Journal of Organometallic Chemistry, 473 (1994) 149–154

Preparation and some reactions of bis(η^5-cyclopentadienyl)hydrido(tosylato)-molybdenum and -tungsten

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(Received December 1, 1993; in revised form December 15, 1993)

Abstract

Hydridotosylato complexes $Cp_2MH(OTs)$ [M = Mo (**3a**) and W (**3b**)] have been synthesized by the treatment of $[Cp_2MH_3]^+OTs^-$ either thermally (M = Mo) or with acetone (M = W) and are characterized spectroscopically. Complex **3a** is so reactive that its reaction with methanol afforded the cationic adduct $[Cp_2MoH(MeOH)]^+OTs^-$. However, **3b** did not react with alcohol but reacted with RO^- to yield the corresponding alkoxo complexes $Cp_2WH(OR)$. Complexes **3** also reacted with tertiary phosphines to give the cationic monohydrido complexes $[Cp_2MH(PR_3)]^+OTs^-$.

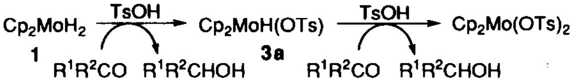
Key words: Molybdenum; Tungsten; Cyclopentadienyl; Hydride; Alkoxide; Tosylato

1. Introduction

The chemistry of the bis(cyclopentadienyl) derivatives of molybdenum and tungsten has been studied extensively since the first preparation of the dihydrides Cp_2MH_2 (**1**) (M = Mo and W; Cp = η^5-C_5H_5) by Green and co-workers [1,2]. These studies include, *e.g.* insertion of the carbon–carbon double or triple bond into the M–H bond to give hydrido-alkyl derivatives [3] and the chemical, photochemical, or thermal generation of highly reactive tungstenocene which can be trapped with the solvent benzene to give the hydridophenyl derivative as a result of aromatic C–H activation [4–7]. One of their typical features is their high basicity. It is reported that their basicities are nearly equal to that of ammonia [8] and these complexes are in fact easily protonated to give cationic trihydrides $[Cp_2MH_3]^+$ [9,10]. The reactions of the latter have also been studied especially with Lewis bases possessing the nitrogen donor atoms [11–13] or allylic alcohols [14–16].

The monohydridohalogeno derivatives, $Cp_2M(H)X$ (X = Cl, Br, I), have also been synthesized [17–19] and their reactivities towards a variety of Lewis bases have been examined [11–13,20]. The preparation of $Cp_2M(H)X$ has been achieved by the partial reduction of Cp_2MX_2 with sodium borohydride [17], by the reaction of **1** (M = W) with CCl_4 (for X = Cl), $CHBr_3$ (for X = Br), or CH_3I (for X = I) [18], or by the protonolysis of $Cp_2WCl(SnMe_3)$ [19]. Since these types of monohydridohalogeno complexes are not necessarily adequate as precursors for other monohydrido derivatives of molybdenocene or tungstenocene [18], the exploitation of an alternate source for such derivatives is anticipated.

Recently, we have demonstrated that the trihydrido-molybdenum and -tungsten cations can be successfully isolated as tosylates when the dihydrides are protonated with *p*-toluenesulfonic acid (TsOH) in nonaqueous solvents. The molybdenum trihydride complex $[Cp_2MoH_3]^+OTs^-$ (**2a**) thus obtained reduced organic carbonyl compounds to the corresponding alcohols in the presence of protonic acids such as RCOOH, HCl or TsOH, with an extremely high diastereoselectivity when 4-t-butylcyclohexanone was reduced [21].



$$\underset{\mathbf{1}}{Cp_2MoH_2} \xrightarrow[R^1R^2CO \quad R^1R^2CHOH]{TsOH} \underset{\mathbf{3a}}{Cp_2MoH(OTs)} \xrightarrow[R^1R^2CO \quad R^1R^2CHOH]{TsOH} Cp_2Mo(OTs)_2 \qquad (1)$$

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0022-328X/94/$7.00
SSDI 0022-328X(93)24386-J

The detailed spectroscopic studies revealed that the reaction proceeds *via* two successive pathways in which $Cp_2MoH(OTs)$ (**3a**) is thought to play a role of key intermediate (eqn.(1)). By carrying out these reactions under controlled conditions, we succeeded in isolating this monohydridotosylato complex in reasonable yield. This paper describes in detail, studies on the syntheses and the reactivities of **3a** as well as its tungsten analog (**3b**). Preliminary communications of parts of this work have been published [10,22,23].

