Syntheses, Structures, and Reactions of Di-μ-hydroxo Dinuclear Complexes of Tungsten(IV) and Molybdenum(IV)

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The title compounds have been prepared in good yields by reaction of Cp_2MH_2 (M = W or Mo) with $Cp_2M(OTs)_2$ (OTs = p-$CH_3C_6H_4SO_3$) in aqueous acetone. The products were investigated by IR, ^1H NMR, and ^{13}C NMR spectroscopy as well as by X-ray crystallography. The molecules of the two compounds are isostructural. The structures comprise a planar four-membered ring consisting of alternating M and O atoms. In methanol solution, ^1H NMR chemical shifts for the cyclopentadienyl units of the complexes are significantly deshielded with respect to those for the parent dihydrides. The reactions between these complexes and tertiary phosphines in alcoholic solvents yield novel alkoxo complexes $[Cp_2M(PR_3)(R'O)]^+(OTs^-)$ (**2**) (R = Et, Bu^n, and Ph; R′ = Me, Et, Pr^i, CF_3CH_2, and Ph). The structure of the complex with (R = Bu^n and R′ = CF_3CH_2, determined by a single-crystal X-ray diffraction study, exhibits a distorted tetrahedral geometry with Mo−P = 2.540 Å and internal angle CP1−Mo−CP2 (CP is the centroid of the cyclopentadienyl ligand) = 132.8°.

Introduction

A variety of binuclear and polynuclear transition-metal complexes have been known for many years, and they continue to be the focus of investigations of their synthesis and reactivity. Especially, these complexes are currently of great interest because of their potential to induce unique catalytic transformations as a result of cooperative interaction between adjacent metals. Various kinds of ligands, such as CO, halides, tertiary phosphines, phosphides, hydride, methylene, or sulfides have been known to bridge two metal centers. In particular, the hydroxy group as a bridging ligand is important, since μ-hydroxo complexes sometimes work as precursors for the μ-oxo complexes.[1] The latter complexes are especially interesting in view of their ability to activate molecular oxygen as well as being used for the syntheses of oxide materials by sol−gel and related hydrothermal syntheses. A number of μ-hydroxo-bridged complexes which included the f- and d-block metals have been reviewed recently.[2]

We have been investigating the chemistry of the molybdenum and tungsten dihydrides Cp_2MH_2 (Cp = η-C_5H_5; M = Mo or W), which are capable of acting as a Lewis base and are easily protonated to give cationic trihydrides $[Cp_2MH_3]^+$.[3] Recently, we reported that molybdenum trihydride complex $[Cp_2MoH_3]^+OTs^-$ (OTs = p-$CH_3C_6H_4SO_3$) was readily converted to hydrido tosylato complex $Cp_2MoH(OTs)$ with accompanying evolution of 1 mol of H_2 when warmed in ethanol.[4] This complex was found to react with a wide variety of substrates, affording molybdenocene derivatives, and hence, it is useful as a precursor of these types of compounds.[5] We also showed that the complex is important as a stereoselective reducing agent in organic synthesis.[6] For example, an extremely high diastereoselectivity was achieved by using this complex in the reduction of 4-*tert*-butylcyclohexanone to cis-4-*tert*-butylcyclohexanol. We have tried to extend this work to tungsten complexes. In contrast to the molybdenum complex, however, tungsten trihydride is found to be so inert owing to the thermostability that the hydrido tosylato complex should be prepared by an alternate

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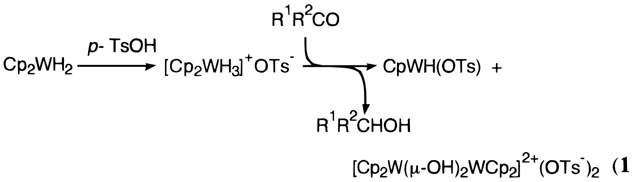
Table 1. Preparation of $[Cp_2M(\mu\text{-}OH)_2MCp_2]^{2+}(OTs^-)_2$ (M = W (1a) and Mo (1b))

	Cp_2MH_2/mmol	$Cp_2M(OTs)_2$/mmol	solvent/mL acetone/H_2O	temp/°C	time/h	yield of **1**/%
M = W	0.231	0.229	20/0.2	50	8	83
M = Mo	1.96	1.94	30/0.2	50	10	97

synthetic route. We have explored the reaction conditions and found that it can be successfully obtained by treating $[Cp_2WH_3]^+OTs^-$ with a hydrogen acceptor such as acetone or 2-butanone (eq 1). In these reactions, we



(1)

1a

have isolated an unexpected novel di-μ-hydroxo dinuclear complex $[Cp_2W(\mu\text{-}OH)_2WCp_2]^{2+}(OTs^-)_2$ (**1a**) though in low yield.[7] Afterwards this complex is most conveniently prepared in high yield via the direct reaction of Cp_2WH_2 with $Cp_2W(OTs)_2$ in aqueous acetone (eq 2).

$$Cp_2WH_2 + Cp_2W(OTs)_2 \longrightarrow \underset{\mathbf{1a}}{[Cp_2W(\mu\text{-}OH)_2WCp_2]^{2+}(OTs^-)_2} \quad (2)$$

The analogous molybdenum complex $[Cp_2Mo(\mu\text{-}OH)_2MoCp_2]^{2+}(OTs^-)_2$ (**1b**) was prepared in a similar fashion to **1a**. Although μ-hydroxo dinuclear molybdenum and tungsten complexes containing H_2O[8] or CO[9] as ligand are well-known, the analogous complex with cyclopentadienyl ligand is relatively rare.[10] In this paper, we report full details on the preparation and the structures of these complexes. We also report the reactions of complexes **1a** and **1b** with tertiary phosphines in alcoholic solvents which result in the formation of novel alkoxo complexes. Some of these results have appeared in a preliminary communication.[11]

Results and Discussion

Formations of $[Cp_2M(\mu\text{-}OH)_2MCp_2]^{2+}(OTs^-)_2$ (M = W (1a) and Mo (1b)). In the reaction of Cp_2WH_2 with TsOH in acetone (eq 1), the detailed observation indicated that purplish complex $Cp_2W(OTs)_2$ was first formed, and then it was converted to grayish complex **1a**. Furthermore, it appears that water takes part in the reaction significantly, since no formation of complex **1a** was observed when the reaction was carried out under rigorously anhydrous conditions. We therefore tried an alternate system that involved the use of water and $Cp_2W(OTs)_2$ (eq 3).

$$Cp_2MH_2 + Cp_2M(OTs)_2 \xrightarrow{(CH_3)_2CO\ -\ H_2O} [Cp_2M(\mu\text{-}OH)_2MCp_2]^{2+}(OTs^-)_2 \quad (3)$$

M = W (**1a**), Mo (**1b**)

Table 2. Spectroscopic Properties of $[Cp_2M(\mu\text{-}OH)_2MCp_2]^{2+}(OTs^-)_2$ (M = W (1a) and Mo (1b))

	IR/cm^{-1} [a]		^1H NMR/ppm[b]	^{13}C NMR/ppm[c]
complex	ν[CH(Cp)]	ν(OH)	δ(Cp)	δ(Cp)
1a (M = W)	3078	3550	6.00	98.5
1b (M = Mo)	3075	3540	5.99	103.6

[a] KBr disk. [b] 270 MHz in CD_3OD. [c] 67.8 MHz in CD_3OD.

