Syntheses and Reactions of Cationic Cyclic (γ-Hydroxypropyl)molybdenum(IV) Derivatives: New Pathway for Molybdenaoxacyclopentanes

Takashi Ito,* Katsuhiko Haji, Fumihiro Suzuki, and Tadashi Igarashi

Department of Materials Chemistry, Faculty of Engineering, Yokohama National University, Tokiwadai 156, Yokohama 240, Japan

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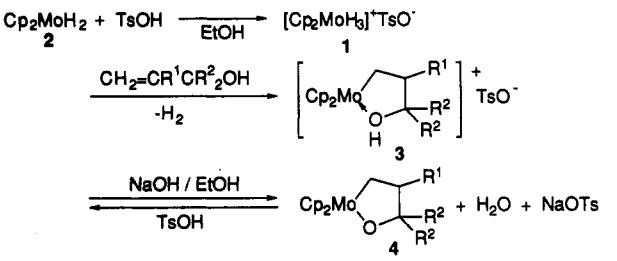
The reaction of Cp_2MoH_2 (Cp = η^5-C_5H_5) with $CH_2{=}C(R^1)C(R^2)_2OH$ ($R^1 = R^2 = H$; $R^1 = H$, $R^2 = CH_3$; $R^1 = CH_3$, $R^2 = H$) in the presence of TsOH (*p*-$CH_3C_6H_4SO_3H$) afforded $[Cp_2MoCH_2CH(R^1)C(R^2)_2OH]^+TsO^-$ (**3**). In the case of allyl alcohol, the reaction was accompanied by the formation of $[Cp_2Mo(\eta^3\text{-allyl})]^+TsO^-$ (**5**). A higher ratio of **3**/**5** in the product mixture was obtained by employing a stronger protonic acid such as gaseous HCl. Complexes **3** were deprotonated by treatment with NaOH in ethanol to give the neutral oxametallacycle $Cp_2MoCH_2CH(R^1)C(R^2)_2O$ (**4**). On protonation with TsOH, **4** reverted to **3**, whereas alkylation at the oxygen atom of **4** with RI (R = CH_3, C_2H_5) yielded the corresponding cationic complexes $[Cp_2MoCH_2CH(R^1)C(R^2)_2OR]^+I^-$ (**6**). A possible reaction pathway for the formation of **3** and **5** was discussed with special reference to the product selectivity.

Introduction

Chemistry of the oxametallacycles of the transition metals, especially those of the early transition metals, is one of the major research themes of current interest in view of its relevance to the olefin oxidation reactions and hetero-metathesis reactions mediated by transition-metal complexes. Many such complexes have been reported, which include saturated and unsaturated four-,[1-6] five-,[7-17] six-,[18-21] and seven-membered[22] oxametallacycles.

General methods for the preparation of these oxametallacycles may be classified into five principal categories: (i) the reactions of aldehydes or ketones with metal carbenes,[1,2] alkene or alkyne complexes,[7,10,11] or metallacycles[18,19,22] and vice versa,[8,9] (ii) the reactions of metal oxides with alkynes,[3] (iii) the insertion of metals into the C–O bond of epoxides,[4,5] (iv) the intramolecular insertion or C–H oxidative addition of metal alkoxides,[6,20] and (v) the formation of oxametallacyclopentadienes as a resonance form of γ-oxoalkenyl complexes[12-17] (Scheme I).

In the course of studies on the reactivity of the cationic bis(cyclopentadienyl)molybdenum trihydride $[Cp_2MoH_3]^+TsO^-$ (**1**; Cp = η^5-C_5H_5, TsO = *p*-$CH_3(C_6H_4)SO_3$), which was formed by the protonation of Cp_2MoH_2 (**2**) with TsOH in MeOH, with various Lewis bases, we found that **1** reacts with allylic alcohols to yield the cyclic γ-hydroxypropyl complex **3**, which is deprotonated with base to give the molybdenaoxacyclopentane derivatives **4** (eq 1).



