm H_2 . Thus both NaBARF_4 and H_2 must be present for the reaction to proceed, although the H_2 activation by **5a** and **6a** would presumably occur after the removal of chloride from the Ru site. The salt NaBARF_4 does not react with H_2 under this condition. In contrast, the tris(μ -sulfido) complex $\text{Cp}^*\text{W}(\mu\text{-S})_3\text{RuCl}(\text{PPh}_3)_2$ (**4a**) reacts readily with NaBARF_4 in the absence of H_2 to give a dark brown solid. Although we were unable to characterize the dark brown product, it is interesting to note that the reaction of **4a** with NaBARF_4 under atmospheric H_2 produces a solid, the ^1H NMR spectrum of which is very similar to that of the above dark brown product. The difference between **4a** and **5a** is the coordination number of Ru, and the chloride at the octahedral Ru seems to be more labile. Taking these observations into account, we propose that the reaction of **5a** with $\text{NaBARF}_4/\text{H}_2$ is initiated by coordination of H_2 to the pentacoordinate Ru as shown in Scheme 3. The resulting octahedral H_2 complex, designated as (A) in Scheme 3, would have facilitated dissociation of chloride in the reaction with NaBARF_4 . Removal of chloride from A leads to the square-pyramidal intermediate with $\eta^2\text{-H}_2$ (B), and subsequently the H_2 molecule splits into the Ru–H and W–OH forms in **7a**. Formation of $\eta^2\text{-H}_2$ complexes prior to the heterolytic H_2 cleavage has occasionally been speculated.^{3b,4, 5c} The mechanism of the H_2 -splitting process from B to **7a** will be discussed below.

Protonation Reactions of the Hydride Complexes. The hydridic centers of transition metal complexes often react with protons (H^+), and evolve H_2 . Contrary to this preconception, we found the oxo ligand of $\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2$ (**5b**) to be protonated when it was treated in THF with an equimolar amount of $[\text{H}(\text{OEt}_2)_2][\text{BARF}_4]$ or HOTf. $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2][\text{BARF}_4]$ (**7a**) and $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2](\text{OTf})$

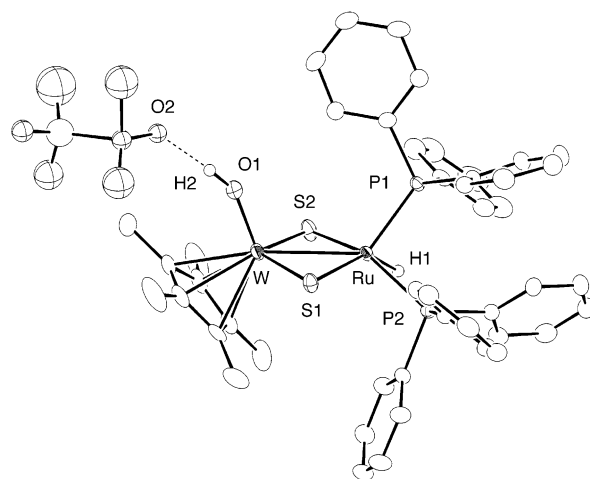
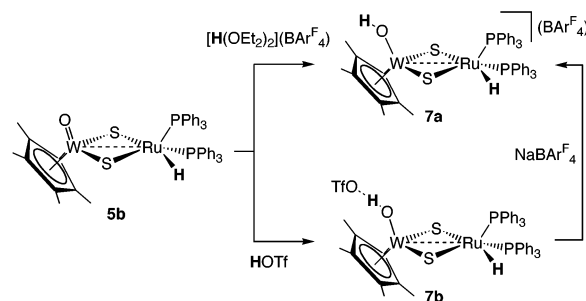


Figure 3. Structure of $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2](\text{OTf})$ (**7b**). The hydrogen bond to Ru was located by the X-ray analysis, and the hydroxyl hydrogen was put at a calculated position.

(**7b**) were isolated in 97% and 87% yields, respectively. In these reactions, the hydridic site at Ru remained intact, and no H_2 evolution was observed. Conversion of **7b** into **7a** was successful on anion exchange with NaBARF_4 in CH_2Cl_2 . The occurrence of protonation at the oxo ligand points to two significant aspects: a) W=O is a more basic site than Ru–H, and b) the OH hydrogen in **7a** or **7b** is acidic in character.

Scheme 4



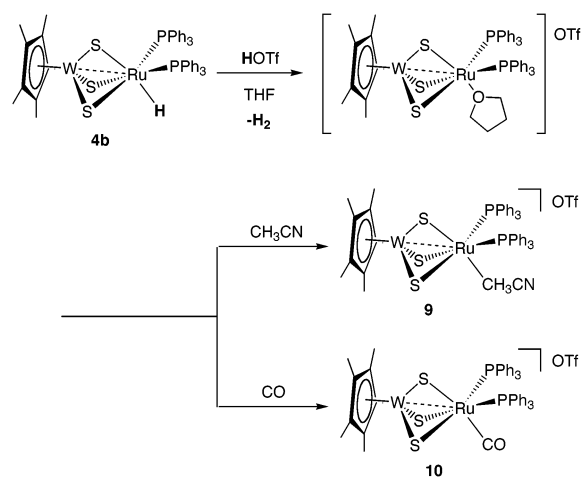
Complex **7b**, isolated as dark purple crystals, was characterized by spectroscopic data and by combustion analysis, and its structure was determined by X-ray analysis. The event of selective protonation at W=O was indicated by the disappearance of the characteristic $\nu(\text{W}=\text{O})$ band, and by the persistence of the Ru–H band at 2015 cm^{-1} in the IR spectrum. Observation of ^1H NMR resonances at δ 10.8 (W–OH) and δ –5.96 (Ru–H) is consistent with the interpretation of the IR spectrum. Similar to **7a**, there appears a single peak in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at room temperature, and the two phosphine ligands are thus fluxional. The molecular structure of **7b** is presented in Figure 3, and selected bond lengths and angles are compared with those of **7a** in Table 2. The most notable feature of the crystal structure is the short contact between the W–OH group and the anion OTf^- . The O–O separation of 2.66(1) Å is indicative of hydrogen bonding. The W–O bond length of 1.858(4) Å is obviously elongated by protonation, as compared with the W=O bond of **5b**, and it is slightly longer than the W–OH distance of **7a**, too. The O–O separation is also longer for **7b** by 0.08 Å. The hydroxyl group of **7a** is hydrogen bonded to the ether oxygen, and the longer W–OH and O–O distances for **7b** suggest that the hydrogen bond with OTf^- is weaker

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[\text{Cp}^*\text{W}(\mu\text{-S})_3\text{RuL}(\text{PPh}_3)_2](\text{OTf})$ ($\text{L} = \text{CH}_3\text{CN}$ (**9**), Co (**10**))

9				10			
W–Ru	2.6264(3)	W–S1–Ru	68.90(2)	W–Ru	2.660(1)	W–S1–Ru	68.5(1)
W–S1	2.2269(8)	W–S2–Ru	66.90(2)	W–S1	2.226(3)	W–S2–Ru	68.38(10)
W–S2	2.2306(9)	W–S3–Ru	67.17(2)	W–S2	2.207(4)	W–S3–Ru	66.40(10)
W–S3	2.2215(8)			W–S3	2.226(4)		
Ru–S1	2.4084(8)			Ru–S1	2.493(4)		
Ru–S2	2.5148(8)			Ru–S2	2.498(4)		
Ru–S3	2.5069(8)			Ru–S3	2.491(4)		
Ru–N	2.046(3)			Ru–C	1.86(2)		

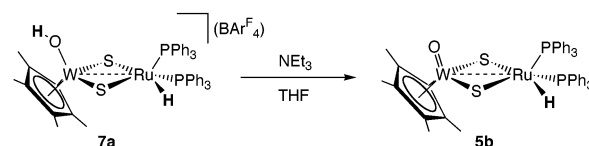
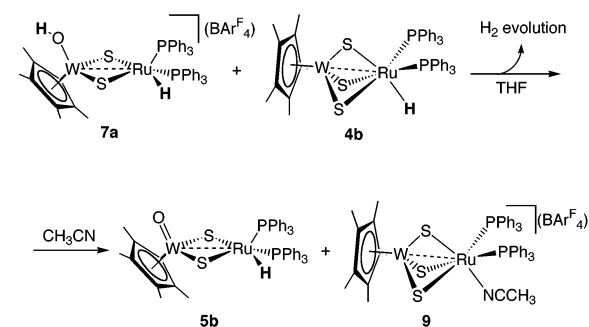
than the interaction with ether. The coordination geometries at W and Ru resemble those of **5b** and **7a**.