The reaction of Cp_2WH_2 with $Cp_2W(OTs)_2$ in aqueous acetone at 50 °C afforded complex **1a** almost quantitatively (Table 1). In this system, we could not observe a side reaction. Namely, the formation of the monohydrido tosylato complex or the trihydride complex was not observed. This procedure was found to be also applicable to the molybdenum analog $[Cp_2Mo(\mu\text{-}OH)_2MoCp_2]^{2+}(OTs^-)_2$ (**1b**) (Table 1). Complexes **1a** and **1b** are moderately air-stable grayish solids and are very soluble in polar solvents such as methanol but not soluble in a nonpolar solvent such as benzene or toluene.

Spectroscopic Properties of $[Cp_2M(\mu\text{-}OH)_2MCp_2]^{2+}(OTs^-)_2$ (M = W (1a) and Mo (1b)). In Table 2, selected spectroscopic data for the complexes **1a**,**b** are collected. The IR spectra of **1a**,**b** show strong bands at 3550 and 3540 cm^{-1}, respectively, due to the bridging O−H stretching vibrations. The C−H stretching bands of Cp ligands are observed at 3078 cm^{-1} for **1a** and at 3075 cm^{-1} for **1b**, both being at lower frequency than that of the parent dihydrides Cp_2MH_2 (M = W or Mo) by about 20 cm^{-1}. In the ^1H NMR spectrum of **1a**, the resonance of the hydrogens of Cp ligands appears as a singlet at $\delta = 6.00$ ppm, which is at lower field than that of the parent complex Cp_2WH_2 by about 1.7 ppm. This downfield shift in **1a** presumably reflects a higher degree of a drift of electron density from Cp ligands to the cationic tungsten metal center as compared with the neutral Cp_2WH_2. The Cp protons of complex **1b** appear at $\delta = 5.99$ ppm, which are almost identical to those of **1a**. The ^{13}C NMR spectra of complexes **1a**,**b** give a signal for cyclopentadienyl carbons at 98.5 and 103.6 ppm, respectively.

Crystal Structure Determinations of Complexes $[Cp_2M(\mu\text{-}OH)_2MCp_2]^{2+}(OTs^-)_2$ (M = W (1a) and Mo (1b)). Figure 1 shows the molecular structure for the tungsten complex **1a** and the numbering scheme for the atoms. This drawing will also serve to represent the molybdenum compound **1b** since the only differences are slight changes in some internuclear distances and angles and the atom numbering schemes are parallel.

The molecular structure is a neat and simple one, as can be clearly seen in Figure 1. The analyses for **1a**,**b** indicate that the molecules are dimeric in the solid state with formulations $\{[Cp_2M(OH)]^+(OTs^-)\}_2$ in which one molecule of water is included as a crystallization solvent. O(24) corresponds to the oxygen atom of the water molecule. Selected interatomic bond distances and angles are presented in Tables 3 and 4. Complexes **1a**,**b**

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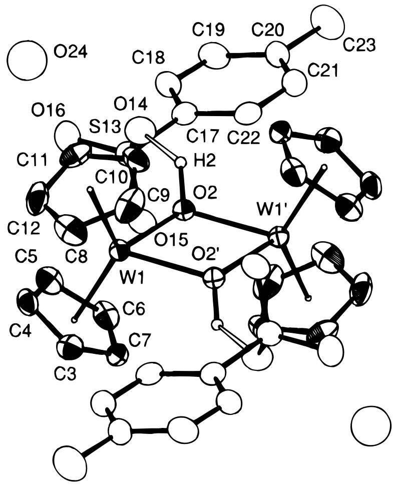


Figure 1. ORTEP drawing of the molecular structure of **1a** with the atom-numbering scheme.

Table 3. Interatomic Distances (Å) and Angles (deg) for 1a

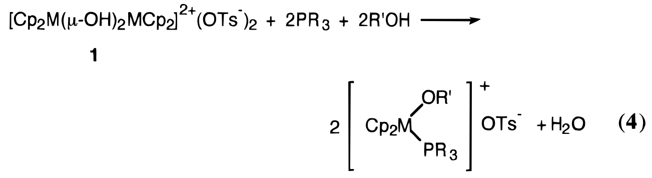
Distances			
W(1)−O(2)	2.076(7)	W(1)−O(2′)	2.099(7)
W(1)−C(3)	2.294(12)	W(1)−C(4)	2.254(12)
W(1)−C(5)	2.278(12)	W(1)−C(6)	2.370(11)
W(1)−C(7)	2.369(13)	W(1)−C(8)	2.357(13)
W(1)−C(9)	2.371(13)	W(1)−C(10)	2.281(14)
W(1)−C(11)	2.261(14)	W(1)−C(12)	2.327(12)
O(2)−H(2)	1.106(7)	O(14)−H(2)	1.711(8)
W(1)−CP1	1.982(0)	W(1)−CP2	1.994(0)
O(2)−O(2′)	2.254(14)	O(2)−O(14)	2.625(11)
O(14)−O(24)	2.952(8)	O(16)−O(24)	3.348(10)
Angles			
O(2)−W(1)−O(2′)	65.35(32)	W(1)−O(2)−W(1′)	114.65(32)
W(1)−O(2)−H(2)	127.21(48)	O(2)−H(2)−O(14)	136.36(45)
CP1−W(1)−CP2	130.95(2)	W(1)−O(2′)−H(2′)	111.69(45)

Table 4. Interatomic Distances (Å) and Angles (deg) for 1b

Distances			
Mo(1)−O(2)	2.092(2)	Mo(1)−O(2′)	2.100(2)
Mo(1)−C(3)	2.314(4)	Mo(1)−C(4)	2.282(4)
Mo(1)−C(5)	2.286(5)	Mo(1)−C(6)	2.365(4)
Mo(1)−C(7)	2.388(5)	Mo(1)−C(8)	2.356(4)
Mo(1)−C(9)	2.365(4)	Mo(1)−C(10)	2.286(5)
Mo(1)−C(11)	2.296(5)	Mo(1)−C(12)	2.323(5)
O(2)−H(2)	0.986(2)	O(14)−H(2)	1.703(3)
Mo(1)−CP1	1.996(5)	Mo(1)−CP2	2.001(5)
O(2)−O(2′)	2.298(5)	O(2)−O(14)	2.679
O(14)−O(24)	2.974	O(16)−O(24)	3.419
Angles			
O(2)−Mo(1)−O(2′)	66.21(10)	Mo(1)−O(2)−Mo(1′)	113.79(10)
Mo(1)−O(2)−H(2)	122.11(18)	O(2)−H(2)−O(14)	171.48(17)
CP1−Mo(1)−CP2	128.3	Mo(1)−O(2′)−H(2′)	124.01(17)

