Bis(η^5-methylcyclopentadienyl)dihydridomolybdenum(IV). Synthesis and Reactions with Nucleophiles in the Presence of Protonic Acids

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$[Mo(\eta^5\text{-MeCp})_2H_2]$ (**3**) (MeCp=C_5H_4Me) which was prepared by the reaction of $MoCl_5$ with Na(MeCp) in the presence of $NaBH_4$ was treated with *p*-toluenesulfonic acid (TsOH) to give $[Mo(\eta^5\text{-MeCp})_2H(OTs)]$. Reactions of **3** with allyl alcohol in the presence of TsOH yielded $[Mo(\eta^5\text{-MeCp})_2(\eta^3\text{-}C_3H_5)]^+TsO^-$ whereas the similar reaction with 2-methyl-2-propen-1-ol yielded $[Mo(MeCp)_2CH_2CH(Me)CH_2OH]^+TsO^-$. When the reactions of **3** with protonic acid HA (HA=TsOH and AcOH) were carried out in the presence of acetone or 4-*t*-butylcyclohexanone, $[Mo(\eta^5\text{-MeCp})_2A_2]$ were formed accompanied by the reduction of ketones to the corresponding alcohols. The results are compared with the similar reactions with cyclopentadienyl analog of **3**.

Since the first synthesis of $[Mo(Cp)_2H_2]$ (Cp=η^5-C_5H_5) (**1**) by Green et al. in 1961,[1] extensively rich chemistry of **1** has been developed.[2] Some of its typical reactions include, for example, the insertion reactions of alkenes or alkynes into its Mo–H bond(s) to give alkyl- or alkenylmolybdenum derivatives,[3—6] photochemical cleavage of Mo–H bonds to generate reactive molybdenocene intermediate,[7,8] reactions with alkyl halides[9] or Lewis acids such as Fe(II), Sn(IV), BuLi, and AlR_3,[10—14] and the protonation with Brønsted acids.[1,15] The trihydridomolybdenum cation derived from the last reaction proved to be an important key compound which shows versatile reactions toward nucleophiles.[15—19]

In view of the fact that most reactions of complex **1** depend upon the basic nature of its metal center, it is interesting to see how these reactivities change by introducing the substituents into the cyclopentadienyl ligands in **1**.

In spite of ample reports on the $[Mo(Cp)_2H_2]$ chemistry as described above, little has been studied on the chemistry of the type **1** complex with the substituted cyclopentadienyl ligands. This may be partially ascribed to the difficulty in the preparation of such complexes, especially that with the permethylcyclopentadienyl ligand, $[Mo(Cp')_2H_2]$ (Cp'=η^5-C_5Me_5) (**2**), as pointed out by Cloke et al.[20,21] Although we recognized that **2** can be prepared by the analogous reaction path used for the preparation of **1**, the yield is not satisfactory for the purpose of utilizing it as a starting complex for various reactions.[21]

In order to see the substituent effect of Cp ligand on the electrophilic reactions of the complex of the type **1**, we prepared the monomethylcyclopentadienyl analog of **1**, $[Mo(MeCp)_2H_2]$ (**3**) (MeCp=η^5-C_5H_4Me) (Chart 1), and examined some of its reactions with Lewis bases.

Results and Discussion

Complex **3**, which is a MeCp analog of **1**, was synthesized by following essentially the same procedure as utilized for the preparation of complex **1**. The complex was isolated as yellow needles after sublimation in vacuo in yield of 33% based on $MoCl_5$ used (Eqs. 1 and 2).

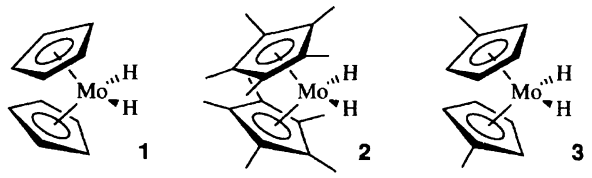


Chart 1.

$$MeCpH + Na \longrightarrow \underset{86\%}{Na(MeCp)} \quad (1)$$

$$Na(MeCp) + MoCl_5 + NaBH_4 \xrightarrow[THF]{reflux} \underset{\mathbf{3}\ 33\%}{[Mo(MeCp)_2H_2]} \quad (2)$$

Spectral data for complex **3** are shown in Table 1. In addition to the characteristic ν(Mo–H) band at 1855 cm^{-1}, stretching and deformation bands of CH_3 group at 2400—3000 cm^{-1} and at 1495 and 1450 cm^{-1}, respectively, are observed in the IR spectrum of **3**. The ν(Mo–H) band at 1855 cm^{-1} is intermediate between those of $[Mo(Cp)_2H_2]$ **1** (1845 cm^{-1}) and $[Mo(Cp')_2H_2]$ **2** (1860 cm^{-1}), in accordance with the electron-donating nature of the methyl substituent on Cp ring.

