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

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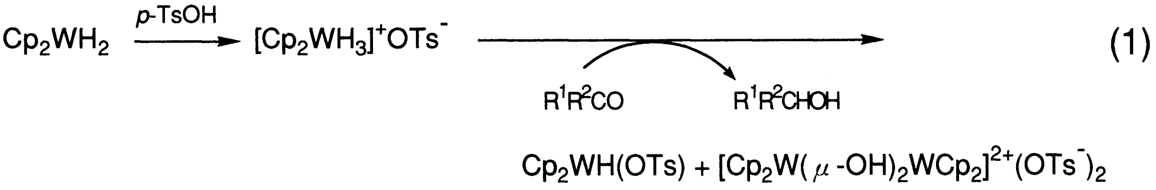
Novel dinuclear complexes $[Cp_2M(\mu\text{-}OH)_2MCp_2]^{2+}(OTs^-)_2$ (M = Mo and W) were prepared by the reaction of Cp_2MH_2 with $Cp_2M(OTs)_2$ in aqueous acetone. Their structures were characterized by spectroscopic methods as well as by X-ray crystallography. The structure comprises a planar four membered ring consisting of alternating M and O atoms.

We have been interested for sevelal years in the chemistry of the molybdenum and tungsten dihydrides Cp_2MH_2 (Cp = $\eta\text{-}C_5H_5$, M = Mo and W) which have the basic character and are easily protonated to give cationic trihydrides $[Cp_2MH_3]^+$.$^{1)}$ In the previous paper, we reported that molybdenum trihydride complex $[Cp_2MoH_3]^+OTs^-$ (OTs = $p\text{-}CH_3C_6H_4SO_3$) was readily converted to hydridotosylato complex $Cp_2MoH(OTs)$ with accompanying evolution of one mol of H_2 when warmed in ethanol.$^{2)}$ This complex is important not only as a highly reactive molybdenocene precursor but also as a stereoselective reducing agent in organic synthesis.$^{3)}$ Unlike the molybdenum complex, tungsten trihydride is so inert that the hydridotosylato complex should be prepared by an alternate route. We have explored the reaction system and found that it can be successfully obtained in the presence of hydrogen acceptor such as acetone or 2-butanone. In these reactions, we have observed unexpected formation of a novel dinuclear complex $[Cp_2W(\mu\text{-}OH)_2WCp_2]^{2+}(OTs^-)_2$ **1a** as a by-product in low yield.$^{4)}$



$$Cp_2WH_2 \xrightarrow{p\text{-TsOH}} [Cp_2WH_3]^+OTs^- \xrightarrow[R^1R^2CO \;\to\; R^1R^2CHOH]{} Cp_2WH(OTs) + [Cp_2W(\mu\text{-}OH)_2WCp_2]^{2+}(OTs^-)_2 \qquad (1)$$

1a

Recently much attention has been focused on the compounds of this type in terms of a precursor for the di-μ-oxo complexes which are particularly interesting in view of their ability to activate molecular oxygen as well as biological aspects.$^{5)}$ We report herein the straightforward synthesis of **1a** including the molybdenum analog $[Cp_2Mo(\mu\text{-}OH)_2MoCp_2]^{2+}(OTs^-)_2$ **1b** and the structual characterization of these complexes. The reaction of **1a** with nucleophiles is also described.

In the reaction of Cp_2WH_2 with p-toluenesulfonic acid, the observation indicated that purplish complex

$Cp_2W(OTs)_2$ was first formed, then it was converted to grayish complex **1a**. Furthermore, it appears that water takes part in the reaction since no formation of complex **1a** was observed under rigorously anhydrous conditions. We therefore tried an alternate system that involved the use of water and $Cp_2W(OTs)_2$.6)

$$Cp_2WH_2 + Cp_2W(OTs)_2 \xrightarrow{(CH_3)_2CO/H_2O} [Cp_2W(\mu\text{-}OH)_2WCp_2]^{2+}(OTs^-)_2 \qquad (2)$$