In contrast to the selective protonation at the oxo ligand of **5b**, the analogous reaction of HOTf with $\text{Cp}^*\text{W}(\mu\text{-S})_3\text{RuH}(\text{PPh}_3)_2$ (**4b**) occurred at the hydride site. Addition of HOTf to a THF solution of **4b** at room temperature caused an immediate evolution of H_2 to afford a dark red solution. Although the dark red product has not been characterized, it is presumed to be a cationic THF complex $[\text{Cp}^*\text{W}(\mu\text{-S})_3\text{Ru}(\text{THF})(\text{PPh}_3)_2][\text{OTf}]$, because a CH_3CN -adduct $[\text{Cp}^*\text{W}(\mu\text{-S})_3\text{Ru}(\text{CH}_3\text{CN})(\text{PPh}_3)_2][\text{OTf}]$ (**9**) and a CO-adduct $[\text{Cp}^*\text{W}(\mu\text{-S})_3\text{Ru}(\text{CO})(\text{PPh}_3)_2][\text{OTf}]$ (**10**) were isolated upon treating the dark red solution with CH_3CN and CO, respectively. The IR spectrum of **9** exhibits bands for CH_3CN at 2210 cm^{-1} , and for OTf^- at 1270, 1220, 1150, and 636 cm^{-1} , while complex **10** was characterized by a strong CO band at 1990 cm^{-1} . Their ^1H NMR spectra agree with the formulation, and the signal for free CH_3CN appeared for **9**, when the measurement was performed in CD_3CN . The structures of **9** and **10** were confirmed by crystallographic analysis, and the selected bond lengths and angles are given in Table 3. Similar to the molecular structures of $\text{Cp}^*\text{W}(\mu\text{-S})_3\text{RuX}(\text{PPh}_3)_2$ (**4a**; $\text{X} = \text{Cl}$, **4b**; $\text{X} = \text{H}$), the two metal centers are bridged by three sulfides, and CH_3CN or CO is coordinated at Ru. A notable difference in the structures of **4a**, **4b**, **9**, and **10** is the Ru–S1 bond lengths trans to chloride (2.4079(7) Å), hydride (2.5387(8) Å), CH_3CN (2.4084(8) Å), and CO (2.493(4) Å), which show the strong trans influence of hydride and CO.

Scheme 5

Deprotonation and H_2 Evolution. Addition of hydrogen at the oxo ligand can be accomplished either by the heterolytic cleavage of H_2 or by protonation. In expectation of obtaining insights into the mechanism of heterolytic H_2 activation, the reverse processes of H–H cleavage and protonation were

investigated. The protic character of the WOH hydrogen was established by the observation that “deprotonation” of the complex cation $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2]^+$ (**7a,b**) was induced selectively by a small excess of NEt_3 , resulting in quantitative formation of $\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2$ (**5b**). Evolution of H_2 , which would produce $[\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{Ru}(\text{NEt}_3)(\text{PPh}_3)_2]^+$, did not take place in this reaction.

Scheme 6**Scheme 7**

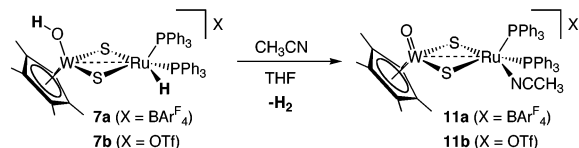
We mentioned earlier in this paper that the hydride of $\text{Cp}^*\text{W}(\mu\text{-S})_3\text{RuH}(\text{PPh}_3)_2$ (**4b**) reacted readily with HOTf. Transition metal hydrides are potential bases, and could interact with the acidic W–OH group. As a matter of fact, treatment of $\text{Cp}^*\text{W}(\mu\text{-S})_3\text{RuH}(\text{PPh}_3)_2$ (**4b**) with **7a** in THF resulted in immediate evolution of H_2 , and the subsequent addition of CH_3CN into the resulting dark-brown solution produced **5b** and $[\text{Cp}^*\text{W}(\mu\text{-S})_3\text{Ru}(\text{CH}_3\text{CN})(\text{PPh}_3)_2][\text{BARF}_4]$ (**9**). Obviously H_2 was formed by an intermolecular coupling of the hydroxyl hydrogen in **7a** and the hydride in **4b**. This facile H_2 formation raises the intriguing question as to why **7a** or **7b** does not evolve H_2 by itself via an intermolecular or intramolecular H–H coupling pathway. They are stable in THF under an inert atmosphere. Hydridic character of the Ru–H bond may be weak, and/or the hydrogen bonding with OTf^- or ether may decrease the acidity of the hydroxyl hydrogen.

Although the complex cation $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2]^+$ is stable in THF, it was found to be labile in the presence of CH_3CN or under CO atmosphere. Upon addition of CH_3CN to a THF solution of **7a** or **7b**, the complex was gradually converted into $[\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{Ru}(\text{CH}_3\text{CN})(\text{PPh}_3)_2](\text{X})$ (**11a**;

Table 4. Selected Bond Distances (Å) and Angles (deg) for [Cp*W(O)(μ -S)₂Ru(CH₃CN)(PPh₃)₂](OTf) (**11b**)

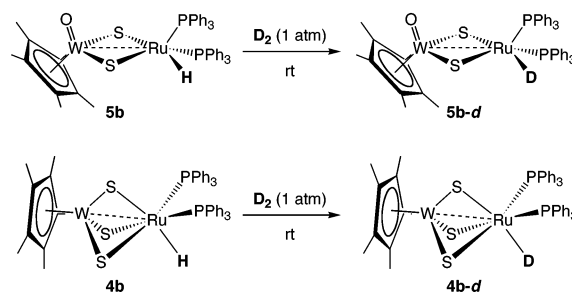
11b	
W–Ru	2.8603(3)
W–O	1.727(3)
W–S1	2.2644(9)
W–S2	2.2650(9)
Ru–S1	2.3648(9)
Ru–S2	2.3354(8)
Ru–N	2.063(3)
W–S1–Ru	76.65(3)
W–S2–Ru	76.87(3)

X = BaR^F₄, **11b**; X = OTf) with evolution of H₂. The product was isolated as a grayish blue crystalline powder in 95% yield. Formation of H₂ was detected by a separate NMR tube experiment in THF-d₈ with a small amount of CH₃CN, where the free H₂ signal appeared at δ 4.55. Complexes **11a** and **11b** were characterized by the IR bands associated with the W=O bond and CH₃CN, and by ¹H and ³¹P{¹H} NMR spectra. As in the case of **5a**, the two phosphine ligands are chemically nonequivalent in the ³¹P NMR spectrum. Crystals suitable for X-ray analysis were grown by layering ether onto a THF solution of **11b**. The X-ray derived geometric parameters are listed in Table 4. There is no short contact between the complex cations and the anions in the crystals. The dinuclear structure of the complex cation is analogous to those of **5a** and **5b**, in which the Ru atom adopts a distorted square pyramidal coordination geometry with an apical PPh₃, and with one PPh₃, two μ -S atoms, and one CH₃CN molecule at the basal positions.