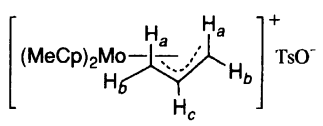
In contrast, ^1H NMR chemical shift values of the hydrido hydrogens of complexes **1**—**3** are not necessarily in the order of electron density of the central metal which is expected from the number of the electron-donating methyl substituent: Thus the chemical shift for **1** (δ=−8.76) is the highest and that for **2** is intermediate value (δ=−8.35). This result may suggest the existence of some other factors such as steric influence which governs the chemical shift of the hydrido hydrogen of this type of complex.

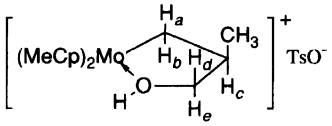
Since unsubstituted dihydride **1** has been known to be protonated with *p*-toluenesulfonic acid (TsOH) in dieth-

Table 1. Spectral Data for MeCp Complexes

Complex	IR/cm^{-1} a)	^{1}H NMR/ppm b)				
	ν (Mo–H)	δ (MoH)	δ (*Me*Cp)	δ (Me*Cp*)	δ (TsO)	Others
$[Mo(MeCp)_2H_2]$ **3**	1855s	−8.21 (s, 2H)	1.87 (s, 6H)	4.22 (s, 4H) 4.46 (s, 4H)	—	—
$[Mo(MeCp)_2H(OTs)]$ **5**	1880m	−9.14 (s, 1H)	1.87 (s, 6H)	4.85 (m, 4H) 5.37 (m, 2H) 5.61 (m, 2H)	2.37 (s, 3H) 7.24 (d, J=8 Hz, 2H) 7.70 (d, J=8 Hz, 2H)	—
$[Mo(MeCp)_2(\eta^3\text{-}C_3H_5)]^+TsO^-$ **6**	—	—	1.85 (s, 3H)	4.84 (m)	2.37 (s, 3H)	2.00 (d, J=3.1 Hz, 2H, H_a)c)
			2.19 (s, 3H)	5.08 (m)	7.22 (d, J=8 Hz, 2H)	3.20 (m, 2H, H_b)c)
				5.20 (m)	7.71 (d, J=8 Hz, 2H)	3.93 (m, 1H, H_c)c)
$[Mo(MeCp)_2CH_2CH(Me)CH_2OH]^+$	—	—	1.74 (s, 3H)	4.99 (m)	2.34 (s, 3H)	0.96 (d, J=5.7 Hz, 3H, Me)d)
TsO^- **7**			1.87 (s, 3H)	5.26 (m)	7.19 (d, J=8 Hz, 2H)	1.25 (d, J=10.6 Hz, 1H, H_b)d)
				5.36 (m)	7.65 (d, J=8 Hz, 2H)	ca. 1.4 (m, 1H, H_c)d) 2.00 (m, 1H, H_a)d) 2.85 (dd, 1H, H_d)d) 3.94 (m, 1H, H_e)d)
$[Mo(MeCp)_2(OCOMe)_2]$ **8**	—	—	1.65 (s, 6H)	4.55 (at, 4H) 5.21 (at, 4H)	—	2.06 (s, 6H, AcO)

a) KBr disc. b) 90 MHz at room temperature. Solvents: C_6D_6 for complexes **3** and **8**, CD_3OD for complexes **5** and **6**, and $(CD_3)_2CO$ for complex **7**. Abbreviations for multiplicity: s, singlet; d, doublet; t, triplet; dd, doublet of doublet; at, apparent triplet; m, multiplet.

c) (6) 

d) (7) 

yl ether at room temperature to give colorless, isolable trihydride cation, $[Mo(Cp)_2H_3]^+TsO^-$,[15] protonation of **3** with TsOH was attempted to compare their basic nature.