The reaction of Cp_2WH_2 with $Cp_2W(OTs)_2$ in aqueous acetone at 50℃ afforded complex **1a** quantitatively.7) In this system, we could not observe a side reaction. This procedure was found to be also applicable to the molybdenum analog **1b**. Complex **1a** was not soluble in a non-polar solvent, such as benzene or toluene, but soluble in methanol and was moderately air-stable solid. The IR spectrum of the complex shows a band at 3546 cm^{-1} due to the O-H stretching vibrations, as well as Cp ligand peaks and those due to the OTs^- counter ion. ^1H NMR spectrum in CD_3OD shows a singlet signal assignable to the Cp protons at δ = 6.00 ppm which is the lower field than the parent complex Cp_2WH_2 by about 1.7 ppm, suggesting that the increased magnetic deshielding effect in complex **1a** is induced by the cationic metal center. The spectroscopic properties of the molybdenum complex **1b** were found to be quite similar to those of **1a**.

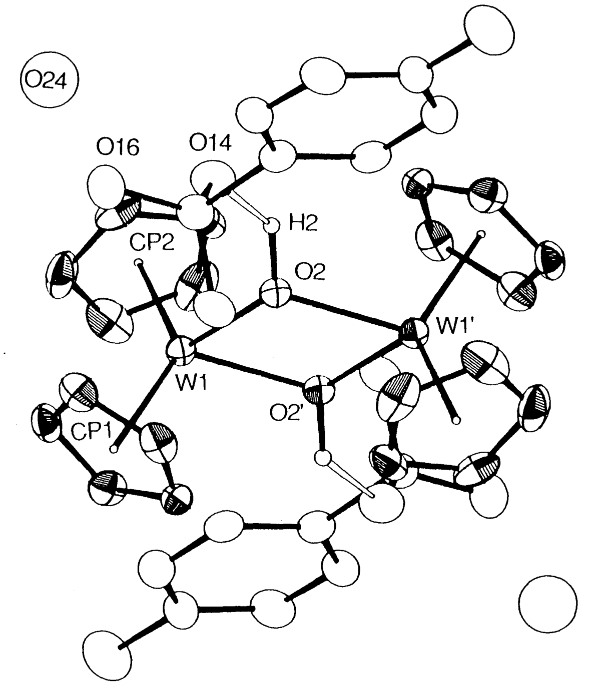
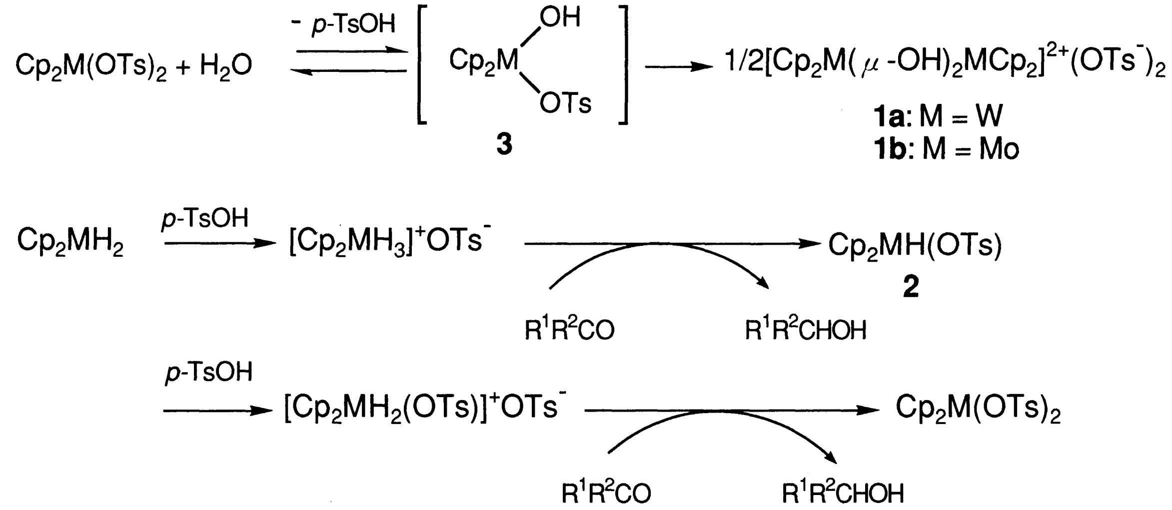


Fig. 1. Structure of **1a**.