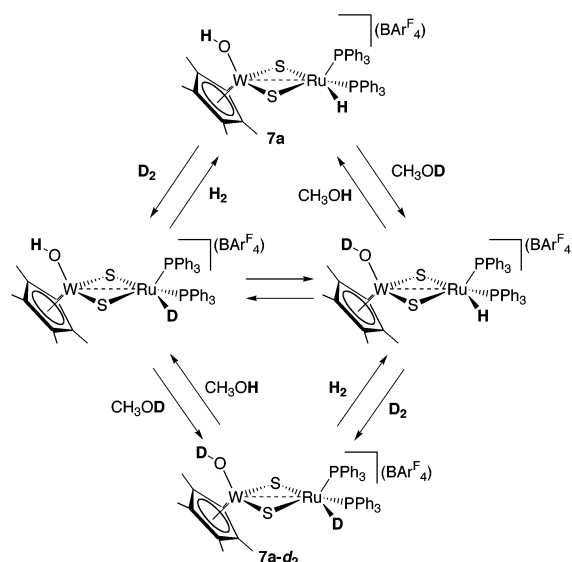
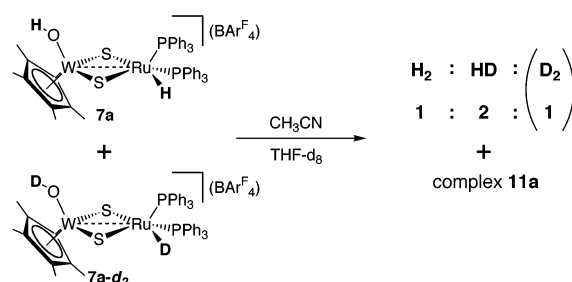
Scheme 8

H/D Exchange Experiments. In the previous section, we mentioned that the hydride complex Cp*W(O)(μ -S)₂RuH(PPh₃)₂ (**5b**) appeared not to react under 10 atm H₂. To ascertain if **5b** is really inert to external H₂, an H/D exchange reaction was conducted in an NMR tube at room temperature, and the reaction was monitored by ¹H NMR. Introduction of D₂ onto a C₆D₆ solution of **5b** gave rise to Cp*W(O)(μ -S)₂RuD(PPh₃)₂ (**5b-d**). Formation of HD and H₂ was noted in the ¹H NMR. The reaction is relatively slow and is nearly completed in 1 day. The exchange between D₂ and the hydride is most likely to proceed through coordination of η^2 -D₂. The tri(μ -sulfido) hydride complex Cp*W(μ -S)₃RuH(PPh₃)₂ (**4b**) was also found to undergo the H/D exchange between the hydride and 1 atm D₂ to produce Cp*W(μ -S)₃RuD(PPh₃)₂ (**4b-d**).

The NMR tube experiments were also carried out for the H/D exchange reactions of [Cp*W(OH)(μ -S)₂RuH(PPh₃)₂][BaR^F₄] (**7a**). Surprisingly, exposure of a THF-d₈ solution of **7a** to D₂ lead to a facile exchange of both hydridic center attached to Ru and protic center on the OH group, giving rise to [Cp*W-(OD)(μ -S)₂RuD(PPh₃)₂][BaR^F₄] (**7a-d₂**) within 1 day, and the formation of HD and H₂ was identified in the ¹H NMR spectrum. More surprisingly, the treatment of **7a** with CH₃OD also resulted in **7a-d₂**. The deuterated complex **7a-d₂** was synthesized in a preparative scale by the reaction of **5a** with

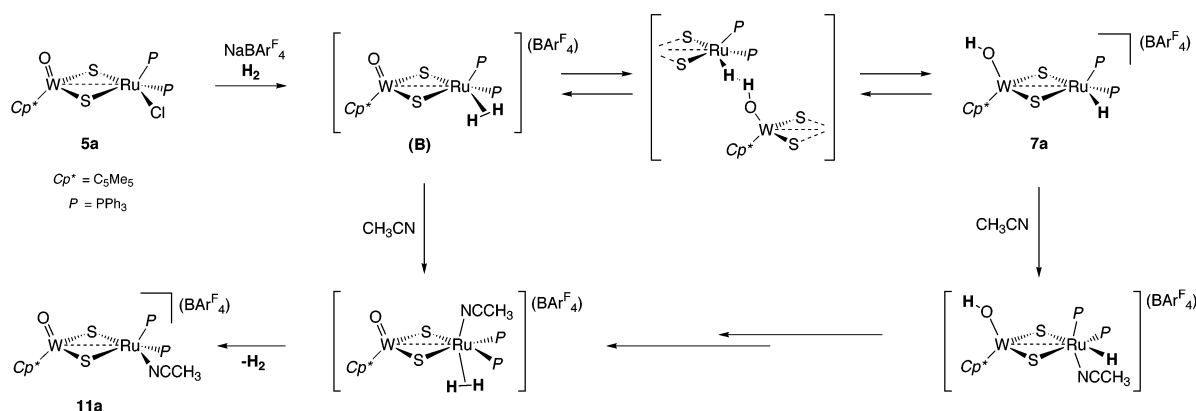
Scheme 9

NaBaR^F₄ under a D₂ atmosphere, and it was characterized by means of ¹H, ²H, and ³¹P NMR spectra. In either of the reactions with D₂ and CH₃OD in NMR tubes, the intensity of the W–OH signal (or the W–OD signal) remains nearly equal to that of the Ru–H signal (or Ru–D signal). In other words, during the H/D exchange, the W–OH and Ru–H proton signals decrease approximately at the same rate, and the situation is similar to the concomitant increases of the corresponding ²H signals.

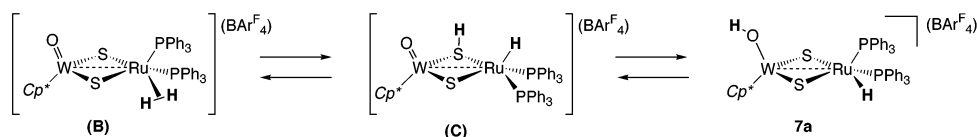
Scheme 10**Scheme 11**

As one might expect, CH₃OD does not react with the hydride of Cp*W(O)(μ -S)₂RuH(PPh₃)₂ (**5b**). It may also be expected that a fast exchange between W–OH and D₂ is unlikely to proceed. Therefore, we propose that the H/D exchange at the W–OH site of **7a** under D₂ is actually initiated by deuteration of the hydride at Ru via D₂ coordination, and the H/D scramble between the W–OH and Ru–D sites follows. Likewise, in the reaction between **7a** and CH₃OD, deuteration probably occurs first at W–OH, which would then scramble over the two sites.

Scheme 12



Scheme 13



Since the H/D exchanges occur simultaneously at W–OH and Ru–H in the ^1H NMR time scale, the H(D) scramble between these sites must be much faster than the deuteration processes at Ru–H with D_2 and at W–OH with CH_3OD .

We have carried out a crossover experiment for the $\text{H}_2(\text{D}_2)$ formation from $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2][\text{BARF}_4]$ (**7a**) and $[\text{Cp}^*\text{W}(\text{OD})(\mu\text{-S})_2\text{RuD}(\text{PPh}_3)_2][\text{BARF}_4]$ (**7a-d2**) in the presence of CH_3CN (see Scheme 11). In an NMR tube, a 1:1 mixture of **7a** and **7a-d2** was dissolved in THF-d_8 and one drop of CH_3CN was added, followed by immediate ^1H NMR measurement. The spectrum clearly shows the signals of H_2 and HD in the 1:2 intensity ratio, and also points to the quantitative formation of $[\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{Ru}(\text{CH}_3\text{CN})(\text{PPh}_3)_2][\text{BARF}_4]$ (**11a**). If the H_2 evolution occurs within each molecule of **7a** and **7a-d2**, H_2 and D_2 would be produced. On the other hand, if the reaction proceeds via an intermolecular pathway, a statistical amount of HD would also be generated, which is in accord with the experimental result. However, the formation of HD may also be explained in terms of a facile intermolecular/intramolecular H/D scrambling between **7a** and **7a-d2** before the H_2 evolution. This possibility could not be ruled out.