$R^1 = R^2 = H$ (**a**), $R^1 = H$, $R^2 = CH_3$ (**b**); $R^1 = CH_3$, $R^2 = H$ (**c**) (1)

The sequence of the reactions not only provides a new approach to the oxametallacycle of a five-membered ring (Scheme I (vi)) but also a possible intermediate in the transition-metal-mediated hydroxyl-directed stereoselec-

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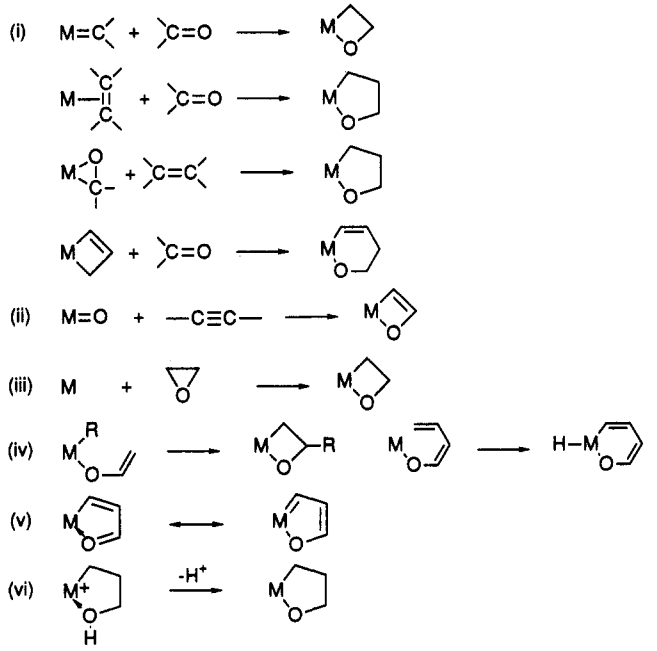
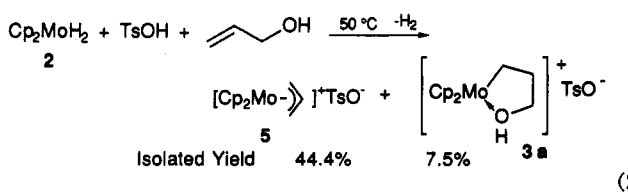
Scheme I. Representative Synthetic Routes to Oxametallacycles



tive olefin hydrogenation.[23] In this report, we describe in detail the preparation and characterization of complexes **3** and **4** and some of their reactions. A part of this work has already been communicated.[24,25]

Results and Discussion

Synthesis of Cationic Cyclic (γ-Hydroxypropyl)molybdenum(IV) Derivatives. In previous communications, we reported that the reaction of allyl alcohol with **2** or with **1** in the presence of TsOH gives the reddish brown cationic η^3-allyl complex **5**.[24,25] Later refinement of the products of the reaction between **2** and an excess amount of allyl alcohol in the presence of an equimolar amount of TsOH, however, revealed that γ-hydroxypropyl complex **3a** is also formed as a minor byproduct, which was separated from **5** as reddish orange crystals by means of fractional crystallization (eq 2).

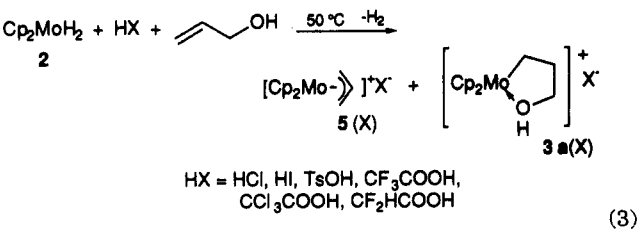


Isolated Yield 44.4% 7.5%

(2)

Both products are soluble in ethanol and insoluble in diethyl ether. Their solubilities in acetone are somewhat different from each other; **3a** is more soluble than **5**. These similarities in physical properties between **3a** and **5** made their separation difficult, giving rise to the low isolation yield. In fact, inspection of the ^{1}H NMR signals assignable to Cp protons of the bulk solid of the reaction products showed the presence of **3a** and **5** in the ratio of 1/2.2. Characterization of **3a** was achieved by spectroscopy as well as by microanalysis. Its IR spectrum showed a strong band at 2900–3000 cm^{-1} assignable to the stretching of the O–H group coordinated to the central metal atom. In the ^{1}H NMR spectrum measured in CD_3OD (Table I), besides the singlet signal due to Cp protons at δ 5.26 ppm, triplet, quintet, and triplet signals at δ 1.94, 1.40, and 3.48 ppm are respectively observed, each assignable to α-, β-, and γ-protons of the molybdenum alkyl group. These results suggest the horizontally symmetrical planar conformation of the metallacyclic ring in **3a**, although for the geometry of the oxygen atom it is not certain whether it is planar or it is accompanied with rapid inversion through oxygen. The hydroxyl proton was not observable, probably due to an exchange with solvent OD.