On stirring the mixture of the equimolar amount of **3** and TsOH in diethyl ether at room temperature, a rapid reaction took place and an oily untractable product was formed immediately. When the reaction mixture was prepared at the liquid nitrogen temperature and the temperature was raised gradually by removing the Dewar bottle, colorless solid came out immediately which was isolated by filtration. The off-white powder thus obtained was so reactive that the attempted purification by dissolving it in tetrahydrofuran (THF) caused decomposition. Identification of the solid as trihydrido cation of the formula $[Mo(MeCp)_2H_3]^+TsO^-$ (**4**) (crude yield, 90%) was achieved by IR and the subsequent reaction with allyl alcohol to give cationic η^3-allyl derivative (vide infra). The higher basic nature at the metal center of **3** than that of **1** induced by a methyl substituent in **3** may be the principal cause of the apparent higher reactivity of **3** toward protonic acid as compared with that of **1**.

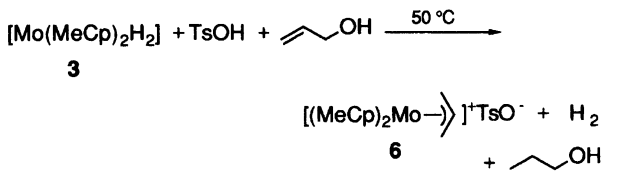
When the equimolar mixture of **3** and TsOH in methanol was stirred in vacuo at 50 °C for 12 h, reddish orange crystals of the neutral complex $[Mo(MeCp)_2H(OTs)]$ (**5**) were obtained in 47% yield accompanied by evolution of quantitative amount of H_2 (Eq. 3).

$$\underset{\mathbf{3}}{[Mo(MeCp)_2H_2]} + TsOH \xrightarrow[MeOH]{50°C} \underset{\mathbf{5}}{[Mo(MeCp)_2H(OTs)]} + H_2 \quad (3)$$

The new monohydridotosylato complex **5** was characterized by IR and ^{1}H NMR spectrum (see Table 1) and elemental analysis (see Experimental section). It is noteworthy that the hydridotosylato complex with Cp ligand, $[Mo(Cp)_2H(OTs)]$, has been known to be converted into the cationic methanol adduct $[Mo(Cp)_2H(MeOH)]^+TsO^-$ on treatment of it with methanol,[15] while no such reaction was observed for the analogous methyl-substituted Cp complex **5**. These results may be again ascribed to the higher electron density at the metal center in **5** than in its Cp analog: Coordination of Lewis basic MeOH may be less facile in the former than the latter.

Reactions of **3** with allyl alcohol and 2-methyl-2-propen-1-ol (methallyl alcohol) at 50 °C in the presence of equimolar amount of TsOH yielded a cationic η^3-allyl complex (**6**) and a cationic cyclic γ-hydroxyalkyl derivative (**7**), respectively (Eqs. 4 and 5), as is reported for the unsubstituted Cp complex.[16,17,19] Both reactions were accompanied by evolution of H_2 (0.89 mol/mol of **3** for allyl alcohol and 0.81 mol/mol of **3** for methallyl alcohol) and formation of the corresponding saturated alcohols as a result of side reaction of allyl

group reduction (0.36 and 0.19 mol/mol of **3**, respectively). The resulting complexes **6** and **7** were characterized by comparing their IR and ^{1}H NMR spectra with the corresponding Cp derivatives as well as by elemental analyses.



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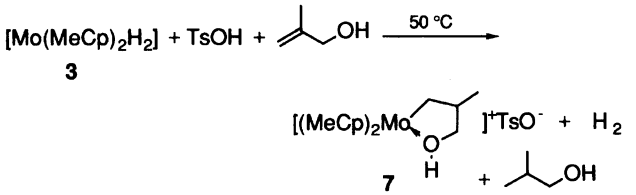
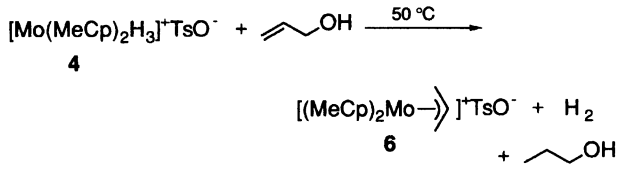


(5)

η^3-Allyl complex **6** was obtained in 76% yield by treating crude cationic trihydride **4** (vide supra) with allyl alcohol at 50 °C. The reaction was also accompanied by formation of H_2 (77%) and 1-propanol (19%) (Eq. 6).



