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Preparation and Some Reactions of the Tungsten Hydridotosylato Complex $Cp_2WH(OTs)$

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Reaction of Cp_2WH_2 ($Cp = \eta\text{-}C_5H_5$) with TsOH (*p*-toluenesulfonic acid) in acetone afforded $Cp_2WH(OTs)$ **2** together with a novel binuclear complex $[Cp_2W(\mu\text{-}OH)_2WCp]^{2+}(OTs^-)_2$ **3**. The determination of the molar conductivity suggest that the complex **2** has less ionic nature as compared to the molybdenum analog. The complex **2** reacted with tertiary phosphines and phosphite to give cationic complexes $[Cp_2WH(PR_3)]^+OTs^-$ **5** (R = Ph, Bu^n, OEt).

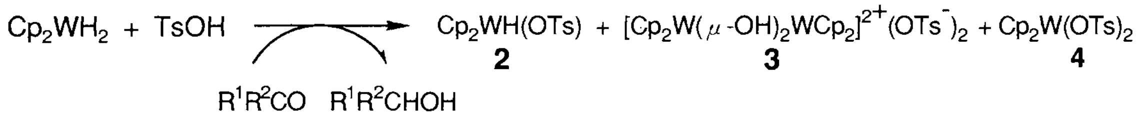
Since the first preparation of the dihydrides Cp_2MoH_2 and Cp_2WH_2 ($Cp = \eta\text{-}C_5H_5$) by Green and coworkers, their chemistries have been widely investigated.1) It has long been known that these complexes have basic character and are easily protonated to give cationic trihydrides $[Cp_2MH_3]^+$. However, their properties have scarcely been studied partly because of the difficulty in their isolation in analytically pure forms due to their tendencies to revert to the parent hydrides in the course of the attempted purification. Recently we have found that the trihydride cation can be successfully isolated as tosylates when the hydrides are protonated with TsOH (*p*-toluenesulfonic acid) in non-aqueous solvent. And we have synthesized many kinds of bis(cyclopentadienyl) molybdenum complexes derived from trihydride species.2,3)

During the course of our studies on this line, we found that molybdenum trihydride complex $[Cp_2MoH_3]^+OTs^-$ was converted to hydridotosylato complex $Cp_2MoH(OTs)$ **1** with accompanying evolution of one mole of H_2 when warmed in ethanol (Eq. 1).2) The complex **1** is of importance not only as intermediates of many reactions but rather as a reagent in organic synthesis. For example, an extremely high diastereoselectivity was achieved by using this complex in the reduction of 4-*t*-butylcyclohexanone to *cis*-4-*t*-butylcyclohexanol.4)

$$Cp_2MoH_2 + TsOH \xrightarrow{EtOH} [Cp_2MoH_3]^+OTs^- \xrightarrow[-\,H_2]{EtOH} \underset{\mathbf{1}}{Cp_2MoH(OTs)} \quad (1)$$

In contrast to the molybdenum complex **1**, it was not easy to prepare tungsten analog: the above method was found to be not applicable due to the inert nature of the W-H bonds in $[Cp_2WH_3]^+$. Here we report the first preparation and the characterization of tungsten hydridotosylato complex $Cp_2WH(OTs)$ **2**. In addition, this paper will describe its reactions with tertiary phosphines and phosphite.

Owing to thermostability, it appears that trihydrido tungsten complex could not liberate hydrogen. Consequently, we surveyed the use of a hydrogen acceptor. Ephritikhine reported that acetone functions as a hydrogen acceptor in the reaction of $[Cp_2MoH_3]^+PF_6^-$ with 1,3-butadiene.5) Furthermore we have found that trihydrido molybdenum complex reduced organic carbonyl compounds to alcohols.4) Based on these facts, the reaction was first examined by using various types of ketonic medium (Eq. 2). Reaction conditions used and results obtained are summarized in Table 1.



$$Cp_2WH_2 + TsOH \xrightarrow[R^1R^2CO \quad R^1R^2CHOH]{} \underset{\mathbf{2}}{Cp_2WH(OTs)} + \underset{\mathbf{3}}{[Cp_2W(\mu\text{-}OH)_2WCp_2]^{2+}(OTs^-)_2} + \underset{\mathbf{4}}{Cp_2W(OTs)_2} \quad (2)$$

Table 1. Preparation of Hydridotosylato Complex **2**

Solvent R^1R^2CO R^1	R^2	ml	Cp_2WH_2/mmol	Temp/℃	Time/h	Yield/%[a)]
CH_3	CH_3	25	1.05	50	7.5	36.0
CH_3	CH_3	15	0.403	r. t. / 50	100 / 8	41.5
CH_3	C_2H_5	20	0.340	r. t. / 50	47 / 8	48.0
CH_3	C_2H_5	15	0.420	50	8	43.0
C_2H_5	C_2H_5	15	0.890	50 / 60	7 / 8	0
CH_3	$(CH_3)_2CH$	10	0.460	50	10	29.0

a) The yields of **3** and **4** are omitted.