have an orthorhombic system. The molecular structures of **1a**,**b** contain a four-membered ring consisting of alternating M and O atoms, and there is an inversion center in the molecule with half the molecule consisting of $\{[Cp_2M(OH)]^+(OTs^-)\}$ being the symmetric unit. The positions of the H(2) and H(2′) atoms were located from difference Fourier maps and included as fixed contributions. The M−O bridge bond distances (the average of M(1)−O(2) and M(1)−O(2′) distances) are 2.088 and 2.096 Å for **1a**,**b**, respectively. This distance (**1b**) is very close to that found by Prout in $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)(\mu\text{-}H)(\mu\text{-}OH)]^{2+}(PF_6^-)_2$ as 2.08 Å.[10] The O(2)−O(14) distance in **1a** is 2.625 Å and in **1b** is 2.679 Å, and it seems reasonable to assume that H(2) forms a hydrogen bond to O(14), one of three oxygen atoms of the counteranion, OTs^-. The bond distances O(24)−O(14) are 2.952 Å in **1a** and 2.974 Å in **1b**, and O(24)−O(16) distances are 3.348 Å in **1a** and 3.419 Å in **1b**, which suggest that hydrogen bondings occur also between the water molecule and oxygen atoms of OTs^- anions. The average C−C bond distances for the Cp ring in **1a** (1.399 Å) and in **1b** (1.392 Å) are comparable to the average C−C bond distance in Prout's complex (1.42 Å). The internal C−C−C ring angles in **1a** range from 102.45 to 110.33° and in **1b** from 103.03 to 110.57°. These angles are compared favorably with the expected internal angle, 108°, for a planar pentagon. The Cp ligands attached to the metal atoms are positioned above and below the M_2O_2 planes. These complexes have geometry typical of bent metallocene with M−CP (CP is the centroid of the cyclopentadienyl ligand) distances close to 2.0 Å and with CP1−M−CP2 angles equal to 130.95° in **1a** and 128.3° in **1b**, and these results are in accord with expectation based on the orbital configuration of tungsten or molybdenum atom and the steric interaction around it.[12] The average metal−ring carbon distances are 2.316 Å in **1a** and 2.326 Å in **1b**; therefore, Mo−ring distances are slightly longer than W−ring distances. The ring angles M−O−M are 114.65° in **1a** and 113.79° in **1b**, and M−M distances are 3.51 Å in **1a** and 3.52 Å in **1b**. The M−M interactions are considered to be nonbonding since the observed separations are substantially longer than the M−M distances of 2.60 Å (M = W) and of 2.72 Å (M = Mo), estimated from the sum of covalent radii.[13]

Reactions of 1a or 1b with Tertiary Phosphines. The hydroxy groups in complex **1a** or **1b** were sufficiently labile to undergo displacement by tertiary phosphines in alcoholic solvents to afford novel mononuclear cationic alkoxo complexes **2** (eq 4). These complexes were stable to air to some extent in the solid state and were found to be soluble in polar solvents such as methanol, ethanol, and acetone but insoluble in hexane or pentane, although tributylphosphine complexes were found to be soluble in benzene.



$$\underset{\mathbf{1}}{[Cp_2M(\mu\text{-}OH)_2MCp_2]^{2+}(OTs^-)_2} + 2PR_3 + 2R'OH \longrightarrow 2\underset{\mathbf{2}}{\left[Cp_2M\begin{matrix}OR'\\PR_3\end{matrix}\right]^+} OTs^- + H_2O \qquad (4)$$

2a-k (M = Mo)	**2a'-k'** (M = W)
a, R = Et, R' = Me	**a'**, R = Et, R' = Me
b, R = Bu^n, R' = Me	**b'**, R = Bu^n, R' = Me
c, R = Et, R' = Et	**c'**, R = Et, R' = Et
d, R = Bu^n, R' = Et	**d'**, R = Bu^n, R' = Et
e, R = Et, R' = Pr^i	**e'**, R = Et, R' = Pr^i
f, R = Bu^n, R' = Pr^i	**f**,' R = Bu^n, R' = Pr^i
g, R = Et, R' = CF_3CH_2	**g'**, R = Et, R' = CF_3CH_2
h, R = Bu^n, R' = CF_3CH_2	**h'**, R = Bu^n, R' = CF_3CH_2
i, R = Ph, R' = CF_3CH_2	**i'**, R = Ph, R' = CF_3CH_2
j, R = Et, R' = Ph	**j'**, R = Et, R' = Ph
k, R = Bu^n, R' = Ph	**k'**, R = Bu^n, R' = Ph

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Table 5. Preparations of Complexes $[Cp_2MPR_3(OR')]^+OTs^-$ (2)

						conditions		
compd (M)	R	R′	complex **1**/mmol	PR_3/mmol	R′OH/mL	temp/°C	time/h	yield/%
2a (Mo)	Et	Me	0.433	1.02	20	r.t.[b]	8	85
2a′ (W)	Et	Me	0.204	0.510	20	r.t.	8	87
2c (Mo)	Et	Et	0.180	0.365	20	r.t.	40	82
2c′ (W)	Et	Et	0.247	0.533	20	r.t.	40	75
2e (Mo)	Et	Pr^i	0.192	0.398	5	50	2.5	92
2e′ (W)	Et	Pr^i	0.100	0.332	10	r.t.	100	83
2h (Mo)	Bu^n	CF_3CH_2	0.195	0.442	3	r.t.	2	97
2h′ (W)	Bu^n	CF_3CH_2	0.152	0.362	3	r.t.	2	97
2i (Mo)	Ph	CF_3CH_2	0.101	0.218	1	r.t.	100	95
2i′ (W)	Ph	CF_3CH_2	0.040	0.115	1	r.t.	100	95
2j (Mo)	Et	Ph	0.246	0.660	3[a]	r.t.	2	88
2j′ (W)	Et	Ph	0.167	0.528	5[a]	r.t.	3	87

[a] $PhOH/Et_2O$ = 1/1 (mL/mL). [b] r.t. = room temperature.

Table 6. Properties and Analytical Data for Complexes $[Cp_2MPR_3(OR')]^+OTs^-$ (2)

				elemental anal.[a]	
compd (M)	R	R′	mp °C	C/%	H/%
2a (Mo)	Et	Me	91.0−93.0	52.19 (52.75)	6.62 (6.45)
2a′ (W)	Et	Me	105.0−107.0	44.81 (45.44)	5.70 (5.56)
2c (Mo)	Et	Et	93.5−95.0	*b*	*b*
2c′ (W)	Et	Et	87.5−89.5	*b*	*b*
2e (Mo)	Et	Pr^i	69.0−71.0	*b*	*b*
2e′ (W)	Et	Pr^i	73.5−74.5	*b*	*b*
2h (Mo)	Bu^n	CF_3CH_2	128.5−129.5	52.76 (53.29)	6.69 (6.63)
2h′ (W)	Bu^n	CF_3CH_2	132.0−133.5	48.04 (47.34)	5.90 (5.89)
2i (Mo)	Ph	CF_3CH_2	102.0−104.0	*b*	*b*
2i′ (W)	Ph	CF_3CH_2	105.0−107.0	52.08 (52.49)	4.19 (4.06)
2j (Mo)	Et	Ph	119.0−121.0	56.86 (57.23)	5.88 (6.13)
2j′ (W)	Et	Ph	121.0−124.0	*b*	*b*

[a] Calculated values in parentheses. [b] Analytically pure sample was not obtainable (see text).

The cationic complexes analogous to **2** with hydride ligand in the place of alkoxide and a halide counteranion have been prepared by Dias et al. starting from Cp_2MoHX (X = Cl, Br, and I)[14] for PPh_3, PMe_2Ph, PEt_2Ph,[15] and the X-ray structure of $[Cp_2MoH(PPh_3)]^+I^-$ was determined to be a distorted tetrahedron.[16]

Preparations, analytical data, and spectroscopic properties for complexes **2a**, **2a′**, **2c**, **2c′**, **2e**, **2e′**, **2h**, **2h′**, **2i**, **2i′**, **2j**, and **2j′** are compiled in Tables 5−7, respectively. The data for complexes **2b**, **2b′**, **2d**, **2d′**, **2f**, **2f′**, **2g**, **2g′**, **2k**, and **2k′** are stored in the Supporting Information as Tables S13−S15. The syntheses of complexes **2** as described in Tables 5 and S13 show the following trends. In methanol, ethanol, or 2-propanol, only basic phosphines such as triethylphosphine or tributylphosphine react with **1a**,**b**. On the other hand, no substitution of the hydroxy bridging groups by triphenylphosphine has been observed in these solvents. Interestingly, in moderately acidic alcohol, such as trifluoroethanol, or in the presence of phenol, the reactions proceeded more smoothly affording **2** in good yields. Moreover, triphenyphosphine reacted also in trifluoroethanol with **1a** or **1b** to give monomeric complexes. Therefore these substitution reactions seem to be effected with both the basicity of tertiary phosphine ligands and the acidity of solvents.