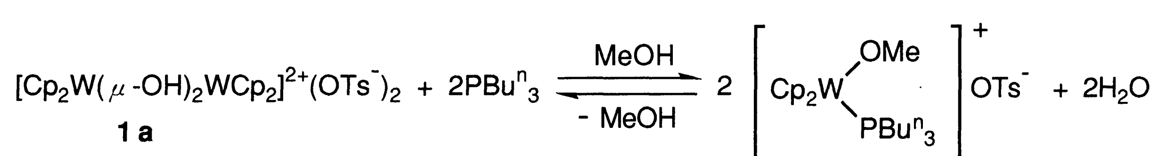
The X-ray structure determination for complex **1a** confirms the dimer formulation in which one molecule of water is included as a crystallization solvent. A view of the molecule is shown in Figure 1.8) In Fig. 1, O(24) corresponds to the oxygen atom of the water molecule. Complex **1a** has an orthorhombic system. The structure comprises an almost planar four-membered ring consisting of alternating W and O atoms, and the conformation shows a C_2 axis passing through the two bridging O(2) atoms. The position of H(2) atom was located from a different Fourier map. The O(2)-O(14) distance is 2.625 Å, and hence it seems reasonable to assume that H(2) forms hydrogen bond to O(14). The Cp ligands attached to the tungsten atoms are positioned above and below the W_2O_2 plane. This complex has geometry typical of bent metallocene with W-CP (CP is the centroid of the cyclopentadienyl ligand) distances close to 2.0 Å and with CP1-W-CP2 angles equal to 130.95°, and these results are in accord with expectations based on the orbital configuration of tungsten atom and the steric interaction around it.9) The bond distances of 2.952 and 3.348 Å for O(24)-O(14) and O(24)-O(16) respectively, suggest that hydrogen bondings occur between the water molecule and oxygen atoms of the TsO anion. The angle W-O-W is 114.65° and W-W distance is 3.51 Å, therefore we think it is too large for tungsten atoms to interact mutually.10) The whole geometry of the molybdenum analog **1b** was found to be virtually identical with that of **1a** on the basis of the X-ray analysis.11) Although at this moment the reaction and in particular the mechanism are not completely understood and are being investigated further, the mechanism suggested in the following scheme can account for the formation of the complexes.



Scheme 1.

The initial stage of this reaction would be replacement of one OTs^- group in $Cp_2M(OTs)_2$ by OH^-. The resulting hydroxo complex **3** may be dimerized into the dinuclear complex **1**, accompanied by the migration of OTs^- group from the inner sphere to the outer. The greater tendency of the OH^- group, as compared with Cl^- and I^-, to act as a bridging ligand, would be responsible for the formation of these dimeric species.12) Complex **1** and monomeric **3** may possibly coexist at equilibrium in solution, though there is no direct evidence to support it. The *p*-toluenesulfonic acid formed would be immediately trapped by basic Cp_2MH_2 affording monohydridotosylato complex $Cp_2MH(OTs)$ **2** through the cationic trihydride intermediate $[Cp_2MH_3]^+ OTs^-$. We believe this neutralization reaction provides the driving force for the whole system. The resulting complex **2** would react with an additional acid to give $Cp_2M(OTs)_2$ which would be subjected to the further reaction as the starting material.

When **1a** was treated with tributylphosphine in methanol, a reddish brown solid was isolated and identified as a mononuclear cationic methoxo complex **4a**.13)



$$[Cp_2W(\mu\text{-}OH)_2WCp_2]^{2+}(OTs^-)_2 + 2PBu^n_3 \underset{-\,MeOH}{\overset{MeOH}{\rightleftharpoons}} 2\,[Cp_2W(OMe)(PBu^n_3)]^+ OTs^- + 2H_2O \qquad (3)$$

1 a **4 a**

Interestingly, this complex has been readily and quantitatively reverted to the original complex **1a** on dissolving in benzene containing trace of water, accompanied by the liberation of the phosphine ligand. While triethylphosphine reacted with **1a** in a similar manner, triphenylphosphine was found to be unreactive, suggesting that basicity of phosphine ligand may play an important role in this reaction.