The satisfactory results were obtained when 2-butanone and acetone were used as solvent. More bulky ketones, such as diethylketone or methylisopropylketone were inferior to them. A typical reaction procedure is as follows: to a solution of Cp_2WH_2 (0.127 g, 0.403 mmol) in acetone (15 ml) was added equimolar amount of TsOH (0.0650 g, 0.400 mmol). The reaction mixture was stirred at ambient temperature for 100 h under argon and an additional stirring was continued for 8 h at 50 ℃. The solution changed from colorless to dark-red, and a grayish precipitate was observed. The reaction was accompanied by the reduction of acetone; formation of 2-propanol was confirmed by gas chromatography. The precipitate and solution were separated by filtration. The resultant solution was concentrated to dryness under reduced pressure and the residue was washed with ether followed by vacuum drying. The reddish powder thus obtained was $Cp_2WH(OTs)$ **2** (0.0810 g, 41.5%).6) The grayish precipitate which was not soluble in acetone, was extracted with methanol. Purification by recrystallization from methanol afforded $[Cp_2W(\mu\text{-}OH)_2WCp_2]^{2+}(OTs^-)_2$ **3** (0.0774 g, 19.1%).7) The residue, which was soluble neither in acetone nor in methanol, was $Cp_2W(OTs)_2$ **4** (0.024 g, 9.0%), identified by comparing its infrared spectrum with that of the authentic sample.8)

The hydridotosylato complex **2** is soluble in methanol, ethanol, THF, CH_3CN, and acetone. In its IR spectrum, W-H stretching band was observed at 1950 cm^{-1}, which is higher frequency than that of the molybdenum hydridotosylato complex **1** (1875 cm^{-1}). ^1H NMR spectra of **2** in CD_3OD showed two singlet signals assignable to the Cp protons at δ 5.08 and hydride proton at δ -12.38, both are higher field than the molybdenum analog **1** by about 0.3 and 3 ppm, respectively. These upfield shifts appear to reflect a difference in the nature of metals. In fact, the hydride protons of the parent Cp_2WH_2 shift ca. 4 ppm upfield compared to that of molybdenum analog.[11)] Molybdenum complex **1** suffered a solvolysis to give the ionic species.[2)] The molar conductivity of **2** in methanol (21.40 S $cm^2 mol^{-1}$) is less than half that of **1** (48.19 S cm^2 mol^{-1}) and the equilibrium appears to lie far to the left in Eq. 3.

$$Cp_2WH(OTs) \xrightleftharpoons[\text{- S}]{\text{+ S (solvent)}} [Cp_2WH(S)]^+ OTs^- \qquad (3)$$

Complex **2** reacted with PR_3 to give corresponding cationic complexes $[Cp_2WH(PR_3)]^+OTs^-$ **5** in a similar manner as reported for molybdenum complex **1** (Eq. 4).[3a)]

$$Cp_2WH(OTs) + PR_3 \longrightarrow \underset{\mathbf{5}}{[Cp_2WH(PR_3)]^+OTs^-} \qquad (4)$$

Table 2. Preparation and Spectroscopic Properties of Cationic Complexes **5**[a)]

PR_3/mmol		**2**/mmol	Solvent/ml	Time/h	Yield of **5**/%[b)]	IR/ cm^{-1} ν (W-H)	^1H NMR/ppm[c)] δ (Cp)	δ (W-H)
PPh_3	1.21	0.596	EtOH 20	68	62.4	1905	4.90	-11.31
							(1.83)	(29.30)
$P(Bu^n)_3$	1.60	0.449	THF 20	40	42.7	1915	5.09	-11.84
							(1.83)	(29.91)
$P(OEt)_3$	0.96	0.479	THF 25	39	(40.7)	1935	5.18	-11.82
							(3.83)	(33.57)

a) Complex **2**, solvent, and PR_3 were combined under argon. The reaction mixture was stirred at ambient temperature. Evaporation to dryness, washing with ether, and extraction with THF yielded **5**.
b) Crude yield in parenthesis. c) 270 MHz in CD_3OD, *J* (P-H) in Hz are in parentheses.

In ^1H NMR spectrum of **5** in CD_3OD, the hydride and cyclopentadienyl resonances are split into doublets due to coupling with phosphorus nuclei. In ^{31}P NMR spectrum of **5**, tungsten satellites were observed [*J* (W-P) = 297.8, 245.6, and 512.8 Hz for PR_3 = PPh_3, $P(Bu^n)_3$, and $P(OEt)_3$, respectively]. These data indicate that the phosphine ligands bind to metal in these complexes.

While the molybdenum analogue of **5** have been also synthesized by Dias and coworkers by the reaction of halohydrides Cp_2MoHX (X = Cl, Br, I) with tertiary phosphines, they have failed in obtaining **5** by this method.[9,10)] We believe that hydridotosylato complex **2** is promising as a highly reactive tungstenocene precursor because of the labile property of the TsO group.

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6) $Cp_2WH(OTs)$ (**1**): IR (KBr) 1950 cm^{-1} [ν (W-H)]; ^1H NMR (CD_3OD) $\delta = 5.08$ (10 H, s, Cp), -12.38 (1H, s, W-H). Resonances due to the TsO group's protons are omitted throughout; Found: C, 41.87; H, 3.69; S, 6.45%. Calcd for $C_{17}H_{18}O_3SW$: C, 41.99; H, 3.73; S, 6.59%.
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