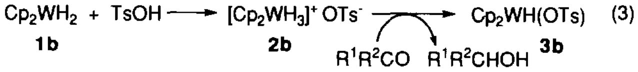
2. Results and discussion

2.1. *Preparation and characterization of hydridosylato complex $Cp_2MH(OTs)$ (3)*

The reaction of molybdenum dihydride Cp_2MoH_2 (**1a**) with TsOH at room temperature in Et_2O afforded the highly reactive cation, $[Cp_2MoH_3]^+OTs^-$ (**2a**) which is so reactive that most common organic solvents reacted with it [10]. The cation **2a** was converted into the hydridosylato complex $Cp_2MoH(OTs)$ (**3a**) with accompanying evolution of 1 mol of H_2 when warmed at 50°C in EtOH or tetrahydrofuran (THF). Complex **3a** was more easily obtained by simply heating the mixture of Cp_2MoH_2 (**1a**) and TsOH in EtOH at 50°C.

$$\underset{\textbf{1a}}{Cp_2MoH_2} + TsOH \xrightarrow{Et_2O} \underset{\textbf{2a}}{[Cp_2MoH_3]^+OTs^-} \xrightarrow[-H_2]{EtOH} \underset{\textbf{3a}}{Cp_2MoH(OTs)} \quad (2)$$

The tungsten analog of **2a**, $[Cp_2WH_3]^+OTs^-$ (**2b**) was similarly obtained using EtOH as solvent [16]. Both complexes **2a** and **2b** are colorless solids and are unstable to air even in the solid state, the former being more easily decomposed in air. In contrast to the molybdenum complex **2a**, the tungsten analog **2b** was stable on heating in the solution, so that the above method of dehydrogenation was found to be not applicable to the synthesis of the tungsten analog **3b**. This may be ascribed to the inert nature of the W–H bonds in $[Cp_2WH_3]^+$ compared with corresponding Mo–H bonds. However, when **2b** was treated with ketonic solvents, the hydrido(tosylato)tungsten complex **3b** was formed accompanied by the formation of the corresponding alcohols and a grayish precipitate.



$$\underset{\textbf{1b}}{Cp_2WH_2} + TsOH \longrightarrow \underset{\textbf{2b}}{[Cp_2WH_3]^+OTs^-} \xrightarrow[R^1R^2CO \quad R^1R^2CHOH]{} \underset{\textbf{3b}}{Cp_2WH(OTs)} \quad (3)$$

It seems likely that the ketonic solvents function as a hydrogen acceptor [21]. Ephritikhine *et al.* [24] also reported that acetone served as a hydrogen acceptor in the reaction of $[Cp_2MoH_3]^+PF_6^-$ with 1,3-butadiene to give the η^3-crotyl derivative. Acetone and ethyl methyl ketone were found to be superior reaction solvents for the synthesis of **3b** compared with the more bulky diethyl ketone or isopropyl methyl ketone, since they allowed isolation of the product in much higher yield.

The reddish powdery complexes **3a** and **3b** are extremely sensitive to air and moisture and are soluble in methanol, ethanol, THF, CH_3CN and acetone. It has been found that complexes **3a** and **3b** suffer a solvolysis to give ionic species of the type $[Cp_2MH(solvent)]^+OTs^-$. The molar conductivity of **3b** in methanol (21.40 S cm^2 mol^{-1}) is less than half that of **3a** (48.19 S cm^2 mol^{-1}) and the equilibrium shown in eqn. (4) appears to lie far to the left for the tungsten complex **3b**. In the case of **3a**, the ionic molybdenum complex $[CpMoH(MeOH)]^+OTs^-$ (**4a**) could be isolated, although the cationic tungsten complex analogous to **4a** could not be observed at all.

$$\underset{\textbf{3}}{Cp_2MH(OTs)} \underset{-\ solvent}{\overset{+\ solvent}{\rightleftharpoons}} \underset{\textbf{4}}{[Cp_2MH(solvent)]^+OTs^-} \quad (4)$$

Spectroscopic data for **3a** and **3b** are given in Table 1. Characteristic M–H bond stretching vibrations in IR spectra of **3a** and **3b** appeared at significantly higher frequency than those of the parent Cp_2MH_2 (1840 cm^{-1} and 1915 cm^{-1} for M = Mo and W, respectively). The ^1H NMR spectra taken in THF-d_8 showed, in addition to the signals due to the TsO ligand, two resonances assignable respectively to Cp protons around 5.1 ppm and the hydrido ligand at −8.95 (**3a**) and −12.08 ppm (**3b**). Since the hydrido protons of the parent Cp_2MoH_2 shift *ca.* 4 ppm low field compared with that of the tungsten analog [25], the low field shifts of the hydrido resonance in molybdenum complex **3a** compared with that in the tungsten analog **3b**