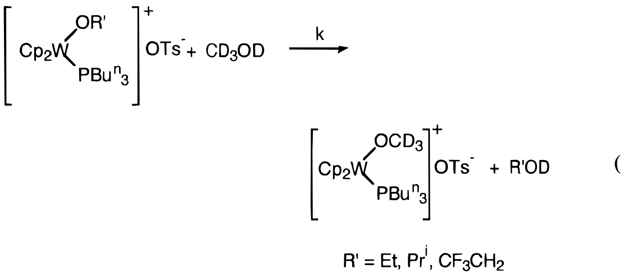
As shown in Table 7, ^1H NMR resonances for the cyclopentadienyl ring protons of **2** appear in the range δ 5.4−5.6 ppm as a doublet coupled to phosphorus; this represents significant deshielding of these protons compared with chemical shifts in parent neutral Cp_2MH_2 (M = W and Mo) complexes (δ 4.2−4.3 ppm) but is compatible with the observed chemical shifts of cationic complex **1a** or **1b**.

The ^1H NMR studies showed that ethoxo, isopropoxo, and trifluoroethoxo complexes were converted slowly to methoxo species in methanol (eq 5). These alkoxo

Table 7. ^1H NMR Spectral Data for $[Cp_2M(OR')(PR_3)]^+(OTs^-)$ (2)

compd (M)[a]	R	R′	δ (ppm)
2a (Mo)	Et	Me	5.58 (d, Cp, $J_{P-H} = 1.22$ Hz, 10H), 3.34 (s, OMe, 3H), 1.94−2.06 (m, PCH_2, 6H), 1.04−1.16 (m, CH_3, 9H)
2a′ (W)	Et	Me	5.55 (d, Cp, $J_{P-H} = 1.22$ Hz, 10H), 3.21 (s, OMe, 3H), 1.87−1.96 (m, PCH_2, 6H), 0.96−1.07 (m, CH_3, 9H)
2c (Mo)	Et	Et	5.55 (d, Cp, $J_{P-H} = 1.83$ Hz, 10H), 2.90 (q, CH_2 of OEt, $J_{H-H} = 6.33$ Hz, 2H), 1.97−2.09 (m, PCH_2, 6H), 1.06−1.18(m, CH_3, 9H), 0.78 (t, CH_3 of OEt, $J_{H-H} = 6.71$ Hz, 3H)
2c′ (W)	Et	Et	5.52 (d, Cp, $J_{P-H} = 7.93$ Hz, 10H), 3.09 (q, CH_2 of OEt, $J_{H-H} = 6.91$ Hz, 2H), 1.97−2.09 (m, PCH_2, 6H), 1.06−1.17(m, CH_3, 9H), 0.72 (t, CH_3 of OEt, $J_{H-H} = 6.71$ Hz, 3H)
2e (Mo)	Et	Pr^i	5.56 (d, Cp, $J_{P-H} = 1.83$ Hz, 10H), 2.92 (dspt, CH of Pr^i, $J_{H-H} = 6.11$ Hz, $J_{P-H} = 1.22$ Hz, 1H), 1.96−2.08 (m, PCH_2, 6H),1.05−1.18 (m, CH_3, 9H), 0.75 (d, CH_3 of Pr^i, $J_{H-H} = 5.49$ Hz, 6H)
2e′ (W)	Et	Pr^i	5.54 (d, Cp, $J_{P-H} = 1.22$ Hz, 10H), 3.23 (dspt, CH of Pr^i, $J_{H-H} = 6.11$ Hz, $J_{P-H} = 1.83$ Hz, 1H), 1.94−2.05 (m, PCH_2, 6H),1.05−1.19 (m, CH_3, 9H), 0.73 (d, CH_3 of Pr^i, $J_{H-H} = 6.11$ Hz, 6H)
2h (Mo)	Bu^n	CH_2CF_3	5.62 (d, Cp, $J_{P-H} = 1.84$ Hz, 10H), 3.16 (q, CH_2 of CH_2CF_3, $J_{F-H} = 9.77$ Hz, 2H), 1.90−2.03 (m, PCH_2, 6H), 1.38−1.50(m, CH_2CH_2, 12H), 0.88−1.00 (m, CH_3, 9H)
2h′ (W)	Bu^n	CH_2CF_3	5.60 (d, Cp, $J_{P-H} = 1.22$ Hz, 10H), 3.36 (q, CH_2 of CH_2CF_3, $J_{F-H} = 9.77$ Hz, 2H), 1.90−2.05 (m, PCH_2, 6H), 1.40−1.55(m, CH_2CH_2, 12H), 0.85−1.02 (m, CH_3, 9H)
2i (Mo)	Ph	CH_2CF_3	7.40−7.63 (m, Ph, 15H), 5.45 (d, Cp, $J_{P-H} = 1.22$ Hz, 10H), 3.84 (q, CH_2 of CH_2CF_3, $J_{F-H} = 9.16$ Hz, 2H)
2i′ (W)	Ph	CH_2CF_3	7.40−7.63 (m, Ph, 15H), 5.45 (d, Cp, $J_{P-H} = 1.22$ Hz, 10H), 3.55 (q, CH_2 of CH_2CF_3, $J_{F-H} = 9.77$ Hz, 2H)
2j (Mo)	Et	Ph	7.01 (t, Ph (meta), $J_{H-H} = 7.33$ Hz, 2H), 6.54 (t, Ph (para), $J_{H-H} = 7.33$ Hz, 1H), 6.19 (d, Ph (ortho), $J_{H-H} = 7.33$ Hz, 2H),5.65 (d, Cp, $J_{P-H} = 1.22$ Hz, 10H), 2.05−2.20 (m, PCH_2, 6H), 1.14−1.26 (m, CH_3, 9H)
2j′ (W)	Et	Ph	7.07 (t, Ph (meta), $J_{H-H} = 7.33$ Hz, 2H), 6.57 (t, Ph (para), $J_{H-H} = 7.33$ Hz, 1H), 6.30 (dd, Ph (ortho), $J_{H-H} = 8.54$ Hz, $J_{P-H} = 1.22$ Hz, 2H), 5.63 (d, Cp, $J_{P-H} = 1.83$ Hz, 10H), 2.05−2.25 (m, PCH_2, 6H), 1.15−1.28 (m, CH_3, 9H)

[a] For complexes **2b**, **2b′**, **2d**, **2d′**, **2f**, **2f′**, **2g**, **2g′**, **2k**, and **2k′**, see the Supporting Information.



(5)

exchange reactions were found to follow the pseudo-first-order kinetics with the rate constants shown in Table 8. At 20 °C, trifluoroethoxo complex was found to be quite stable, whereas relatively slow transformation was observed at 60 °C.