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6) $Cp_2W(OTs)_2$: The mixture of Cp_2WH_2 (0.407 g, 1.29 mmol) and *p*-toluenesulfonic acid (0.445 g, 2.59 mmol) in acetone (30 ml) was stirred at ambient temperature for 8 h under argon. Evaporation to dryness and washing the residual solid with ether yielded $Cp_2W(OTs)_2$ (0.771 g, 90.5%).

7) $[Cp_2W(\mu\text{-}OH)_2WCp_2]^{2+}(OTs^-)_2$ **1a**: The mixture of Cp_2WH_2 (0.0727 g, 0.231 mmol) and $Cp_2W(OTs)_2$ (0.151 g, 0.229 mmol) in acetone (20 ml) and water (0.2 ml) was heated at 50℃ for 8 h under argon. The grayish precipitate thus obtained was separated by filtration, extracted with methanol, and solvent was removed under vacuum. Purification 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 material that analyzed as $[Cp_2W(\mu\text{-}OH)_2WCp_2]^{2+}(OTs^-)_2$ **1a** in almost quantitative yield (0.193 g, 84%). This procedure is also applicable to the molybdenum analog **1b** (yield = 66%). **1a**: IR (KBr) 3546 cm^{-1} [ν (O-H)]; 3078 cm^{-1}[ν (C-H)]: ^1H NMR (CD_3OD): δ = 7.68 (4H, d, meta-tolyl, *J* = 7.9 Hz), 7.27 (4H, d, ortho-tolyl, *J* = 7.9 Hz), 6.00 (20H, s, Cp), 2.38 (6H, s, Me-tolyl); Found: C, 40.44; H, 4.14; S, 6.32%. Calcd for $C_{34}H_{36}O_8S_2W_2$: C, 40.66; H, 3.61; S, 6.38%. $[Cp_2Mo(\mu\text{-}OH)_2MoCp_2]^{2+}(OTs^-)_2$ **1b**: IR (KBr) 3540 cm^{-1} [ν (O-H)]; 3075 cm^{-1}[ν (C-H)]: ^1H NMR (CD_3OD): δ = 7.70 (4H, d, meta-tolyl, *J* = 7.9 Hz), 7.27 (4H, d, ortho-tolyl, *J* = 7.9 Hz), 6.00 (20H, s, Cp), 2.38 (6H, s, Me-tolyl). Found: C,49.02; H, 4.47; S, 7.72%. Calcd for $C_{34}H_{36}O_8S_2Mo_2$: C, 49.27; H, 4.38; S, 7.74%.

8) Crystal data for **1a**: $C_{34}H_{38}O_9S_2W_2$, M = 1022.50, orthorhombic, space group *P*bna, a = 15.262(3), b = 16.101(4), c = 13.049(3) Å, V = 3207 $Å^3$, Z = 4, Dc = 2.118 g cm^{-3}, Mo-Kα radiation (λ = 0.71069 Å), R = 0.044, Rw = 0.050 for 2057 reflections [$Fo > 3\sigma(Fo)$].

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10) Covalent radius of a tungsten atom is 1.30 Å. J. A. Deans, "Lange's Handbook of Chemistry," McGraw-Hill Book Company, New York (1985), p. 3-126.

11) A more detailed report of the complex **1b** will be presented elsewhere.

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13) **4a**: IR (KBr) 2750 cm^{-1} [ν (C-H of OMe)]. ^1H NMR (CD_3OD): δ = 7.69 (2H, d, meta-tolyl, *J* = 7.9 Hz), 7.24 (2H, d, ortho-tolyl, *J* = 7.9 Hz), 5.54 (10H, d, Cp, *J* (H-P) = 1.8 Hz), 3.21 (3H, s, OMe), 2.37 (3H, s, Me-tolyl), 1.91-2.01 (6H, m, $PBu^n{}_3$), 1.40-1.50 (12H, m, $PBu^n{}_3$), 0.94-0.99 (9H, m, $PBu^n{}_3$). Found: C, 49.43; H, 6.91; S, 5.11%. Calcd for $C_{30}H_{47}O_4PSW$: C, 50.15; H, 6.59; S, 4.46%.

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