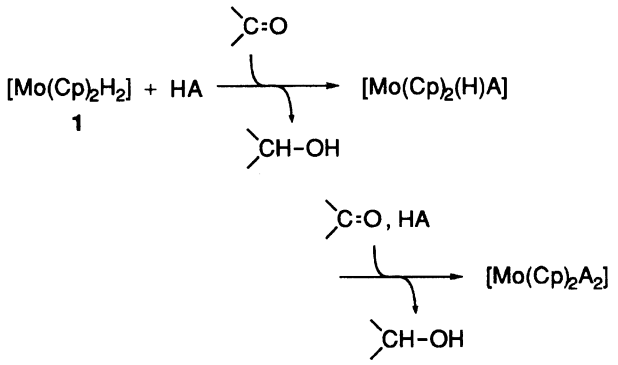
(6)

The fact that the similar results were obtained in the reactions of allylic compounds with **3** and **1** suggests that the analogous reaction path as proposed for the reaction with **1**[16,19] may be applicable to the present system too (Scheme 1).

In Scheme 1, coordination of methallyl alcohol through its alcoholic oxygen atom is postulated to give intermediate **B** although the coordinating ability of methanol to **3** was found to be weak as mentioned above. The formation of stable 5-membered ring via insertion of the C–C double bond into the Mo–H bond may be a driving force for this reaction to proceed.

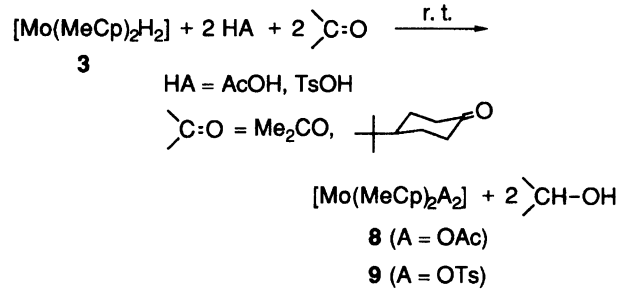
Contrary to the results with complex **1** where corresponding cationic cyclic γ-alkyl complex was obtained by its reaction with 2-methyl-3-buten-1-ol,[15,16,19] complex **3** did not react similarly with the same alcohol but yielded hydridotosylato complex **5** instead (yield 50%) indicating that the methyl substituents on the Cp rings may hinder the approach of bulky 2-methyl-3-buten-1-ol, the tertiary alcohol, to the metal center of intermediate **A** in Scheme 1.

Since the system composed of dihydride **1** and protonic acid such as TsOH or carboxylic acid has been reported to reduce carbonyl groups of aldehyde and ketone quantitatively (Eq. 7),[23] the similar reactions of acetone and 4-*t*-butylcyclohexanone were examined in which complex **3** was employed in place of **1**.



(7)

The reaction of **3** with either acetone or 4-*t*-butylcyclohexanone at room temperature in the presence of excess amount of acetic acid or TsOH as protonic acid afforded corresponding alcohol in high yield together with diacetato complex (**8**) and ditosylato complex (**9**), respectively (Eq. 8).

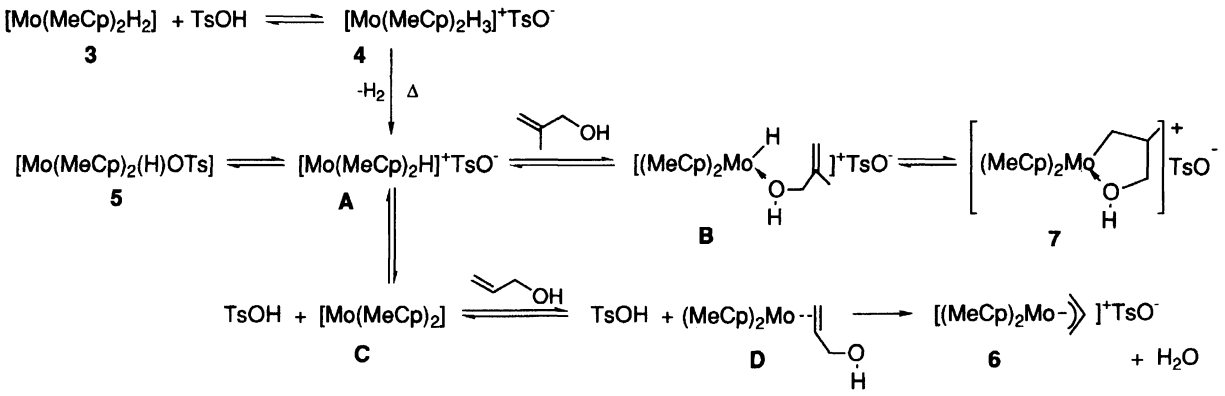


(8)