Molecular Structure of [$Cp_2Mo(PBu^n_3)(CF_3CH_2O)]^+(OTs^-)$ (2h). While the spectroscopic analyses of complexes **2** established their overall structures, we were interested in further details of the structure. Consequently, the structure of complex **2h** (R = Bu^n; R′ = CF_3CH_2) was confirmed by single-crystal X-ray analysis. A dark-red crystal suitable for X-ray analysis was obtained by recrystallization from benzene. An ORTEP view, together with the atom-numbering scheme, is shown in Figure 2. Bond lengths and bond angles appear in Table 9. The crystals belong to the triclinic system. The structure of the complex shows that molybdenum is surrounded by a distorted tetrahedral array of the center of two cyclopentadienyl ligands, the phosphine atom of PBu^n_3, and the oxygen atom of CF_3CH_2O. This structure can be compared and contrasted with that of the neutral phosphine complex $Cp_2Mo(PBu^n_3)$ (**3**), which was synthesized and characterized by our group.[5a]

The cyclopentadienyl rings are bound to molybdenum in an η^5 fashion, and each of the ring carbon atoms are coplanar. The internal ligand C−C−C bond angles average 107.6°, which is approximately equal to that of complex **3** (107.9°). The C−C bond distances for Cp rings average 1.38 Å, which is a little shorter than that of complex **3** by ca. 0.03 Å. The Mo−CP1 (CP1 is the centroid of the cyclopentadienyl ligand) bond distance is 1.96 Å, and it closely resembles that found in **3** (Mo−CP1 = 1.95 Å). The CP1−Mo−CP2 angle is 132.8° and differs notably from the angle CP1−Mo−CP2 in **3** (143.8°). This clearly reflects the steric repulsion between the large cyclopentadienyl ligand and the trifluoroethoxo ligand. The PBu^n_3 molecule is coordinated to molybdenum atom with a Mo−P bond distance of 2.540 Å. It appears to be long in contrast to the known Mo−P bond length of 2.494 Å in complex **3**, again reflecting the bulkiness of the trifluoroethoxo ligand.

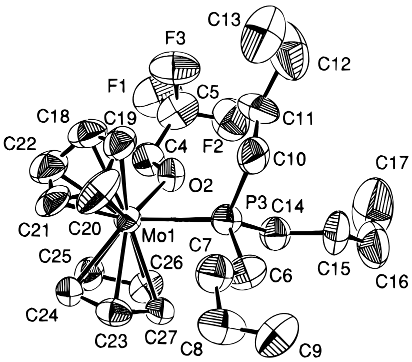


Figure 2. ORTEP drawing of the molecular structure of **2h** with the atom-numbering scheme.

Table 8. Pseudo-First-Order Rate Constants for the Reactions of [$Cp_2W(PBu^n_3)(OR')]^+(OTs^-)$ with Methanol[a]

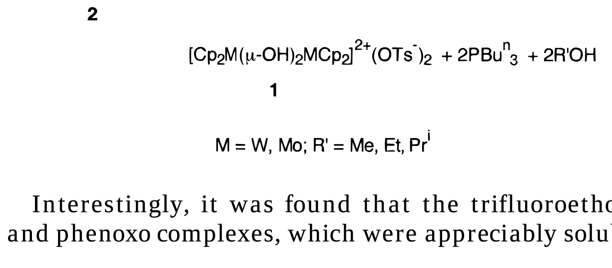
complex	R′	rate const k/s^{-1}
2d′	Et	4.86×10^{-5} [b]
2f′	Pr^i	3.70×10^{-4} [b]
2h′	CF_3CH_2	4.98×10^{-5} [c]

[a] The progress of the reaction was monitored by observing the liberation of the corresponding alcohol from the complex with an ^1H NMR spectrometer. [b] The measurement was carried out at 20 °C. [c] The measurment was carried out at 60 °C.

Table 9. Interatomic Distances (Å) and Angles (deg) for 2h

Distances			
Mo(1)−P(3)	2.540(4)	Mo(1)−O(2)	2.019(8)
Mo(1)−C(18)	2.31(2)	Mo(1)−C(19)	2.30(2)
Mo(1)−C(20)	2.25(2)	Mo(1)−C(21)	2.28(2)
Mo(1)−C(22)	2.30(2)	Mo(1)−C(23)	2.30(1)
Mo(1)−C(24)	2.26(1)	Mo(1)−C(25)	2.24(1)
Mo(1)−C(26)	2.31(1)	Mo(1)−C(27)	2.36(1)
O(2)−C(4)	1.39(2)	C(4)−C(5)	1.50(2)
P(3)−C(6)	1.83(2)	P(3)−C(10)	1.84(2)
P(3)−C(14)	1.82(1)	C(6)−C(7)	1.46(2)
C(7)−C(8)	1.58(3)	C(8)−C(9)	1.39(3)
C(10)−C(11)	1.24(3)	C(14)−C(15)	1.51(2)
C(15)−C(16)	1.52(3)	C(16)−C(17)	1.27(3)
Cp−Mo(1)	1.96		
Angles			
P(3)−Mo(1)−O(2)	74.4(3)	Mo(1)−P(3)−C(6)	117.9(6)
Mo(1)−P(3)−C(10)	118.0(5)	Mo(1)−P(3)−C(14)	111.1(5)
Mo(1)−O(2)−C(4)	121.4(8)	O(2)−C(4)−C(5)	110(1)
C(19)−C(18)−C(22)	114(2)	C(18)−C(19)−C(20)	107(2)
C(19)−C(20)−C(21)	101(2)	C(20)−C(21)−C(22)	113(2)
C(18)−C(22)−C(21)	103(2)	C(24)−C(23)−C(27)	106(1)
C(23)−C(24)−C(25)	108(1)	C(24)−C(25)−C(26)	107(1)
C(25)−C(26)−C(27)	108(1)	C(23)−C(27)−C(26)	109(1)
Cp(1)−Mo(1)−Cp(2)	132.8		

Reaction of [$Cp_2M(PBu^n_3)(OR')]^+OTs^-$ (R′ = Me, Et, Pr^i) with H_2O. The complexes [$Cp_2MPBu^n_3(OR')]^+OTs^-$ (**2**) (M = Mo, W; R′ = Me, Et, Pr^i) have been readily and quantitatively reverted to the original complex **1a** or **1b** on dissolving the former in benzene containing a small quantity of water, accompanied by the liberation of the phosphine ligand (eq 6). On the other hand, triethylphosphine complexes were not soluble in benzene at all and they were unreactive to water.



(6)

Interestingly, it was found that the trifluoroethoxo and phenoxo complexes, which were appreciably soluble

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(14) Dias, A. R.; Romão, C. C. *J. Organomet. Chem.* **1982**, *233*, 223.

(15) Azevedo, C. G.; Dias, A. R.; Martins, A. M.; Romão, C. C. *J. Organomet. Chem.* **1989**, *368*, 57.

(16) Azevedo, C. G.; Calhorda, M. J.; Carrondo, M. A. F. d. C. T.; Dias, A. R.; Felix, V.; Romão, C. C. *J. Organomet. Chem.* **1990**, *391*, 345.

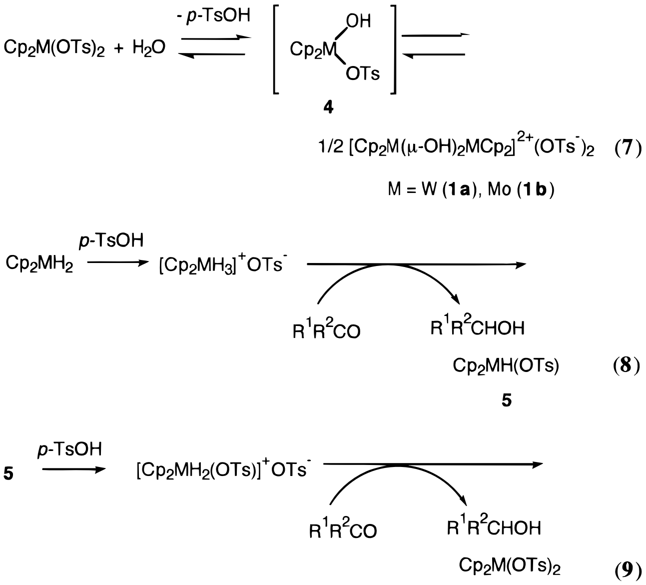
(17) Carmona, E.; Marìn, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1987**, *6*, 1757.