Mechanistic Aspects of the Reversible H_2 Activation. We emphasized in Scheme 3 that the H_2 activation reaction of $\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{RuCl}(\text{PPh}_3)_2$ (**5a**) with NaBARF_4 could be initiated by formation of an $\eta^2\text{-H}_2$ complex $\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{RuCl}(\text{H}_2)(\text{PPh}_3)_2$ (**A**), and that dissociation of chloride from the intermediate, leading to another $\eta^2\text{-H}_2$ intermediate $[\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{Ru}(\text{H}_2)(\text{PPh}_3)_2][\text{BARF}_4]$ (**B**), would then be facilitated by NaBARF_4 . In this section, the mechanism of the subsequent H_2 splitting process of **B** to give $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2][\text{BARF}_4]$ (**7a**) is discussed (Scheme 12). This process can be reversible, which would account for the mechanisms of H/D exchange reactions of **7a** (and **7b**) and facile H_2 evolution in CH_3CN to generate $[\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{Ru}(\text{CH}_3\text{CN})(\text{PPh}_3)_2][\text{BARF}_4]$ (**11a**). An alternative mechanism of the H_2 evolution is also implicated at the bottom of Scheme 12, where addition of CH_3CN to Ru of **7a** precedes the H–H coupling.

It has been known that the enhanced acidity of molecular hydrogen bound to electron deficient transition metal centers

results in heterolytic H–H bond splitting. A proton is transferred to a counteranion, an external base, or to a basic site within the molecule. In the $\eta^2\text{-H}_2$ intermediate (**B**), the oxo group, the bridging sulfides, and the counteranion $[\text{BARF}_4]^-$ may act as proton acceptors. However, proton abstraction by $[\text{BARF}_4]^-$ is unlikely to occur, because a proton is only lost when a conjugate base such as Et_2O or H_2O is present to give $[\text{H}(\text{OEt})_2][\text{BARF}_4]$ or $[\text{H}_3\text{O}][\text{BARF}_4]$, while the reaction of **5a** with H_2 was carried out in CH_2Cl_2 . A direct intramolecular proton abstraction by $\text{W}=\text{O}$ is also ruled out, because the $\text{W}=\text{O}$ group is far away from the Ru coordination sphere.

Thus a plausible pathway for the H_2 activation is the one involving an intermolecular H–H splitting as shown in Scheme 12. This mechanism is analogous to the known deprotonation reactions of metal-bound $\eta^2\text{-H}_2$ molecules promoted by external bases. Another way to view this mechanism is that the reaction proceeds via the intermediate having an intermolecular interaction between the hydridic Ru–H site and the protic W–OH site. This Ru–H–H–O–W interaction is relevant to the so-called nonclassical hydrogen-bonding found in some transition metal hydride complexes,¹⁹ e.g., the Ir–H–H–N interaction in $[\text{Ir}\{\text{H}(\eta^1\text{-SC}_5\text{H}_4\text{NH})\}_2(\text{PCy}_3)_2]\text{BF}_4$ ^{4a} and the Ir–H–H–O interaction observed in $[\text{Ir}(\text{H})_2\{(\text{C}_9\text{H}_6\text{N})\text{NC}(\text{OH})\text{Me}\}(\text{PPh}_3)_2](\text{SbF}_6)$.^{4b}

On the other hand, a possibility of proton migration over the $\mu\text{-S}$ sites, by way of the $\mu\text{-SH}$ intermediate $[\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})(\mu\text{-SH})\text{RuH}(\text{PPh}_3)_2][\text{BARF}_4]$ (**C**), is not ruled out (Scheme 13). The bridging sulfide in (**B**) is in close vicinity to the molecular hydrogen at Ru, a lone pair of which is capable of abstracting a proton from the $\eta^2\text{-H}_2$ molecule. The resulting mercapto group is acidic, and would deliver the proton readily to the more basic oxo group. The heterolytic cleavage of H_2 by dinuclear $\mu\text{-sulfido}$ complexes have been reported to generate a $\mu\text{-SH}$ bond and a M–H bond.^{6b,c,d}

(19) (a) Crabtree, R. H.; Siegbahn, P. E. M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. *Acc. Chem. Res.* **1996**, 29, 348, and references therein. (b) Stevens, R. C.; Bau, R.; Milstein, D.; Blum, O.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1990**, 1429.

Experimental Section

General Procedures. All reactions and the manipulations of air-sensitive compounds were performed under nitrogen or argon atmosphere using standard Schlenk techniques. Solvents were dried, degassed and distilled from sodium/benzophenone ketyl (hexane, Et₂O, toluene, DME, THF) or from CaH₂ (CH₃CN, CH₂Cl₂) under nitrogen. Deuterated solvents were vacuum-transferred from sodium (benzene-d₆, toluene-d₈, THF-d₈) or CaH₂ (CD₃CN, CD₂Cl₂, CDCl₃).

¹H and ³¹P NMR spectra were acquired on a Varian INOVA-500 spectrometer at 500 and 202 MHz, respectively. ¹H NMR spectra were referenced to the residual proton resonances of the deuterated solvents. ³¹P chemical shifts were relative to the external reference of 85% H₃-PO₄. Infrared spectra were recorded on a Parkin Elmer 2000 FT-IR spectrometer or a JASCO A3 spectrometer. ESI-MS spectra were obtained from a Perkin-Elmer Sciex API 300 ion spray mass spectrometer or a Micromass LCT TOF-MS spectrometer. Elemental analyses for C, H, N, and S were performed on a LECO CHNS-932 elemental analyzer where the crystalline samples were sealed in silver capsules under argon. FAB-MS spectra were obtained on a JEOL JMS-LCMATE mass spectrometer, where 3-nitrobenzyl alcohol was used as the matrix. X-ray diffraction data were collected on a Rigaku RASA-7 Quantum system and a Rigaku AFC7R equipped with an ADSC Quantum1 CCD detector by using graphite-monochromated MoK α radiation.

The following compounds were prepared according to the literature procedures. (PPh₄)[Cp*W(S)₃] (**1**),^{10a} (PPh₄)[Cp*W(S)₂(O)] (**2**),^{10b} RuCl₂(PPh₃)₃, RuClH(PPh₃)₃,¹² NaBAR^F₄ and [H(OEt₂)₂]BAR^F₄.¹⁸

Synthesis of (PPh₄)[Cp*W(S)₂(NPh)] (3**).** (PPh₄)[Cp*W(O)(S)₂] (**2**; 110 mg, 0.15 mmol) was dissolved in CH₃CN (15 mL) under nitrogen atmosphere, to which PhNCO (17 mL, 0.16 mmol) was added with stirring at 40 °C, and the reaction mixture was kept stirring for 2 h. The CH₃CN was removed under vacuum, and the residue was washed with hexane to give (PPh₄)[Cp*W(S)₂(NPh)] (**3**) as an orange powder (118 mg, 98%). ¹H NMR (CD₃CN): δ 8.0–7.6 (m, 20 H, PPh₄), 7.21–6.70 (m, 5 H, NPh), 1.99 (s, 15 H, Cp*). IR (KBr pellet): 1350 (s, W=NPh), 455, 434 (s, W=S) cm⁻¹. ESI-MS (CH₃CN): *m/z* 474 ([Cp*W(S)₂(NPh)]⁺). Anal. Calcd for C₄₀H₄₀NS₂PW: C 59.04; H 4.95; N 1.72; S 7.88 Found: C 58.27; H 5.16; N 1.76; S 7.85.