Replacement of TsOH with nonaqueous HCl in the reaction (2) under similar conditions resulted in the formation of complexes analogous to **3a** and **5** with chloride ion as a counteranion instead of tosylate in the ratio of 2.0/1.0. The chloride analog of **3a** (**3a**(Cl)) was isolated in the analytically pure state by working up the reaction mixture, and its spectral data are included in Tables I and II.



HX = HCl, HI, TsOH, CF_3COOH, CCl_3COOH, CF_2HCOOH

(3)

As the ratio of **3a** and **5** was found to change drastically by replacing TsOH with HCl, the dependence of the ratio **3a**/**5** on the kind of protonic acid HA in the reaction (3) was examined by monitoring the signal intensities of the Cp resonances of the crude reaction product. As shown in Table III, preference of the formation of γ-hydroxypropyl complex **3a** to that of η^3-allyl complex **5** seems to increase as the acidity of HA increases. Addition of an equimolar amount of water to the CF_3COOH system increased the acidity, giving rise to the increased selectivity of **3a**. The exceptionally low yield in the case of CCl_3COOH is ascribed to the formation of a fairly large amount of byproduct, which was characterized spectroscopically as Cp_2MoCl_2.[26]

The reactions similar to (2) using substituted allyl alcohols such as 2-methyl-3-buten-2-ol and β-methallyl alcohol in place of allyl alcohol also afforded the corresponding (γ-hydroxyalkyl)molybdenum cations **3b** (45%) and **3c** (74%), respectively. Interestingly, no η^3-allyl type complexes were formed in these reactions. Brown crystalline complexes of **3b** and **3c** were characterized with ^{1}H and ^{13}C NMR spectra (Tables I and II). A singlet signal for Cp's and equivalence of the methylene protons of 4-hydroxy-3-methylbutyl complex **3b** reflect its symmetrical conformation, as is the case for **3a**. This is in contrast to **3c**, where we observe two Cp singlets and complicated metal alkyl proton signals, reflecting the horizontal asymmetry of the molecule due to the single methyl substituent.

As shown in eq 2, complexes **3b** and **3c** were also formed in 44 and 79% yield, respectively, by treatment of the corresponding allylic alcohols with the trihydride cation **1**, which was derived from the dihydride **2** and TsOH.

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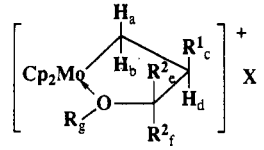
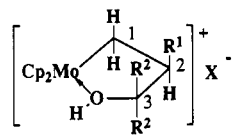
Table I. ^{1}H NMR Spectral Data for the Complexes[a]



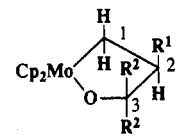
complex	R^1	R^2	R	X	chem shift (δ/ppm) and coupling constant (J/Hz) Cp	H_a	H_b	R^1_c	H_d	R^2_e	R^2_f	R_g
3a	H	H	H	TsO	5.26 s	1.94 t (^3J = 6.16)		1.40 qn (^3J = 6.16)		3.84 t (^3J = 6.16)		
3b	H	CH_3	H	TsO	5.27 s	1.90 at (^3J = 6.4)		1.45 at (^3J = 6.6)		1.17 s		
3c	CH_3	H	H	TsO	5.22 s 5.30 s	1.35 d (^2J = 10.7)	2.12 ad	0.98 d (^3J = 5.3)	1.56 at (J = 8.3)	2.75 dd (^3J = 8.3, ^2J = 11.6)	3.80 m	
3a(Cl)	H	H	H	Cl	5.30 s	1.98 t (^3J = 6.10)		1.44 qn (^3J = 6.10)		3.51 t (^3J = 6.10)		
3c(Cl)	CH_3	H	H	Cl	5.26 s 5.34 s	1.41 d	2.17 ad	1.00 d	1.54 m	2.79 dd	3.84 m	
3c(CF_3CO_2)	CH_3	H	H	CF_3CO_2	5.26 s 5.33 s	1.40 d	2.17 ad	1.00 d	1.56 m	2.78 dd	3.84 m	
6a$_m$	H	H	CH_3	I	5.42 s	1.87 t (^3J = 6.11)		1.56 qn (^3J = 6.11)		3.84 t (^3J = 6.11)		3.60 s
6a$_e$	H	H	C_2H_5	I	5.42 s	1.85 t (^3J = 5.86)		1.50 qn (^3J = 5.86)		3.49 t (^3J = 5.86)		3.85 q (^3J = 7.08), 1.17 t (^3J = 7.08)
6c$_m$	CH_3	H	CH_3	I	5.40 s 5.47 s	1.32 d (^3J = 11.07)	2.13 ad	0.98 d (^3J = 6.12)	1.72 m	3.05 dd (^3J = 5.69, ^2J = 7.79)	3.55 m	3.54 s
6c$_e$	CH_3	H	C_2H_5	I	5.42 s 5.48 s	1.22 d (^3J = 11.23)	2.29 dd	0.99 d (^3J = 5.86)	1.72 m	2.03 dd (^3J = 7.08, ^2J = 1.96)	3.83 ddd	3.73 m, 1.14 t