TABLE 1. IR and ^1H NMR data for complexes **3a** and **3b**

Complex	IR (cm^{-1}) [a]	^1H NMR (ppm) [b]		
	ν(M–H)	M–H	δ(Cp)	δ(OTs)
$Cp_2MoH(OTs)$ **3a**	1875m	−8.95 (s)	5.17 (s)	2.30 (s) 7.37 (d) 7.07 (d) J(H–H) = 8.54 Hz
$Cp_2WH(OTs)$ **3b**	1950m	−12.08 (s) J(W–H) = 64.8 Hz	5.05 (s)	2.31 (s) 7.36 (d) 7.08 (d) J(H–H) = 8.54 Hz

[a] KBr disc. [b] 270 MHz in THF-d_8.

TABLE 2. Preparation and spectroscopic data for hydridoalkoxo complexes $Cp_2WH(OR)$ (**5b**)

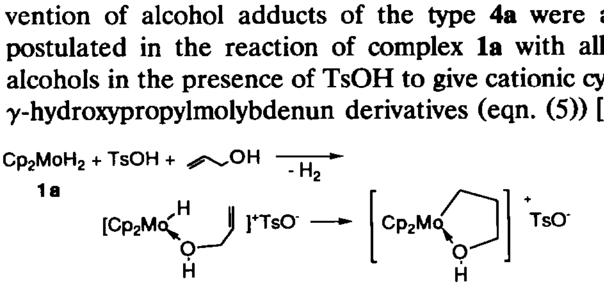
Complex R	**3b**/RO^- (mmol)	Solvent (ml)		Time (h)	Yield of **5b** (%)	IR (cm^{-1}) [a] ν(W–H)	^1H NMR (ppm) [b] δ(Cp)	 δ(W–H)
C_2H_5	0.146/1.08	EtOH	13	6	64	1900s	4.43	−10.51
CH_2=$CHCH_2$	0.211/1.20	CH_2=$CHCH_2OH$	10	21	38	1885s	4.44 J(W–H) = 81 Hz	−10.54
CH_2=$C(CH_3)CH_2$	0.216/6.19	THF	14	6	26	1880s	4.45 J(W–H) = 81 Hz	−10.48

[a] KBr disc. [b] In C_6D_6, 90 MHz for R = C_2H_5 and CH_2=$C(CH_3)CH_2$ and 270 MHz for R = CH_2=$CHCH_2$. All signals are singlets unless otherwise specified.

appear to reflect a difference in the nature of the metals. However, the contribution from the equilibrium shown in eqn. (4) to the apparent low field resonance in the case of **3a** may not be ruled out to some extent.

2.2. *Reactions of hydridotosylato complexes 3a and 3b with bases*

As described above, the hydridotosylatomolybdenum complex **3a** reacts with methanol to give the cationic methanol adduct $[CpMoH(MeOH)]^+OTs^-$ (**4a**). Intervention of alcohol adducts of the type **4a** were also postulated in the reaction of complex **1a** with allylic alcohols in the presence of TsOH to give cationic cyclic γ-hydroxypropylmolybdenun derivatives (eqn. (5)) [16].



(5)

The IR spectrum of **4a** showed the ν(Mo–H) absorption at 1840 cm^{-1} with medium intensity. Multiplet bands with large intensity at 2400–2800 cm^{-1} are assigned to the ν(O–H) of coordinated MeOH. Their significant low frequency shifts compared with the normal O–H stretching band may suggest the existence of the hydrogen bond between the coordinated OH group and the TsO anion. The ^1H NMR spectrum taken in CD_3OD showed two singlet signals at 5.37 (10H) and −9.35 (1H) ppm assignable to Cp protons and Mo–H, respectively, in addition to the characteristic signals assignable to the TsO anion. Signals due to the coordinated MeOH were not observable because of an exchange with the solvent CD_3OD, although those assignable to one equivalent of the liberated MeOH were observed in the NMR spectrum of **4a** taken in CD_3OD.