Synthesis of Cp*W(μ -S)₃RuCl(PPh₃)₂ (4a**).** A mixture of (PPh₄)[Cp*W(S)₃] (**1**) (0.37 g, 0.50 mmol) and RuCl₂(PPh₃)₃ (0.47 g, 0.49 mmol) in CH₃CN (60 mL) was stirred at room temperature for 4 h. After removal of the solvent under vacuum, the black-brown residue was washed with THF (20 mL) and CH₃CN (40 mL) to afford Cp*W(μ -S)₃RuCl(PPh₃)₂ (**4a**) as a brown powder (0.41 g, 77%). X-ray quality crystals were grown by layering hexane onto the CH₂Cl₂ solution of **4a** at room temperature. ¹H NMR (CDCl₃): δ 7.48–7.45 (m, 12 H, PPh₃), 7.23–7.20 (m, 6 H, PPh₃), 7.10–7.06 (m, 12 H, PPh₃), 2.10 (s, 15 H, Cp*). ³¹P{¹H} NMR (CDCl₃): δ 31.7 (s, PPh₃). Anal. Calcd for C₄₆H₄₅ClP₂RuS₃W·CH₂Cl₂: C, 48.61; H, 4.08; S, 8.28. Found: C, 48.29; H, 4.14, S, 8.54.

Synthesis of Cp*W(μ -S)₃RuH(PPh₃)₂ (4b**).** CH₃CN (120 mL) was added to a mixture of (PPh₄)[Cp*W(S)₃] (**1**) (1.21 g, 1.61 mmol) and RuClH(PPh₃)₃ (1.59 g, 1.56 mmol). The suspension was stirred at room temperature for 1 day to yield brown precipitation. After decanting brown solution off, the brown residue was extracted with toluene (80 mL), and centrifuged to remove PPh₄Cl. After removal of the solvent in vacuo, the brown residue was washed with CH₃CN (30 mL) to afford Cp*W(μ -S)₃RuH(PPh₃)₂ (**4b**) as a brown crystalline powder (1.35 g, 83%). X-ray quality crystals were grown by layering hexane onto the toluene solution of **4b** at room temperature. ¹H NMR (CDCl₃): δ 7.53–7.49 (m, 12H, PPh₃), 7.15–7.02 (m, 18 H, PPh₃), 2.06 (s, 15 H, Cp*), –10.47 (t, ²J_{PH} = 29 Hz, 1 H, RuH). ³¹P{¹H} NMR (CDCl₃): δ 57.3 (s, PPh₃). ¹H NMR (C₆D₆): δ 7.88–7.85 (m, 12 H, PPh₃), 7.00–6.94 (m, 18 H, PPh₃), 1.91 (s, 15 H, Cp*), –10.30 (t, ²J_{PH} = 30 Hz, 1 H, RuH). ³¹P{¹H} NMR (C₆D₆): δ 58.5 (s, PPh₃).

IR (Nujol): 1930 (w, ν_{Ru-H}) cm⁻¹. Anal. Calcd for C₄₆H₄₆P₂RuS₃W: C, 53.02; H, 4.45; S, 9.23. Found: C, 52.82; H, 4.52, S, 9.18.

Synthesis of Cp*W(O)(μ -S)₂RuCl(PPh₃)₂ (5a**).** The procedure is similar to the one used for the synthesis of **4a**. The reaction of (PPh₄)[Cp*W(S)₂(O)] (**2**) (0.94 g, 1.27 mmol) with RuCl₂(PPh₃)₃ (1.21 g, 1.27 mmol) in CH₃CN (125 mL) gave Cp*W(O)(μ -S)₂RuCl(PPh₃)₂ (**5a**) as a green powder (1.10 g, 82%). X-ray quality crystals were grown from hexane/CH₂Cl₂ at room temperature. ¹H NMR (CDCl₃): δ 7.28–7.00 (m, 30 H, PPh₃), 1.88 (s, 15 H, Cp*). ³¹P{¹H} NMR (CDCl₃): δ 68.8 (d, ²J_{PP} = 30 Hz, PPh₃), 26.4 (d, ²J_{PP} = 30 Hz, PPh₃). IR (Nujol): 895 (s, $\nu_{W=O}$) cm⁻¹. Anal. Calcd for C₄₆H₄₅ClO₂P₂RuS₂W·CH₂Cl₂: C, 49.29; H, 4.14; S, 5.60. Found: C, 48.81; H, 4.30; S, 5.46.

Synthesis of Cp*W(O)(μ -S)₂RuH(PPh₃)₂ (5b**).** The synthetic procedure is analogous to that of **4b**. The reaction of (PPh₄)[Cp*W(S)₂(O)] (**2**) (0.97 g, 1.32 mmol) with RuClH (PPh₃)₃ (1.31 g, 1.28 mmol) in CH₃CN (125 mL) afford Cp*W(O)(μ -S)₂RuH(PPh₃)₂ (**5b**) as a greenish brown crystalline powder (1.14 g, 86%). X-ray quality crystals were grown from a hexane/toluene solution at room temperature. ¹H NMR (C₆D₆): δ 7.64–7.60 (m, 12 H, PPh₃), 6.93–6.88 (m, 18 H, PPh₃), 1.86 (s, 15 H, Cp*), –8.17 (t, ²J_{PH} = 33 Hz, 1 H, RuH). ³¹P{¹H} NMR (C₆D₆): δ 68.5 (s, PPh₃). IR (Nujol): 2022 (w, ν_{Ru-H}), 901 (s, $\nu_{W=O}$) cm⁻¹. Anal. Calcd for C₄₆H₄₆O₂P₂RuS₂W: C, 53.83; H, 4.52; S, 6.25. Found: C, 53.98; H, 4.65; S, 6.54.

Synthesis of Cp*W(NPh)(μ -S)₂RuCl(PPh₃)₂ (6a**).** By following a procedure similar to that **4a**, the reaction of (PPh₄)[Cp*W(S)₂(NPh)] (**3**) (0.31 g, 0.38 mmol) with RuCl₂(PPh₃)₃ (0.36 g, 0.38 mmol) in CH₃CN (15 mL) gave Cp*W(NPh)(μ -S)₂RuCl(PPh₃)₂ (**6a**) as a green powder (0.23 g, 54%). ¹H NMR (CDCl₃): δ 7.30–6.98 (m, 30 H, PPh₃), 6.86 (brt, 2 H, NPh), 6.67 (brt, 1 H, NPh), 6.17 (brd, 2 H, NPh), 1.88 (s, 15 H, Cp*). ³¹P{¹H} NMR (CDCl₃): δ 69.5 (d, ²J_{PP} = 30 Hz, PPh₃), 26.4 (d, ²J_{PP} = 30 Hz, PPh₃). IR (KBr pellet): 1336 (s, $\nu_{W=NPh}$) cm⁻¹. FAB-MS⁺ (CH₂Cl₂): *m/z* 1135 ([Cp*W(NPh)(μ -S)₂RuCl(PPh₃)₂]⁺), 1100 ([Cp*W(NPh)(μ -S)₂Ru(PPh₃)₂]⁺), 873 ([Cp*W(NPh)(μ -S)₂RuCl(PPh₃)₂]⁺), 838 ([Cp*W(NPh)(μ -S)₂Ru(PPh₃)₂]⁺). Anal. Calcd for C₅₂H₅₀NP₂RuS₂W: C, 55.00; H, 4.44; N, 1.23; S, 5.65. Found: C, 55.00; H, 4.69; N, 1.30; S, 5.63.