[a] 90 MHz in CD_3OD. Abbreviations for multiplicity: s, singlet; d, doublet; t, triplet; qr, quartet; qn, qunitet; dd, doublet of doublets; ddd, doublet of doublet of doublets; ad, apparent double; at, apparent triplet; m, multiplet.

Table II. ^{13}C NMR Spectral Data for the Complexes[a]



3



4

complex	R^1	R^2	X	chem shift (δ/ppm) Cp	C_1	C_2	C_3	R^1	R^2
3a	H	H	TsO	96.5	31.9	14.7	72.9		
3b	H	CH_3	TsO	96.4 d	9.4 t	44.5 t	87.4 s		28.1 qn
3c	CH_3	H	TsO	96.4 d, 97.0 d	23.8 t	39.1 d	77.9 t	17.2 qr	
3c(Cl)	CH_3	H	Cl	96.5 d, 97.0 d	24.0 t	39.4 d	78.2 t	17.4 qr	
3c(CF_3CO_2)	CH_3	H	CF_3CO_2	96.5 d, 97.0 d	24.0 t	39.4 d	78.0 t	17.4 qr	
4b	H	CH_3		93.9 d	11.5 t	47.6 t	82.9 s		30.8 qn
4c	CH_3	H		93.9 d	26.7 dd	42.5 ad	84.5 dd	19.4 qn	

[a] 22.5 MHz, in CD_3OD for complexes **3** and in C_6D_6 for complexes **4**. Multiplicity data are those observed in the off-resonance spectra. Abbreviations for multiplicity: s, singlet; d, doublet; t, triplet; qr, quartet; dd, doublet of doublets; ad, apparent doublet.

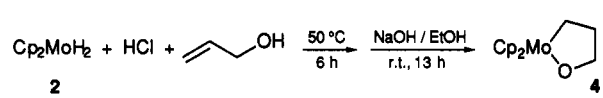
Table III. Dependence of the Ratio 3a/5 on the Protonic Acid

HA	pK_a[a]	reacn conditions	yield (3a + 5)[b] (%)	3a/5
HCl (gas)	−6.1	50 °C, 6 h	95	2.00/1.00
HI	−9.5	50 °C, 6 h	81	1.60/1.00
$TsOH·H_2O$	1.7	50 °C, 6 h	97	0.45/1.00
CF_2HCOOH	1.33	50 °C, 7 h	77	0.55/1.00
CF_3COOH/H_2O	0.50	50 °C, 6 h	79	0.50/1.00
CF_3COOH	0.50	50 °C, 6 h	73	0.34/1.00
CCl_3COOH	0.52	50 °C, 8 h	13	0.11/1.00

[a] pK_a values in water at 25 °C taken from: Dean, J. A. Ed. *Lange's Handbook of Chemistry*, 13th ed.; McGraw-Hill: New York, 1985; pp 5-14–5-60. [b] Crude yield.

Syntheses of Molybdenaoxacyclopentanes. Treatment of cyclic γ-hydroxyalkyl complexes **3** with an equimolar amount of NaOH in ethanol at room temperature gave the neutral molybdenaoxacyclopentane derivatives **4a** (yield 77%), **4b** (91%), and **4c** (70%) accompanied by the formation of a quantitative amount of NaOTs (eq 1). The resulting orange crystalline oxametallacycles, which are soluble in benzene, toluene, tetrahydrofuran, and ethanol and partially soluble in hexane, are moderately sensitive to oxygen and highly moisture sensitive.