In these reactions, carbonyl groups play a role of a hydrogen acceptor according to the process shown in Eq. 7. Yields of alcohols are in the range of 142—186% on the basis of **3** (see Experimental) which are much the same as reported for the similar reactions using unsubstituted complex **1**.[18] The resulting diacetato complex **8** is more soluble in common solvents than the corresponding Cp derivative and was found to be soluble even in diethyl ether from which the complex was recrystallized to give brown needles. The ^{1}H NMR data are included in Table 1.

In the case of reduction of 4-*t*-butylcyclohexanone, mixture of *cis*- and *trans*-4-*t*-butylcyclohexanol was obtained and their selectivity was again similar to that obtained for the similar reactions using unsubstituted complex **1**.[18] In contrast to [Mo(Cp)$_2$(OTs)$_2$] which was not soluble in most solvents, ditosylato complex **9** was slightly soluble in acetone from which it was recrystallized to give analytically pure deep green needles.

In conclusion, reactions of [Mo(MeCp)$_2$H$_2$] (**3**) with



Scheme 1. Possible reaction pathway for the formation of η^3-allyl complex **6** and cyclic γ-hydroxyalkyl complex **7**.

protonic acids were found to proceed much easier than $[Mo(MeCp)_2H_2]$ (**1**) reflecting its higher electron density at the metal center. The resulting protonated cation of the former, the complex **4**, showed less facile reactivity toward Lewis base such as alcohols than that of the latter which may be ascribed to the same reason. The new complexes with bis(methylcyclopentadienyl) ligand, such as hydridotosylato complex (**5**), cationic η^3-allyl (**6**), and cyclic γ-hydroxyalkyl complexes (**7**), were formed by the similar reactions employed in the preparation of the Cp analogs. Furthermore, higher solubility of the MeCp complexes in solvent as compared with Cp analogs was observed in the new diacetato and ditosylato complexes **8** and **9**.

Experimental

Most manipulations were carried out either under dry, oxygen-free argon or nitrogen or in vacuo with Schlenk-type flasks. Solvents were dried and purified in the usual manner, and stored under an atmosphere of argon.

Infrared spectra were recorded on a JASCO A-202 spectrometer using KBr disks prepared under inert atmosphere. ^{1}H and ^{13}C NMR spectra were measured on the JEOL FX-90Q spectrometer. GLC was recorded on Shimadzu GC-3BT (for H_2; a Molecular Sieve 5A column), GC-7A or GC-14A (for organic compounds; 3,3′-oxybis[1,2-propandiol] and capillary column of CBP20-M25-025) gas chromatographs.

Methylcyclopentadiene was prepared by a thermal cracking of its commercial dimer. Guaranteed grade commercial *p*-toluenesulfonic acid monohydrate was dried in vacuo and stored under argon. Guaranteed grade commercial allylic alcohols and alkyl halides were degassed prior to use.

Synthesis of Bis(η^5-methylcyclopentadienyl)dihydridomolybdenum (IV) (3). Preparation of Sodium Methylcyclopentadienide, Na(MeCp): To the THF (100 ml) solution containing sodium dispersion (25.3 g, 1.10 g-atom) cooled at 0 °C, methylcyclopentadiene (120 ml, ca. 1.2 mol) in dry THF (120 ml) was added slowly with stirring. After the addition which took ca. 2 h to complete, the mixture was stirred further for 3.5 h at 0 °C to give pale orange solution. Evaporating off the solvent from the mixture left orange solid, which was dried in vacuo at the elevated temperature, washed with hexane, and dried in vacuo to give orange solid of Na(MeCp): Yield 96.6 g (86% on the basis of sodium dispersion used).