Synthesis of Cp*W(NPh)(μ -S)₂RuH(PPh₃)₂ (6b**).** The procedure is similar to that of **4b**. The reaction of (PPh₄)[Cp*W(S)₂(NPh)] (**3**) (0.34 g, 0.42 mmol) with RuClH (PPh₃)₃ (0.39 g, 0.42 mmol) in CH₃CN (10 mL) afford Cp*W(NPh)(μ -S)₂RuH(PPh₃)₂ (**6b**) as a brown powder (0.35 g, 76%). ¹H NMR (C₆D₆): δ 7.72–7.68 (m, 12 H, PPh₃), 7.46–7.40 (m, 1 H, NPh), 6.98–6.94 (m, 2 H, NPh), 6.92–6.88 (m, 6 H, PPh₃), 6.86–6.80 (m, 12 H, PPh₃), 6.76–6.74 (m, 2 H, NPh), 1.79 (s, 15 H, Cp*), –10.81 (t, ²J_{PH} = 33 Hz, 1 H, Ru–H). ³¹P{¹H} NMR (C₆D₆): δ 69.3 (s, PPh₃). IR (KBr pellet): 1348 (s, $\nu_{W=NPh}$) cm⁻¹.

Formation of [Cp*W(OH)(μ -S)₂RuH(PPh₃)₂](BAR^F₄) (7a**) from **5b**, H₂ gas, and NaBAR^F₄.** A mixture of **5b** (0.15 g, 0.14 mmol) and NaBAR^F₄ (0.13 g, 0.15 mmol) in CH₂Cl₂ (10 mL) was stirred under H₂ atmosphere (1 atm) at room temperature for 1 h. The solution quickly turned purple. After being centrifuged to remove NaCl, the solvent was removed under vacuum. The purple residue was washed with small amount of hexane to afford [Cp*W(OH)(μ -S)₂RuH(PPh₃)₂](BAR^F₄) (**7a**) as a purple powder (0.23 g, 84%). The NMR, IR, and ESI-MS spectra were measured using this purple powder. X-ray quality crystals were grown by cooling an ether solution of **7a** at –78 °C. ¹H NMR (THF-d₈): δ 9.07 (brs, 1 H, WOH), 7.80 (br, 8 H, BAR^F₄), 7.58 (br, 4 H, BAR^F₄) 7.4–7.1 (m, 30 H, PPh₃), 1.99 (s, 15 H, Cp*), –3.37 (t, ²J_{PH} = 32 Hz, 1 H, RuH). ³¹P{¹H} NMR (THF-d₈): δ 70.8 (s, PPh₃). ¹H NMR (CDCl₃): δ 7.70 (br, 8 H, BAR^F₄), 7.50 (br, 4 H, BAR^F₄) 7.4–7.1 (m, 30 H, PPh₃), 1.93 (s, 15 H, Cp*), –1.70 (t, ²J_{PH} = 32 Hz, 1 H, RuH). ³¹P{¹H} NMR (CDCl₃): δ 67.1 (s, PPh₃). IR (KBr pellet): 3453 (m, ν_{WO-H}), 2019 (w, ν_{Ru-H}) cm⁻¹. ESI-MS (THF): *m/z* 1026 ([Cp*W(OH)(μ -S)₂RuH(PPh₃)₂–H]⁺). Anal. Calcd for C₇₈H₅₉BF₂₄OP₂RuS₂W·C₄H₁₀O: C, 50.14; H, 3.54; S, 3.26. Found: C, 50.07; H, 3.68; S, 3.09.

Formation of [Cp*W(NHPh)(μ -S)₂RuH(PPh₃)₂](BAR^F₄) (8**) from **6b**, H₂ gas, and NaBAR^F₄.** The procedure is analogous to that used for

Table 5. Crystal Data for $\text{Cp}^*\text{W}(\mu\text{-S})_3\text{RuCl}(\text{PPh}_3)_2\cdot\text{CH}_2\text{Cl}_2$ (**4a**· CH_2Cl_2), $\text{Cp}^*\text{W}(\mu\text{-S})_3\text{RuH}(\text{PPh}_3)_2$ (**4b**), $\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{RuCl}(\text{PPh}_3)_2\cdot\text{CH}_2\text{Cl}_2$ (**5a**· CH_2Cl_2), $\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{RuCl}(\text{PPh}_3)_2\cdot\text{C}_6\text{H}_5\text{CH}_3$ (**5b**· $\text{C}_6\text{H}_5\text{CH}_3$), $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2](\text{BAR}^{\text{F}}_4)\cdot 2\text{C}_4\text{H}_{10}\text{O}$ (**7a**· $2\text{C}_4\text{H}_{10}\text{O}$), $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2]\text{OTf}$ (**7b**), $[\text{Cp}^*\text{W}(\mu\text{-S})_3\text{RuL}(\text{PPh}_3)_2](\text{OTf})$ ($\text{L} = \text{CH}_3\text{CN}$ (**9**), CO (**10**)), and $[\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{Ru}(\text{CH}_3\text{CN})(\text{PPh}_3)_2](\text{OTf})$ (**11b**)

	4a · CH_2Cl_2	4b	5a · CH_2Cl_2	5b · $\text{C}_6\text{H}_5\text{CH}_3$
formula	$\text{C}_{46}\text{H}_{45}\text{ClP}_2\text{S}_3\text{RuW}\cdot\text{CH}_2\text{Cl}_2$	$\text{C}_{46}\text{H}_{46}\text{P}_2\text{S}_3\text{RuW}$	$\text{C}_{46}\text{H}_{45}\text{ClP}_2\text{S}_2\text{ORuW}\cdot\text{CH}_2\text{Cl}_2$	$\text{C}_{46}\text{H}_{46}\text{P}_2\text{S}_2\text{ORuW}\cdot\text{C}_6\text{H}_5\text{CH}_3$
mol wt (g mol^{-1})	1161.29	1041.92	1145.23	1118.00
crystal system	orthorhombic	triclinic	orthorhombic	triclinic
space group	$Pbca$ (No. 61)	$P\bar{1}$ (No.2)	$Pna2_1$ (No.33)	$P\bar{1}$ (No.2)
color of crystal	red	red	green	red
a (Å)	34.5808(3)	11.5969(8)	23.7028(5)	10.1719(5)
b (Å)	18.2206(1)	12.611(1)	14.8984(1)	12.1015(7)
c (Å)	14.4798(1)	16.3226(2)	12.9654(1)	19.543(1)
α (°)		84.380(1)		87.3157(6)
β (°)		75.862(3)		88.1864(9)
γ (°)		65.3699(7)		76.985(1)
V (Å ³)	9123.47(10)	2104.3(2)	4578.52(8)	2339.6(2)
Z	8	2	4	2
R	0.027	0.020	0.026	0.035
R_w	0.052	0.022	0.042	0.055
GOF	1.81	1.00	2.02	1.89

	7a · $2\text{C}_4\text{H}_{10}\text{O}$	7b	9	10	11b
formula	$\text{C}_{78}\text{H}_{59}\text{F}_{24}\text{BP}_2\text{S}_2\text{ORuW}\cdot 2\text{C}_4\text{H}_{10}\text{O}$	$\text{C}_{47}\text{H}_{47}\text{F}_3\text{P}_2\text{S}_3\text{O}_4\text{RuW}$	$\text{C}_{49}\text{H}_{48}\text{F}_3\text{NP}_2\text{S}_4\text{O}_3\text{RuW}$	$\text{C}_{48}\text{H}_{45}\text{F}_3\text{P}_2\text{S}_4\text{O}_4\text{RuW}$	$\text{C}_{49}\text{H}_{48}\text{F}_3\text{NP}_2\text{S}_3\text{O}_4\text{RuW}$
mol wt (g mol^{-1})	2038.33	1175.93	1231.03	1217.98	1214.97
crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.2)	$P2_1/c$ (No.14)	$P2_1/n$ (No.14)
color of crystal	purple	purple	red	orange	dark blue
a (Å)	13.929(1)	9.2932(6)	12.5670(6)	14.857(2)	12.9743(6)
b (Å)	14.281(2)	13.7152(7)	13.764(1)	16.402(3)	24.498(2)
c (Å)	23.637(3)	18.4144(6)	14.728(1)	22.9772(8)	14.9406(2)
α (°)	103.543(3)	104.7569(6)	77.6218(6)		
β (°)	104.860(1)	95.1659(1)	77.0646(5)	94.7078(8)	91.9160(3)
γ (°)	95.669(1)	91.219(1)	82.866(1)		
V (Å ³)	4354.7(7)	2258.0(2)	2417.4(2)	5580(1)	4746.2(3)
Z	2	2	2	4	4
R	0.058	0.042	0.028	0.075	0.028
R_w	0.069	0.054	0.051	0.091	0.036
GOF	1.60	2.20	1.91	4.71	2.04