Table 10. Crystallographic Data for Complexes 1a,b

complex	**1a**	**1b**
formula	$C_{34}H_{38}O_9S_2W_2$	$C_{34}H_{38}O_9S_2Mo_2$
fw	1022.5	846.37
cryst system	orthorhombic	orthorhombic
space group	*Pbna* (No. 50)	*Pbna* (No. 50)
a/Å	15.262(3)	15.436(10)
b/Å	16.101(4)	16.308(9)
c/Å	13.049(3)	12.963(7)
V/Å^3	3207	3263
Z	4	4
μ/cm^{-1}	75.04	9.27
F(000)	1976	1720
ρ_{calcd} g cm^{-3}	2.118	1.723
temp/°C	25(1)	25(1)
cryst size/mm	0.20 × 0.35 × 0.53	0.28 × 0.33 × 0.80
2θ range/deg	3.0−50.0	3.0−50.0
Scan rate/deg min^{-1}	4	6
h, k, l	$0 \le h \le 18, 0 \le k \le 19, 0 \le l \le 15$	$0 \le h \le 18, 0 \le k \le 20, 0 \le l \le 15$
unique reflcns	2771	3188
reflcns used ($F_o \ge 3\sigma(F_o)$)	2057	2456
R^a	0.044	0.042
$R_w{}^b$	0.050	0.047
weighting scheme	$[\{\sigma(F_o)\}^2 + \{0.020(F_o)\}^2]^{-1}$	$[\{\sigma(F_o)\}^2 + \{0.020(F_o)\}^2]^{-1}$

[a] $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [b] $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w|F_o|^2]^{1/2}$.

Scheme 1



in benzene, were unreactive to water. The results may be ascribed to the fact that both trifluoroethanol and phenol are more acidic than water. It is particularly interesting in light of the fact that the nucleophilicity of trifluoroethoxo or phenoxo group is weaker than that of ethoxo or methoxo group, and thereby the former seems to bind to the metals more weakly.

Mechanistic Considerations for the Formation of Complex 1a or 1b. Although several mechanisms for the formation of complexes **1a**,**b** can be considered, the mechanism suggested in Scheme 1 can account for the reaction most adequately, since Cp_2MH_2 and $Cp_2M(OTs)_2$ are essential for the formation of complexes **1a**,**b** and the source of the bridging OH seems to be water.

The initial stage of this reaction is replacement of one OTs^- group in ditosylato complex $Cp_2M(OTs)_2$ by OH^-. Although the equilibrium might lie well over to the left in this hydrolysis process, trapping of *p*-toluenesulfonic acid formed by Cp_2MH_2 as described later may cause the displacement of the position of the equilibrium. The resulting hydroxy complex **4** is dimerized into the dinuclear complex **1**, accompanied by the migration of OTs^- group from the inner sphere to the outer (eq 7). Apparently the greater tendency of the OH^- group, as compared with halide anions such as Cl^- and I^-, to act as a bridging ligand would be responsible for the formation of these dimeric species.[17] Complex **1** and monomeric **4** may possibly coexist at equilibrium in solution, though there is no direct evidence to support it. Only one signal for Cp protons was observed in the ^1H NMR of complex **1**. *p*-Toluenesulfonic acid formed in eq 7 is immediately trapped by basic Cp_2MH_2 affording monohydrido tosylato complex $Cp_2MH(OTs)$ (**5**) through the cationic trihydride intermediate $[Cp_2MH_3]^+OTs^-$ (eq 8). We believe this neutralization reaction provides the driving force for the whole system, especially for the protonolysis of $Cp_2M(OTs)_2$ with such a weak acid as H_2O. The resulting complex **5** reacts with an additional acid to give ditosylato complex $Cp_2M(OTs)_2$ (eq 9). This process is thought to occur via the dihydrido M(VI) intermediate with a subsequent dehydrogenation reaction affording the ditosylato complex, which is subjected to the further reaction as the starting material. Consequently, Cp_2MH_2 plays an important role not only as a stimulator of the reaction but also as a source for the starting material $Cp_2M(OTs)_2$.

Further investigations of the reactions of complexes **1a**,**b** with various kinds of nucleophiles and the mechanism of the formation are now in progress.

Experimental Section

General Comments. Unless indicated otherwise, all manipulations were conducted under purified argon or nitrogen. Air-sensitive reagents and products were handled by standard Schlenk techniques. Commercially available chemicals were used as such without any further purification.

Infrared spectra were determined on a JASCO A-202 spectrometer or a Perkin-Elmer 1600 series spectrometer. NMR spectra were recorded on a JEOL JNMEX-270 spectrometer. ^1H and ^{13}C NMR chemical shifts were referenced to tetramethylsilane (TMS). All solvents were dried by

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(18) Fan, F. SAPI 85, Chinese Academy of Science, Beijing, China, 1985.

Table 11. Fractional Atomic Coordinates and B_{iso}/B_{eq} Values (Å^2) for Complex 1a

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*
W(1)	0.897 33(2)	0.479 98(2)	0.055 75(2) f	2.54(1)
O(2)	0.970 78(44)	0.555 04(44)	−0.041 00(47)	2.79(16)
C(3)	0.830 51(80)	0.353 18(77)	0.038 12(81)	3.93(32)
C(4)	0.767 21(75)	0.417 06(81)	0.030 12(89)	4.02(32)
C(5)	0.783 45(87)	0.464 93(78)	−0.055 55(86)	4.02(33)
C(6)	0.856 48(81)	0.427 73(89)	−0.107 21(80)	4.06(33)
C(7)	0.883 66(72)	0.361 24(81)	−0.050 25(96)	3.91(32)
C(8)	0.854 85(111)	0.470 54(96)	0.229 05(98)	5.42(45)
C(9)	0.936 67(105)	0.503 20(102)	0.229 14(93)f	5.33(44)
C(10)	0.934 72(96)	0.576 96(87)	0.175 38(109)	5.10(38)
C(11)	0.844 17(101)	0.591 94(87)	0.139 48(98)	4.93(39)
C(12)	0.799 07(87)	0.524 53(101)	0.190 57(111)	5.20(41)
S(13)	0.859 82(19)	0.673 73(19)	−0.234 52(22)	3.74(7)
O(14)	0.892 32(53)	0.681 81(56)	−0.128 04(60)	4.56(24)
O(15)	0.876 08(54)	0.591 01(53)	−0.275 90(77)	4.70(24)
O(16)	0.771 29(57)	0.700 91(53)	−0.248 06(74)	5.26(25)
C(17)	0.925 57(74)	0.743 03(69)	−0.306 53(74)	3.22(28)
C(18)	0.890 41(74)	0.797 25(74)	−0.376 79(105)	4.04(32)
C(19)	0.945 01(92)	0.847 02(81)	−0.431 47(92)	4.56(35)
C(20)	1.034 96(74)	0.845 83(77)	−0.421 22(90)	3.93(31)
C(21)	1.070 96(81)	0.791 82(80)	−0.350 56(102)	4.39(34)
C(22)	1.016 22(77)	0.739 45(68)	−0.294 30(96)	4.02(32)
C(23)	1.093 65(105)	0.901 97(108)	−0.483 96(136)	6.60(51)
O(24)	0.750 0(0)	0.750 0(0)	0.000 0(0)	9.76(0)
H(2)	0.96146(0)	0.622 13(0)	−0.05577(0)	2.79(0)
Cp(1)	0.824 3(10)	0.404 8(10)	−0.028 9(10)	2.00(0)
Cp(2)	0.873 9(10)	0.533 4(10)	0.190 8(10)	2.00(0)