Bis(η^5-methylcyclopentadienyl)dihydridomolybdenum(IV) (3): To the THF (40 ml) solution containing Na(MeCp) (1.72 g, 16.9 mmol) and $NaBH_4$ (1.51 g, 39.9 mmol), $MoCl_5$ (1.09 g, 3.98 mmol) was added portion by portion at −78 °C. After the addition, the mixture was heated under reflux for 4 h while the color of the solution changed from deep red to black. The solvent was evaporated off in vacuo and the residual solid was crushed and pulverized and the resulting fine powder was submitted for vacuum sublimation to give yellow crystalline $[Mo(MeCp)_2H_2]$ (**3**): Yield, 0.334 g (32.7% on the basis of $MoCl_5$). Recrystallization of the product from ethanol gave yellow needles. Found: C, 56.25; H, 6.29%. Calcd for $C_{12}H_{16}Mo$: C, 56.21; H, 6.40%. IR and ^{1}H NMR (see Table 1). ^{13}C NMR (C_6D_6) δ=16.47 (Me), 73.89 and 79.31 (unsubstituted carbons of Cp ring), and 97.46 (ipso-carbon of Cp ring).

Synthesis of Bis(η^5-methylcyclopentadienyl)hydrido(tosylato)molybdenum(IV) (5): To the flask containing $[Mo(MeCp)_2H_2]$ (80.1 mg, 0.313 mmol) and $TsOH\cdot H_2O$ (58.0 mg, 0.305 mmol) was added methanol (4 ml) by the trap-to-trap method under vacuum. Stirring the mixture at 50 °C for 12 h caused the color change of the solution from yellow to red. Evolution of H_2 (1.02 mol/mol of **3**) was detected by GLC. Evaporating off the solvent and washing the residue with diethyl ether gave orange solid of $[Mo(MeCp)_2H(OTs)]$ (**5**) (122.4 mg, crude yield 91.6%). Recrystallization from ethanol afforded analytically pure reddish orange needles of **5** (63.1 mg, 47.3%). Found: C, 53.41; H, 5.17%. Calcd for $C_{19}H_{22}O_3SMo$: C, 53.52; H, 5.20%. IR and ^{1}H NMR (see Table 1).

Synthesis of Bis(η^5-methylcyclopentadienyl)(η^3-allyl)molybdenum(IV) Tosylate (6): To the flask containing $[Mo(MeCp)_2H_2]$ (**3**) (73.3 mg, 0.286 mmol) and $TsOH\cdot H_2O$ (53.3 mg, 0.280 mmol) was added allyl alcohol (4 ml) by the trap-to-trap method under vacuum. Stirring the mixture at 50 °C for 5 h caused the color change of the solution from yellow through red to deep red. Evolution of H_2 (0.892 mol/mol of **3**) was detected by GLC. Solvent was removed from the solution by the trap-to-trap method to leave red residue which was washed with diethyl ether. GLC measurement of the recovered solvent showed the presence of 1-

propanol (36.4%). The resulting solid was extracted with ethanol. Evaporating off the solvent from the extract and washing the residue with diethyl ether gave red solid of [Mo(MeCp)$_2$(η^3-C$_3$H$_5$)]$^+$TsO$^-$ (**6**) (81.7 mg, 61.1%). Found: C, 56.68; H, 5.63%. Calcd for $C_{22}H_{26}O_3SMo$: C, 56.65; H, 5.61%. IR and ^{1}H NMR (see Table 1).

Synthesis of Bis(η^5-methylcyclopentadienyl)(3-hydroxy-2-methylpropyl-C^1,O)molybdenum(IV) Tosylate (7). To the flask containing [Mo(MeCp)$_2$H$_2$] (**3**) (126.5 mg, 0.493 mmol) and TsOH·H$_2$O (93.5 mg, 0.492 mmol) was added methallyl alcohol (4 ml) by the trap-to-trap method under vacuum. Stirring the mixture at 50 °C for 5 h caused the color change of the solution from yellow through red to deep red. Evolution of H$_2$ (0.811 mol/mol of **3**) was detected by GLC. Solvent was removed from the solution by the trap-to-trap method to leave red residue which was washed with diethyl ether (crude yield, 94.5%). GLC measurement of the recovered solvent showed the presence of 1-propanol (18.6%). The resulting solid was extracted with ethanol. Evaporating off the solvent from the extract and recrystallizing the residue from acetone gave red crystals of [Mo(MeCp)$_2$CH$_2$CH(Me)CH$_2$OH]$^+$TsO$^-$ (**7**) (111.8 mg, 45.4%). Found: C, 55.48; H, 6.17; S, 6.09%. Calcd for $C_{23}H_{30}O_4SMo$: C, 55.42; H, 6.27; S, 6.43%. IR and ^{1}H NMR (see Table 1).