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$, $GOF = [\sum w(|F_o|^2 - |F_c|^2)^2 / (N_o - N_p)]^{1/2}$, where N_o and N_p denote the number of data and parameters.

the synthesis of **7a**. The reaction of $\text{Cp}^*\text{W}(\text{NPh})(\mu\text{-S})_2\text{RuCl}(\text{PPh}_3)_2$ (**6b**) (0.090 g, 0.079 mmol) with $\text{NaBAR}^{\text{F}}_4$ (0.070 g, 0.079 mmol) under H_2 atmosphere at room temperature gave $[\text{Cp}^*\text{W}(\text{NPh})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2](\text{BAR}^{\text{F}}_4)$ (**8**) as a dark-brown powder (0.148 g, 95%). ^1H NMR (THF-d_8): δ 7.80 (br, 8 H, BAR^{F}_4), 7.58 (br, 4 H, BAR^{F}_4), 7.4–7.0 (m, 30 H, PPh_3), 6.9–6.7 (m, 5 H, NPh), 5.69 (brs, 1 H, NHP), 1.74 (s, 15 H, Cp^*), -3.98 (t, $^2J_{\text{PH}} = 32$ Hz, 1H, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF-d_8): δ 68.43 (s, PPh_3). IR (KBr pellet): 3303 (m, $\nu_{\text{N-H}}$) cm^{-1} . ESI-MS ($\text{CH}_2\text{-Cl}_2$): m/z 1103 ($[\text{Cp}^*\text{W}(\text{NPh})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2 + \text{H}]^+$). Anal. Calcd for $\text{C}_{84}\text{H}_{64}\text{BF}_{24}\text{NP}_2\text{RuS}_2\text{W}$: C, 51.34; H, 3.28; N, 0.71; S, 3.26. Found: C, 50.97; H, 3.59; N, 0.79; S, 2.83.

Reaction of $\text{Cp}^*\text{W}(\text{O})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2$ (5b**) with $[\text{H}(\text{OEt}_2)_2](\text{BAR}^{\text{F}}_4)$.** A THF (5 mL) solution of $[\text{H}(\text{OEt}_2)_2](\text{BAR}^{\text{F}}_4)$ (0.096 g, 0.095 mmol) was added to a solution of **5b** (0.10 g, 0.10 mmol) in THF (10 mL) with stirring at room temperature. The solution immediately turned purple and was stirred for 2 h. Solvent was removed under vacuum, and the purple residue was washed with a small amount of hexane to afford **7a** as a purple powder (0.19 g, 97%).

Formation of $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2](\text{OTf})$ (7b**) from **5b** and TfOH .** Addition of TfOH (0.17 mmol) to a THF (20 mL) solution of **5b** (0.17 g, 0.17 mmol) formed a purple solution. The mixture was stirred at room temperature for 2.5 h. After removal of a solvent in vacuo, the purple residue was extracted with DME (3 mL). Then layering ether and hexane onto DME purple solution yields $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2](\text{OTf})$ (**7b**) as dark purple crystals (0.17 g, 87%). ^1H NMR (THF-d_8): δ 10.8 (brs, 1 H, WOH), 7.32–7.28 (m, 12 H, PPh_3), 7.24–7.21 (m, 6 H, PPh_3), 7.12–7.09 (m, 12 H, PPh_3), 1.95 (s, 15 H, Cp^*), -5.96 (t, $^2J_{\text{PH}} = 32$ Hz, 1 H, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF-d_8): δ 68.9 (s, PPh_3). ^1H NMR (CDCl_3): δ 7.29–7.24 (m, 18 H, PPh_3), 7.14–7.11 (m, 12 H, PPh_3), 1.96 (s, 15 H, Cp^*), -4.81 (t, $^2J_{\text{PH}} = 32$ Hz, 1 H, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 66.4 (s, PPh_3). IR (KBr pellet): 2015 (w, $\nu_{\text{Ru-H}}$) cm^{-1} . Anal. Calcd for $\text{C}_{47}\text{H}_{47}\text{F}_3\text{O}_4\text{P}_2\text{RuS}_3\text{W}$: C, 48.00; H, 4.03; S, 8.18. Found: C, 48.23; H, 4.15; S, 8.22.

Anion exchange of $[\text{Cp}^*\text{W}(\text{OH})(\mu\text{-S})_2\text{RuH}(\text{PPh}_3)_2](\text{OTf})$ (7b**) with $\text{NaBAR}^{\text{F}}_4$.** A THF (30 mL) solution of $\text{NaBAR}^{\text{F}}_4$ (0.32 g, 0.36 mmol) was added to a THF (20 mL) solution of **7b** prepared from the reaction of **5b** (0.37 g, 0.36 mmol) with TfOH in situ at room temperature, and the reaction mixture was stirred for 20 min. Solvent was removed in vacuo, and the purple residue was extracted with CH_2Cl_2 . After being centrifuged to remove NaCl , the purple solution was evaporated under vacuum. The purple residue was washed with hexane to yield **7a** as a purple powder (0.60 g, 88%).

Formation of $[\text{Cp}^*\text{W}(\mu\text{-S})_3\text{Ru}(\text{CH}_3\text{CN})(\text{PPh}_3)_2](\text{OTf})$ (9**) from **4b**, TfOH , and CH_3CN .** Addition of TfOH (0.28 mmol) to a solution of **4b** (0.29 g, 0.28 mmol) in THF (40 mL) led to evolution of H_2 . The mixture was stirred at room temperature for 2 h, and centrifuged. After removal of the solvent under vacuum, the brown residue was dissolved in CH_3CN (10 mL). The mixture was stirred at room temperature for 1 h. After removal of the solvent in vacuo, the brown residue was washed with DME (2 mL) to afford $[\text{Cp}^*\text{W}(\mu\text{-S})_3\text{Ru}(\text{CH}_3\text{CN})(\text{PPh}_3)_2](\text{OTf})$ (**9**) as a brown crystalline powder (0.30 g, 89%). X-ray quality crystals were grown by layering ether onto the DME/ CH_3CN solution of **9** at room temperature. ^1H NMR (CD_3CN): δ 7.44–7.40 (m, 18 H, PPh_3), 7.31–7.28 (m, 12 H, PPh_3), 2.19 (s, 15 H, Cp^*), 1.97 (s, 3 H, free CH_3CN). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): δ 37.5 (s, PPh_3). IR (Nujol): 2210 (w, $\nu_{\text{CH}_3\text{CN}}$) cm^{-1} . ESI-MS (CH_3CN): m/z 1082 ($[\text{Cp}^*\text{W}(\mu\text{-S})_3\text{Ru}(\text{CH}_3\text{CN})(\text{PPh}_3)_2 + \text{H}]^+$).

(CH₃CN)(PPh₃)₂]⁺), 1041 ([Cp*W(μ -S)₃Ru(PPh₃)₂]⁺). Anal. Calcd for C₄₉H₄₈F₃NO₃P₂RuS₄W: C, 47.80; H, 3.93; N, 1.14; S, 10.42. Found: C, 47.52; H, 4.00; N, 1.14; S, 11.08.