In contrast to the hydridotosylatomolybdenum complex **3a**, the reaction of the tungsten analog **3b** with MeOH did not lead to the methanol adduct as described earlier, however it reacted with the more basic RO^- anions to yield the corresponding alkoxo complexes **5b**.

$$\underset{\textbf{3b}}{Cp_2WH(OTs)} + NaOR \longrightarrow \underset{\textbf{5b}}{Cp_2WH(OR)} + NaOTs \qquad (6)$$

$$R = C_2H_5,\ CH_2{=}CHCH_2,\ CH_2{=}C(CH_3)CH_2$$

TABLE 3. Preparation and spectroscopic data for complexes $[Cp_2MH(PR_3)]^+TsO^-$ (**6**)

Complex R	**3**/PR_3 (mmol)	Solvent (ml)	Time (h)	Yield of **6** [a] (%)	IR (cm^{-1}) [b] ν(M–H)	^1H NMR (ppm) [c] δ(Cp)	 δ(M–H)
(M = Mo)							
Ph	1.34/2.96	EtOH 10	20	58	1820m	4.96 (1.83)	− 8.06 (34)
Et	0.63/1.26	THF 10	10	(92)	1855m	5.11 (1.50)	−8.51 (35)
^nBu	0.49/0.74	THF 10	15	73	1845m	5.13 (2.44)	−8.51 (35)
cyclo-C_6H_{11}	1.17/1.76	THF 10	22	17	1865m	5.15 (1.22)	−8.38 (35)
OEt	0.81/1.22	THF 10	4	50	1855m	5.23 (1.83)	−8.69 (39)
(M = W)							
Ph	0.60/1.21	EtOH 20	68	62	1905m	4.90 (1.83)	−11.31 (29) J(W–H) = 73 Hz
^nBu	0.45/1.60	THF 20	40	43	1915m	5.09 (1.83)	−11.84 (30) J(W–H) = 71 Hz
OEt	0.48/0.96	THF 25	39	(41)	1935m	5.18 (3.83)	−11.82 (34) J(W–H) = 69 Hz

[a] Crude yields in parentheses. [b] KBr disc. [c] 270 MHz in CD_3OD, J(P–H) in Hz are in parentheses. All signals are doublets unless otherwise specified.

The reaction conditions and the spectroscopic data for complexes **5b** are given in Table 2.

Although the ethoxo(hydrido) complex of the type **5b** has been prepared by the reaction of $Cp_2WH(Ph)$ with EtOH in the presence of CO_2 [26], the present method is advantageous for the following reasons: (a) the reaction of $Cp_2WH(Ph)$ with alcohol requires strict temperature control; (b) the product can be readily separated from the reaction mixture. Apart from the alkoxo-bridged multinuclear complexes, well-defined mononuclear alkoxo complexes of tungsten have seldom been reported and this method seems to be effective for their syntheses.

The success in the preparation of alkoxo complexes **5b** by the nucleophilic attack of the alkoxide anion to **3b** prompted us to examine the possibility of the formation of alkyl derivatives by the action of the carbanion on **3b**. The reaction of an excess amount of n-butyllithium with **3b** in hexane at room temperature, however, did not lead to the isolation of the expected n-butylhydrido species, but resulted in messy products, in which n-butane (192%), 1-butene (6.8%), and a small amount of dihydride **1b** were detected either by GLC or IR. The results indicate that n-butyllithium did react with **3b** to give the intermediary n-butyl(hydrido) molybdenum species which releases n-butane by reductive elimination and 1-butene and **1b** by β-elimination. The reason for the formation of an excess amount of n-butane has not yet been clarified.

The hydrido(tosylato)molybdenum complex **3a**, which was formed from **2a** *in situ*, reacted with PPh_3 to give $[Cp_2MoH(PPh_3)]^+OTs^-$ (**6a**). The same cation with PF_6^- counter anion has been prepared by Green *et al.* *via* different routes [27]. When the trihydrido cation **2b** is allowed to react with PEt_3, the latter worked as a Lewis base to trap dissociated TsOH yielding the parent complex **1a** together with the triethylphosphonium salt. The cationic monohydrido(tertiary phosphine) complexes of the type $[Cp_2MH(PR_3)]^+$-OTs^- (**6**) were prepared for various phosphines by their reactions with **3a** or **3b** (eqn. (7) and Table 3).

$$\underset{\mathbf{3}}{Cp_2MH(OTs)} + PR_3 \longrightarrow [Cp_2MH(PR_3)]^+ OTs^- \qquad (7)$$

6a (M = Mo; R = Ph, Et, Bu^n, cyclo-C_6H_{12}, OEt)
6b (M = W; R = Ph, Bu^n, OEt)