Reaction of [Mo(MeCp)$_2$H$_2$] (3) with Acetone in the Presence of Acetic Acid. To the flask containing [Mo(MeCp)$_2$H$_2$] (**3**) (56.4 mg, 0.220 mmol), acetone (3 ml) and acetic acid (0.63 ml, 11 mmol) were added by the trap-to-trap method under vacuum. Stirring the mixture at room temperature for 14 h caused the color change of the solution from yellow through red to black. Gas evolution was not observed in the reaction. From the mixture, volatile portion was separated by the trap-to-trap method, from which 2-propanol (186.4% on the basis of **3**) was detected by GLC. The residual solid was washed with hexane and extracted with toluene. Evaporating off the solvent from the extract and recrystallization of the residue from diethyl ether gave brown needles of [Mo(MeCp)$_2$(OCOCH$_3$)$_2$] (**8**) (45.0 mg, 55.0%). Found: C, 51.54; H, 5.47%. Calcd for $C_{16}H_{20}O_4Mo$: C, 51.62; H, 5.42%. ^{1}H NMR (see Table 1).

Reaction of [Mo(MeCp)$_2$H$_2$] (3) with 4-*t*-Butylcyclohexanone in the Presence of Acetic Acid. To the flask containing [Mo(MeCp)$_2$H$_2$] (**3**) (72.1mg, 0.281 mmol) and 4-*t*-butylcyclohexanone (103.5 mg, 0.671 mmol), acetic acid (0.81 ml, 14 mmol) in THF (2 ml) was added by the trap-to-trap method under vacuum. On stirring the mixture at room temperature for 28 h color of the solution changed gradually from yellow through red to black. Evolution of H$_2$ (2.5%) was observed in the reaction mixture. GLC analysis of the reaction mixture showed the presence of 4-*t*-butylcyclohexanol in 142.3% yield based on **3** [60.7% d.e.(cis)]. From the mixture, the volatile portion was evaporated off and the residual solid was washed with hexane and recrystallized from diethyl ether to give brown needles of [Mo(MeCp)$_2$(OCOCH$_3$)$_2$] (**8**) (50.7 mg, 48.4%).

Reaction of [Mo(MeCp)$_2$H$_2$] (3) with Acetone in the Presence of TsOH. To the flask containing [Mo(MeCp)$_2$H$_2$] (**3**) (53.8 mg, 0.210 mmol) and TsOH·H$_2$O (100.4 mg, 0.528 mmol) was added acetone (3 ml) by the trap-to-trap method under vacuum. Stirring the mixture at room temperature for 14 h caused the color change of the solution from yellow to green and the green solid was precipitated. In the volatile portion which has been separated by the trap-to-trap method, 2-propanol (164.2%) was observed. The residue was washed with diethyl ether to give green powdery [Mo(MeCp)$_2$(OTs)$_2$] (**9**) (120.6 mg, 96.2%). A portion of the solid was recrystallized from acetone to give green needles. Found: C, 52.32; H, 4.75; S, 10.75%. Calcd for $C_{26}H_{28}O_6S_2Mo$: C, 52.35; H, 4.73; S, 10.75%.

Reaction of [Mo(MeCp)$_2$H$_2$] (3) with 4-*t*-Butylcyclohexanone in the Presence of TsOH. To the flask containing [Mo(MeCp)$_2$H$_2$] (**3**) (88.0 mg, 0.343 mmol), 4-*t*-butylcyclohexanone (118.3 mg, 0.767 mmol), and TsOH·H$_2$O (131.5 mg, 0.691 mmol), was added THF (4 ml) by the trap-to-trap method under vacuum. Stirring the mixture at room temperature for 17 h caused the color change of the solution from yellow to red, which then gradually changed to green with the concomitant precipitation of the green solid. The volatile portion was evaporated off from the mixture to leave a dark green solid which was washed with hexane and diethyl ether. [Mo(MeCp)$_2$(OTs)$_2$] (**9**) thus obtained weighed 181.2 mg (88.7%). From the hexane and diethyl ether washings, solvent was evaporated off and the THF solution of the residue was submitted for GLC analysis to show the presence of 4-*t*-butylcyclohexanol in 150.4% based on **3** [78.9% d.e.(cis)].

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