Formation of [Cp*W(μ -S)₃Ru(CO)(PPh₃)₂](OTf) (10) from 4b, TfOH, and CO. After the reaction mixture of TfOH (0.35 mmol) and 4b (0.36 g, 0.35 mmol) in THF (30 mL) was stirred at room temperature for 30 min, where generation of H₂ was noticed, CO (1 atm) was introduced and the solution was stirred for 2 h. The THF solution was concentrated, and addition of ether (50 mL) gave rise to an orange precipitation. After decantation, the orange solid was washed with ether to afford [Cp*W(μ -S)₃Ru(CO)(PPh₃)₂](OTf) (10) as a orange powder (0.19 g, 46%). X-ray quality crystals were grown from hexane/THF at room temperature. ¹H NMR (CDCl₃): δ 7.44–7.38 (m, 6 H, PPh₃), 7.3–7.2 (m, 24 H, PPh₃), 2.27 (s, 15 H, Cp*). ³¹P{¹H} NMR (CDCl₃): δ 37.2 (s, PPh₃). IR (Nujol): 1990 (w, ν_{CO}) cm⁻¹. ESI-MS (CH₃CN): m/z 1069 ([Cp*W(μ -S)₃Ru(CO)(PPh₃)₂]⁺). Anal. Calcd for C₄₈H₄₅F₃NO₄P₂RuS₄W: C, 47.33; H, 3.72; S, 10.53. Found: C, 46.81; H, 4.05; S, 10.68.

Reaction of [Cp*W(OH)(μ -S)₂RuH(PPh₃)₂](BARF₄) (7a) with Et₃N. A resealable NMR tube was charged with a THF-d₈ (0.6 mL) solution of 7a (0.039 g, 0.021 mmol), and one drop of Et₃N was added. The NMR tube was shaken repeatedly at room temperature, and immediately placed in the NMR spectrometer. The spectrum showed a quantitative formation of Cp*W(O)(μ -S)₂RuH(PPh₃)₂ (5b).

Reaction of [Cp*W(OH)(μ -S)₂RuH(PPh₃)₂](BARF₄) (7a) with Cp*W(μ -S)₃RuH(PPh₃)₂ (4b). A resealable NMR tube containing the reaction mixture of 7a (0.022 g, 0.012 mmol) and 4b (0.012 g, 0.012 mmol) in THF-d₈ (0.6 mL) was shaken, and was set on an NMR spectrometer. Generation of H₂ and a quantitative amount of Cp*W(O)(μ -S)₂RuH(PPh₃)₂ (5b) was observed in the ¹H NMR spectrum together with uncharacterizable signals. Then, a small amount of CH₃CN was added to the solution. The NMR tube was shaken and was subjected for the NMR measurement. The resulting ¹H and ³¹P {¹H} NMR spectra revealed a quantitative formation of [Cp*W(μ -S)₃Ru(CH₃CN)(PPh₃)₂](BARF₄) (9) and 5b.

Formation of [Cp*W(O)(μ -S)₂Ru(CH₃CN)(PPh₃)₂](BARF₄) (11a) from 7a and CH₃CN. To an ether (5 mL) solution of 7a (0.122 g, 0.065 mmol) was added CH₃CN (0.1 mL) at room temperature. Evolution of H₂ was observed, and the resulting yellow solution was stirred for 10 min. The solvent was removed in vacuo, and the residue was washed with hexane to give [Cp*W(O)(μ -S)₂Ru(CH₃CN)(PPh₃)₂](BARF₄) (11a) as a blue powder (0.118 g, 95%). ¹H NMR (CDCl₃): δ 7.70 (br, 8 H, BARF₄), 7.52 (br, 4 H, BARF₄), 7.4–6.8 (m, 30 H, PPh₃), 1.91 (s, 3 H, CH₃CN), 1.90 (s, 15 H, Cp*). ³¹P{¹H} NMR (CDCl₃): δ 68.7 (d, ²J_{PP} = 26 Hz, PPh₃), 32.8 (d, ²J_{PP} = 26 Hz, PPh₃). IR (Nujol): 2279 (w, $\nu_{\text{CH}_3\text{CN}}$), 912 (s, $\nu_{\text{W=O}}$) cm⁻¹. ESI-MS (CH₂Cl₂): m/z 1066 ([Cp*W(O)(μ -S)₂Ru(CH₃CN)(PPh₃)₂]⁺). Anal. Calcd for C₈₀H₆₀BF₂₄NOP₂RuS₂W: C, 49.81; H, 3.13; N, 0.73; S, 3.32. Found: C, 49.49; H, 3.30; N, 0.85; S, 3.22.

Formation of [Cp*W(O)(μ -S)₂Ru(CH₃CN)(PPh₃)₂](OTf) (11b) from 7b and CH₃CN. To a THF (50 mL) solution of 7b prepared

from the reaction between 5b (0.36 g, 0.35 mmol) and TfOH in situ was added CH₃CN (3 mL) at room temperature. Evolution of H₂ was observed, and the resulting yellow solution was stirred for 2 h. The solvent was removed in vacuo, and yellow residue was washed with ether and toluene to give [Cp*W(O)(μ -S)₂Ru(CH₃CN)(PPh₃)₂](OTf) (11b) as a blue powder (0.40 g, 95%). X-ray quality crystals were grown from ether/THF. ¹H NMR (CDCl₃): δ 7.46–6.88 (m, 30 H, PPh₃), 2.30 (s, 3 H, CH₃CN), 1.89 (s, 15 H, Cp*). ³¹P{¹H} NMR (CDCl₃): δ 68.4 (d, ²J_{PP} = 26 Hz, PPh₃), 32.7 (d, ²J_{PP} = 26 Hz, PPh₃). IR (Nujol): 2277 (w, $\nu_{\text{CH}_3\text{CN}}$), 899 (s, $\nu_{\text{W=O}}$) cm⁻¹. ESI-MS (CH₂Cl₂): m/z 1066 ([Cp*W(O)(μ -S)₂Ru(CH₃CN)(PPh₃)₂]⁺). Anal. Calcd for C₄₉H₄₈F₃NO₄P₂RuS₂W: C, 48.44; H, 3.98; N, 1.15; S, 7.92. Found: C, 48.37; H, 4.12; N, 1.29; S, 7.88.

X-ray Crystal Structure Determination. Crystal data and refinement parameters for the structurally characterized complexes are summarized in Table 5. Single crystals were coated with oil (Immersion Oil, type B: Code 1248, Cargille Laboratories, Inc.) and mounted on loops. Diffraction data were collected at –80 °C (for 4a, b, 5a, b, 7b, 9, 10, and 11b) or –100 °C (for 7a) under a cold nitrogen stream on a Rigaku AFC7 equipped with a rotating anode and a MSC/ADSC Quantum 1 CCD detector (for 7a, b, 10, and 11b), or on a Rigaku AFC5 equipped with an ADSC CCD detector (for 4a, b, 5a, b, and 9) by using graphite-monochromated Mo K α radiation (λ = 0.710690 Å). Four preliminary data frames were measured at 0.5° increments of ω , to assess the crystal quality and preliminary unit cell parameters. The intensity images were also measured at 0.5° intervals of ω . The frame data were integrated using an MSC d*TREK program package, and the data sets were corrected for absorption using a REQAB program. All calculations were performed with a TEXSAN program package. All structures were solved by direct methods. The remaining heavy atoms were found in subsequent Fourier maps, and the structures were refined by full-matrix least-squares. Anisotropic refinement was applied to all non-hydrogen atoms, except for the disordered OTf anion in 7b were isotropically refined. The OTf anion in 7b is disordered over two positions, with occupancy factors of 50:50. The hydrogen atoms bound to Ru in 4b, 5b, 7a, and 7b were located in the Fourier maps, and were refined isotropically, while the other hydrogen atoms were put at calculated positions. Additional data are available as Supporting Information.

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Supporting Information Available: X-ray crystallographic information files (CIF) for the structures of 4a, 4b, 5a, 5b, 7a, 7b, 9, 10, and 11b. This material is available free of charge via the World Wide Web at <http://pubs.acs.org>.

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