The cationic complexes analogous to **6a** with halide or PF_6- counter anions, $[Cp_2MoH(PR_3)]^+X^-$, have been prepared by Dias *et al.* starting from Cp_2MoHX (X = Cl, Br, and I) for PPh_3, PMe_2Ph, $PEtPh_2$, and $Ph_2PCH_2CH_2PPh_2$ [20], and the X-ray structure of $[Cp_2MoH(PPh_3)]^+I^-$ was determined to be a distorted tetrahedron [28]. The spectroscopic data of complexes **6** together with their synthetic conditions are listed in Table 3. In the ^1H NMR spectra of **6** in CD_3OD, hydride and cyclopentadienyl resonances split into doublets due to coupling with phosphorus nuclei indicating that the phosphine ligands are bonded to metal in these complexes. In addition, in ^{31}P NMR spectra of **6b**, tungsten satellites were observed in the signals due to coordinated PR_3 [J(W–P) = 297.8, 245.6 and 512.8 Hz for $PR_3 = PPh_3$, P^nBu_3 and $P(OEt)_3$, respectively]. Since Azevedo *et al.* reported that they failed to obtain the tungsten analog (**6b**) of molybdenum complexes (**6a**) by the reaction of halohydrides Cp_2WHX (X = Cl, Br, and I) with tertiary phosphines [20], the present method provides us with a convenient method of preparing these types of cationic hydrido(tertiary phosphine) complexes of both molybdenum and tungsten. This may be ascribed to the more labile property of the TsO group as ligand than the halide ligand.

In summary, the synthesis and reactivities of hydridotosylatomolybdenum and -tungsten complexes are described in this paper. They reacted with some bases (MeOH, RO^- and PR_3) readily and were found to be more reactive than analogous halohydrides because of the labile property of the TsO ligand. Obviously, these hydridotosylato complexes seem to have high synthetic potential for preparing new molybdenocene and tungstenocene derivatives.

3. Experimental details

All manipulations were performed using standard Schlenk techniques in an atmosphere of nitrogen or argon. Cp_2MoH_2 and Cp_2WH_2 were synthesized by the published methods [1,29]. Solvents were dried over appropriate desiccants. Guaranteed commercial grade p-toluenesulfonic acid hydrate was dried *in vacuo* and stored under argon. Unhydrated p-toluenesulfonic acid was prepared by refluxing the hydrate in benzene for 5 h followed by crystallization by allowing the resulting solution to stand at ambient temperature. All other chemicals were used as received without further purification.

The infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR and a Jasco A-202 spectrometer using KBr discs prepared under an inert atmosphere. ^1H NMR spectra were recorded on a Jeol JNM EX-270 or a JNM FX-90Q instrument. The chemical shifts are expressed in parts per million relative to tetramethylsilane. A conductivity cell (TOA Electronics, CG-511B) was used for the molar conductivity measurements.

3.1. *Preparation of bis(η^5-cyclopentadienyl)hydrido(p-toluenesulfonato)molybdenum(IV), $Cp_2MoH(OTs)$ (3a)*

The mixture of Cp_2MoH_2 (1.05 g, 4.62 mmol) and p-toluenesulfonic acid hydrate (0.79 g) in EtOH (10 ml) was stirred at 80°C for 4 h. The solution changed from yellow to colorless and then finally to reddish brown.

The volatile liquid was removed from the solution by evaporation *in vacuo*. The residual solid was washed with ether ten times and dried *in vacuo*. The reddish brown powder thus obtained was $Cp_2MoH(OTs)$ (1.84 g, 99%). Anal. Found: C, 51.77; H, 4.70; S, 7.91. $C_{17}H_{18}O_3SMo$ calc.: C, 51.26; H, 4.55; S, 7.91%.

3.2. *Preparation of bis(η^5-cyclopentadienyl)hydrido(p-toluenesulfonato)tungsten, $Cp_2WH(OTs)$ (3b)*

To a solution of Cp_2WH_2 (0.108 g, 0.340 mmol) in ethyl methyl ketone (20 ml) was added an equimolar amount of unhydrated TsOH (0.0585 g). The reaction mixture was stirred at ambient temperature for 46 h under argon and additional stirring was continued for 8 h at 50°C. The solution changed from colorless to dark red, and a grayish precipitate was observed. The reaction was accompanied by the reduction of ethyl methyl ketone as exemplified by the detection of 2-butanol by GLC. The precipitate and solution were separated by filtration. Volatile liquid was removed from the filtrate by evaporation *in vacuo*. The residual solid was washed with ether and dried *in vacuo*. The reddish powder thus obtained was $Cp_2WH(OTs)$ (0.0810 g, 41.5%). Anal. Found: C, 41.87; H, 3.69; S, 6.45. $C_{17}H_{18}O_3SW$ calc.: C, 41.99; H, 3.73; S, 6.59%.