Table 12. Fractional Atomic Coordinates and B_{iso}/B_{eq} Values (Å^2) for Complex 1b

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*
Mo(1)	0.898 21(2)	0.479 22(2)	0.054 37(2)	2.58(0)
O(2)	0.972 01(25)	0.557 14(14)	−0.038 75(16)	3.22(5)
C(3)	0.828 24(31)	0.355 58(25)	0.029 36(32)	4.84(11)
C(4)	0.767 48(25)	0.417 28(29)	0.026 74(32)	4.80(11)
C(5)	0.785 31(29)	0.469 13(29)	−0.058 75(34)	5.17(13)
C(6)	0.856 23(29)	0.433 35(29)	−0.110 92(31)	4.80(11)
C(7)	0.881 14(28)	0.364 09(28)	−0.056 98(34)	4.78(11)
C(8)	0.589 29(35)	0.465 13(29)	0.229 01(32)	5.34(13)
C(9)	0.937 49(32)	0.497 80(32)	0.228 82(32)	5.23(13)
C(10)	0.933 38(32)	0.573 09(32)	0.177 93(35)	5.81(13)
C(11)	0.844 04(35)	0.587 22(28)	0.147 31(34)	5.46(13)
C(12)	0.801 74(29)	0.517 63(35)	0.182 90(35)	5.57(13)
S(13)	0.858 87(6)	0.673 16(6)	−0.240 40(7)	4.23(2)
O(14)	0.887 82(20)	0.679 45(19)	−0.133 55(22)	5.44(8)
O(15)	0.875 85(19)	0.592 70(16)	−0.283 17(25)	5.04(8)
O(16)	0.770 98(19)	0.700 74(19)	−0.255 16(25)	5.68(8)
C(17)	0.925 77(23)	0.742 03(22)	−0.308 24(28)	3.51(8)
C(18)	0.890 19(25)	0.797 52(25)	−0.377 53(32)	4.19(10)
C(19)	0.945 61(29)	0.849 75(25)	−0.432 89(32)	4.55(11)
C(20)	1.033 79(29)	0.846 77(26)	−0.419 4 6(34)	4.84(12)
C(21)	1.068 37(26)	0.792 30(28)	−0.348 93(37)	4.87(11)
C(22)	1.013 70(28)	0.739 58(25)	−0.293 97(34)	4.63(11)
C(23)	1.091 46(38)	0.903 09(35)	−0.477 70(53)	7.23(18)
O(24)	0.750 0(0)	0.750 0(0)	0.000 0(0)	8.25(0)
H(2)	0.946 42(0)	0.604 56(0)	−0.074 57(0)	3.22(0)
Cp(1)	0.823 8(4)	0.407 9(4)	−0.034 1(4)	
Cp(2)	0.875 1(4)	0.528 2(4)	0.193 2(4)	

Table 13. Crystallographic Data for 2h

formula	$C_{31}H_{46}F_3O_4MoSP$
fw	698.67
cryst system	triclinic
space group	$P\bar{1}$ (No. 2)
a/Å	10.351(2)
b/Å	17.025(7)
c/Å	10.128(3)
α/deg	105.64(3)
β/deg	101.69(3)
γ/deg	86.98(3)
Z	2
temp/°C	25(1)
μ/cm^{-1}	46.25
$F(000)$	728.00
ρ_{calcd}/g cm^{-1}	1.379
cryst size/mm	0.28 × 0.22 × 0.06
2θ range/deg	48.2−49.8
scan rate/deg min^{-1}	16.0
unique reflcns	3618
reflcns used	3464
R^a	0.059
$R_W{}^b$	0.078
weighting scheme	$[\sigma^2(F_o)]^{-1}$
function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$

[a] $R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$. [b] $R_w = [\sum_w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum_w F_o{}^2]^{1/2}$.

standard methods and distilled before use. Literature methods were used to prepare Cp_2WH_2, $Cp_2W(OTs)_2$, Cp_2MoH_2, and $Cp_2Mo(OTs)_2$, and they were judged pure by IR and NMR spectroscopy.[3,11] *p*-Toluenesulfonic acid was dehydrated by the use of the benzene azeotrope.

X-ray Crystallographic Studies of 1a,b. Crystals of complexes **1a**,**b** suitable for diffraction analyses were grown in methanol at −40 °C. The dark green crystals thus obtained were mounted in glass capillary tubes under argon. The unit-cell parameters were obtained by least-squares refinement of 2θ values of reflections with $3° \leq 2\theta \leq 50°$. Four crystallographically independent molecules were found to be present in a unit cell. Intensities were collected on a Rigaku AFC-5 four-circle diffractometer. Mo Kα radiations were used (λ = 0.710 69 Å) with μ = 75.04 cm^{-1} (**1a**) and 9.27 cm^{-1} (**1b**), and $F(000)$ = 1976 Å (**1a**) and 1720 Å (**1b**). The parameters used during the collection of diffraction data are given in Table 10.

Calculations were carried out with the program systems SAPI 8518 on a FACOM A-70 computer. The structures were solved by common Fourier methods. A full-matrix least-squares refinement procedure was used with anisotropic thermal parameters or with isotropic thermal parameters for the non-hydrogen atoms. Positions of hydrogen atoms of hydroxo groups were located from the Fourier difference map. All other hydrogen atoms were located at a distance of 1.00 Å from the carbon atoms by assuming idealized geometry. The listings of atomic coordinates are provided in Tables 11 and 12.

Preparation of $[Cp_2W(\mu\text{-}OH)_2WCp_2]^{2+}(OTs^-)_2$ (1a) and $[Cp_2Mo(\mu\text{-}OH)_2MoCp_2]^{2+}(OTs^-)_2$ (1b). A mixture of 0.0727 g of Cp_2WH_2 (0.231 mmol) and 0.151 g of $Cp_2W(OTs)_2$ (0.229 mmol) in acetone/H_2O (20 mL/0.2 mL) was heated at 50 °C for 8 h under argon. The grayish precipitate thus obtained was separated by filtration, and extracted with methanol, and solvent was removed under vacuum. Purification of the residue by recrystallization from methanol afforded a good columnar solid suitable for the X-ray analysis. Exhaustive washing with ether removed the water included as crystallization solvent and produced the material that analyzed as $[Cp_2W(\mu\text{-}OH)_2WCp_2]^{2+}(OTs^-)_2$ (**1a**) (0.193 g) in yield of 84%. This procedure is also applicable to the synthesis of the molybdenum analog **1b**, $[Cp_2Mo(\mu\text{-}OH)_2MoCp_2]^{2+}(OTs^-)_2$ (yield = 97%). **1a**: mp 115 °C dec; IR ν(OH) 3550 cm^{-1}, ν(CH) 3078 cm^{-1}; ^{1}H NMR (CD_3OD) δ 7.68 (d, 7.9 Hz, 4H, *meta*-tolyl), 7.27 (d, 7.9 Hz, 4H, *ortho*-tolyl), 6.00 (s, 20H, *Cp*), 2.38 (s, 6H, *Me*-tolyl); ^{13}C NMR (CD_3OD) δ 143.48, 141.92, 129.95, 126.63 (*tolyl*), 98.47 (*Cp*), 21.35 (*Me*-tolyl). Anal. Calcd for $C_{34}H_{36}O_8S_2W_2$: C, 40.66; H, 3.61; S, 6.38. Found: C, 40.44; H, 4.14; S, 6.32. **1b**: mp 115 °C dec; IR ν(OH) 3540 cm^{-1}, ν(CH) 3075 cm^{-1}; ^{1}H NMR (CD_3OD) δ 7.70 (d, 7.9 Hz, 4H, *meta*-tolyl), 7.27 (d, 7.9 Hz, 4H, *ortho*-tolyl), 6.00 (s, 20H, *Cp*), 2.38 (s, 6H, *Me*-tolyl); ^{13}C NMR (CD_3OD) δ 143.45, 141.92, 129.95, 126.93 (*tolyl*), 103.59 (*Cp*), 21.35 (*Me*-tolyl). Anal. Calcd for $C_{34}H_{36}O_8S_2Mo_2$: C, 49.27; H, 4.38; S, 7.74. Found: C, 49.02; H, 4.47; S, 7.72.