The product was recrystallized from acetone to give pale reddish brown needles. M.p. (under Ar) 176°C (dec.).

3.3. *Reaction of 3a with MeOH*

The addition of MeOH (2 ml) to $Cp_2MoH(OTs)$ (**3a**) (0.0695 g, 0.148 mmol) *in vacuo* afforded a brown solution. After stirring at ambient temperature for 44 h, the solvent was evaporated off to leave a brown solid which was washed with ether to yield $[Cp_2MoH(MeOH)]^+OTs^-$ (**4a**) (yield 97%).

3.4. *Reaction of 3b with RO^- (R = Et, allyl, and methallyl)*

To an alcohol solution of RONa, which was prepared by the reaction of NaH with ROH, was added $Cp_2WH(OTs)$ (**3b**). The reaction mixture was stirred at ambient temperature under argon. Evaporation to dryness and extraction with benzene/hexane yielded $Cp_2WH(OR)$ (**5b**). The reaction conditions and yields are given in Table 2.

3.5. *Preparation of the tertiary phosphine adducts 6*

3.5.1. *Preparation of 6a ($PR_3 = PPh_3$) starting from Cp_2MoH_2 (1a)*

To a solution of $[Cp_2MoH_3]^+OTs^-$ (**2a**) (0.141 g, 0.352 mmol), which was prepared by the reaction of Cp_2MoH_2 (**1a**) with an equimolar amount of TsOH, in EtOH (5 ml) was added PPh_3 (0.112 g, 0.426 mmol). The reaction mixture was stirred at ambient temperature for 17 h *in vacuo*. The solution changed from colorless to yellow and the evolution of H_2 (104%) was detected by Toepler pump and GLC. From the resulting solution, the solvent was evaporated to dryness under reduced pressure. The residue was washed with ether, then extracted with EtOH/THF. Diethyl ether was added to the extract to precipitate $[Cp_2MoH(PPh_3)]^+OTS^-$ (yield 93%).

3.5.2. *Preparation of 6a ($PR_3 = PPh_3$) starting from $Cp_2MoH(OTs)$ (3a)*

A solution containing $Cp_2MoH(OTs)$ (**3a**) (0.353 g, 1.34 mmol) and PPh_3 (0.705 g, 2.96 mmol) in EtOH (10 ml) was stirred at room temperature for 20 h; the solution changed from reddish brown to yellow. Working up the solution as above gave $[Cp_2MoH(PPh_3)]^+OTs^-$ in 94% yield. Recrystallization of the product from acetone at −30°C yielded yellow prismatic crystals (58%). Anal. Found: C, 63.78; H, 5.14; S, 4.95. $C_{35}H_{33}MoPO_3S$ calc.: C, 63.64; H, 5.04; S, 4.85%.

Similarly obtained were the yellow to dark yellow compounds **6a** and **6b** with various tertiary phosphines by the reactions of **3a** and **3b**, respectively, with the corresponding phosphines. The conditions for each reaction are listed in Table 3.

$[Cp_2MoH(P^nBu_3)]^+OTs^-$: Anal. Found: C, 57.50; H, 7.73; S, 5.52. $C_{29}H_{45}MoPO_3S$ calc.: C, 57.99; H, 7.55; S, 5.34%.

$[Cp_2MoH\{P(cyclo\text{-}C_6H_{11})_3\}]^+OTs^-$: Anal. Found: C, 61.64; H, 7.53; S, 4.56. $C_{35}H_{51}MoPO_3S$ calc.: C, 61.93; H, 7.57; S, 4.72%.

$[Cp_2MoH\{P(OEt)_3\}]^+OTs^-$: Anal. Found: C, 48.54; H, 5.96; S, 5.83. $C_{23}H_{33}MoPO_6S$ calc.: C, 48.94; H, 5.89; S, 5.68%.

Acknowledgment

This work was supported by a Grant-in Aid for Scientific Research No. 04453097 and by a Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 05236104 from the Ministry of Education, Science and Culture, Japan. We wish to thank Dr. Masako Tanaka of the Tokyo Institute of Technology for elemental analyses and Mr. Takashi Nakamura for technical assistance.

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