Reaction of 1a,b with Tertiary Phosphines. A typical procedure is as follows. A solution containing **1a** or **1b** and the tertiary phosphine in either methanol, ethanol, 2-propanol, or trifluoroethanol was stirred under the conditions given in Tables 5 and S13. During the stirring, the solution changed from green to red. From the resulting solution, the solvent

Table 14. Fractional Atomic Coordinates and B_{iso}/B_{eq} Values (Å^2) for 2h

atom	x/a	y/b	z/c	B
Mo(1)	0.1579(1)	−0.18045(7)	0.1864(1)	6.06(3)
S(35)	0.8797(4)	−0.1409(3)	0.6942(5)	8.2(1)
P(3)	0.2808(4)	−0.2109(2)	0.4108(4)	7.3(1)
F(1)	0.100(1)	−0.4845(7)	−0.132(1)	14.0(4)
F(2)	0.176(1)	−0.4724(6)	0.082(1)	13.5(4)
F(3)	0.286(1)	−0.4303(6)	−0.035(1)	13.3(4)
O(2)	0.1727(8)	−0.3032(5)	0.1420(9)	6.6(2)
O(3)	0.981(1)	−0.1886(7)	0.633(1)	11.2(4)
O(4)	0.790(1)	−0.1028(7)	0.600(1)	11.7(4)
O(5)	0.933(1)	−0.0852(6)	0.829(1)	9.5(3)
C(4)	0.102(2)	−0.353(1)	0.019(2)	8.2(5)
C(5)	0.166(2)	−0.435(1)	−0.016(2)	10.3(7)
C(6)	0.289(2)	−0.131(1)	0.574(2)	10.4(6)
C(7)	0.348(2)	−0.053(1)	0.582(2)	11.4(7)
C(8)	0.352(2)	0.022(1)	0.707(3)	13.2(7)
C(9)	0.372(3)	0.007(2)	0.837(2)	14.8(9)
C(10)	0.454(2)	−0.244(1)	0.420(2)	11.4(6)
C(11)	0.474(2)	−0.324(1)	0.323(2)	13.2(7)
C(12)	0.614(3)	−0.372(2)	0.322(4)	20(1)
C(13)	0.690(3)	−0.323(2)	0.310(3)	18(1)
C(14)	0.202(1)	−0.2936(9)	0.448(2)	8.1(4)
C(15)	0.267(2)	−0.322(1)	0.575(2)	11.8(6)
C(16)	0.192(3)	−0.391(2)	0.595(3)	15.0(9)
C(17)	0.192(5)	−0.458(2)	0.503(3)	23(1)
C(18)	0.290(3)	−0.205(1)	0.021(3)	10.3(8)
C(19)	0.368(2)	−0.172(2)	0.148(3)	10.1(7)
C(20)	0.317(4)	−0.091(2)	0.202(3)	13(1)
C(21)	0.224(3)	−0.085(1)	0.094(4)	11.0(8)
C(22)	0.200(2)	−0.159(3)	−0.016(3)	13.0(9)
C(23)	0.024(1)	−0.0834(9)	0.296(2)	8.0(5)
C(24)	−0.023(2)	−0.102(1)	0.150(2)	9.3(6)
C(25)	−0.060(1)	−0.183(1)	0.102(2)	8.7(5)
C(26)	−0.044(2)	−0.214(1)	0.220(2)	8.1(5)
C(27)	0.004(1)	−0.153(1)	0.336(2)	7.4(5)
C(28)	0.782(1)	−0.2133(8)	0.734(1)	6.2(4)
C(29)	0.676(2)	−0.1846(9)	0.796(1)	7.7(4)
C(30)	0.606(1)	−0.238(1)	0.836(2)	7.9(5)
C(31)	0.642(2)	−0.317(1)	0.821(2)	8.4(5)
C(32)	0.749(2)	−0.3431(9)	0.760(2)	8.7(5)
C(33)	0.821(1)	−0.2912(10)	0.719(1)	7.6(4)
C(34)	0.546(2)	−0.373(1)	0.859(2)	12.5(7)

[a] $B_{eq} = {}^{8}/_{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha$.

was evaporated to dryness under reduced pressure. The residue was washed with hexane and ether and then extracted with either methanol (for complexes **2a**, **2a′**, **2b**, and **2b′**), ethanol (for complexes **2c**, **2c′**, **2d**, and **2d′**), 2-propanol (for complexes **2e**, **2e′**, **2f**, and **2f′**) or trifluoroethanol (for complexes **2g**, **2g′**, **2h**, **2h′**, **2i**, and **2i′**). Ether was added to the extract to precipitate $[Cp_2MPR_3(OR')]^+OTs^-$ (**2**) as a reddish powder. For complexes **2j**, **2j′**, **2k**, and **2k′**, this extraction procedure was not carried out.

Examples listed in Tables 5 and S13 were carried out under essentially the same conditions. Analytical data and spectroscopic properties of complexes **2** are given in Tables 6 and S14 and Tables 7 and S15, respectively. Elemental analyses of complexes **2c**, **2c′**, **2d**, **2e**, **2e′**, **2f**, **2f′**, **2i**, and **2j′** failed to provide useful information because of impurities which were difficult to remove.

X-ray Crystallographic Study of 2h. Crystals of complex $[Cp_2Mo(PBu^n{}_3)(CF_3CH_2O)]^+OTs^-$ (**2h**) suitable for X-ray crystallography were grown in benzene at 10 °C, and a dark-red plate-shaped crystal thus obtained was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer by using Cu Kα radiation ($\lambda = 1.541\,78$ Å) with $\mu = 46.25$ cm^{-1} and $F(000) = 728.00$ Å.

The unit-cell parameters were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $48.16° \leq 2\theta \leq 49.81°$. The parameters used during the collection of diffraction data are given in Table 13. The structure was solved and expanded by using Fourier techniques.[19] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Final results are summarized in Table 14.

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Supporting Information Available: Tables S1−S15, listing fractional atomic coordinates and thermal parameters, anisotropic thermal factors, and all bond distances and angles for **1a**,**b** and **2h** and experimental details and characterization data for complexes **2b**, **2b′**, **2d**, **2d′**, **2f**, **2f′**, **2g**, **2g′**, **2k**, and **2k′** (37 pages). Ordering information is given on any current masthead page.

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