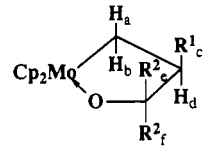
A higher overall yield for **4a** (51%) was attained by employing a one-pot reaction starting from Cp_2MoH_2 (**2**) and gaseous HCl. The mixture of **3a** and **5** is treated with ethanolic NaOH without isolating the former (eq 4).



(4)

Complexes **4** were characterized by NMR spectra (Tables II and IV) as well as by elemental analyses. As in the case of the cationic cyclic γ-hydroxyalkyl complexes **3**, NMR signals for **4a** and **4b** are consistent with the molecular structure possessing a symmetry plane composed of the oxametallacycle, whereas those for **4c** are diagnostic of the horizontally asymmetric structure. The Cp protons in **4** resonate at δ 4.5 ppm, which is higher than those in **3** by 0.8 ppm, reflecting the higher electron density

Table IV. ^{1}H NMR Spectral Data for the Complexes[a]



complex	R^1	R^2	chem shift (δ/ppm) and coupling constant (J/Hz)						
			Cp	H_a	H_b	R^1_c	H_d	R^2_e	R^3_f
4a	H	H	4.47 s	2.05 t		1.75 qn		3.81 t	
4b	H	CH_3	4.53 s	2.10 at (^3J = 5.8)		1.77 at (^3J = 6.1)		1.19 s	
4c	CH_3	H	4.51 s 4.60 s	2.14 dd (^2J = 2.3, ^3J = 5.0)	1.70 dd (^2J = 2.3, ^3J = 7.2)	1.27 d (^3J = 5.4)	1.8 m	3.07 dd (^2J = 10.3, ^3J = 9.0)	4.4 m

[a] 90 MHz, in C_6D_6. Abbreviations for multiplicity: s, singlet; t, triplet; qn, quintet; dd, doublet of doublets; at, apparent triplet; m, multiplet.

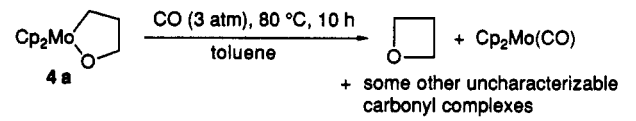
around the metal center in the neutral complexes **4** as compared with the cationic **3**. The ^{13}C NMR signals of the carbon α to the metal in **4** appeared at δ 11.5 (**4b**) and 26.7 (**4c**) ppm, which are considerably higher field than that reported for $(\eta\text{-}C_5Me_5)_2\overline{TiCH_2CH_2CH(Me)O}$ (55.8 ppm).[7] This implies the electron density at the metal center in the Mo(IV) complexes is higher than in Ti(IV) in spite of the opposite order of the propensity for the electron-donating ability between C_5H_5 and C_5Me_5 ligands.

As shown in Table IV, protons attached to the carbon β to the metal in **4** (R^1_C and H_d) resonate at higher field than those attached to the α-carbon (H_a and H_b). A similar tendency was observed for the parent cationic complexes **3** (Table I). These are unusual in view of the ordinary trend of the chemical shifts of this type of oxametallacycle, *e.g.*, $(\eta\text{-}C_5Me_5)_2\overline{TiCH_2CH_2CH(Me)O}$[7] or $(PMe_3)_2(C_2H_4)\overline{WCH_2CH_2CH_2O}$,[8] where β-protons and α-protons resonate at 2.5 and 0.2–2.2 ppm, respectively. The origin of the discrepancy in **4** is not clarified. For the cationic complexes with a simple alkyl ligand of the type $[Cp_2Mo(R)PR_3]^+$, α-protons have been reported to resonate at 0.01–1.12 ppm in their NMR measured in CD_3OD or in $(CD_3)_2CO$.[27,28]

In the mass spectra of **4b** and **4c** taken at 20 eV, parent peaks are observed at *m/e* 314 and 300, respectively, and an intense band at *m/e* 228 is assignable to the Cp_2Mo fragment. The absence of any peaks above *m/e* 320 supports the mononuclear oxametallacycle formulation for these complexes.

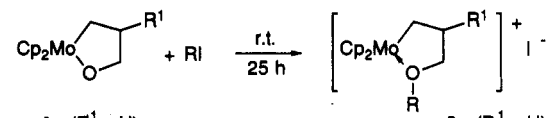
Reactions of Molybdenaoxacyclopentanes and Related Complexes. Thermolysis of **4a** in toluene at 80 °C afforded a trace amount of oxetane as observed by GLC. Its yield increased by purging the system with CO (3 atm), although the amount of the product was still too little to estimate the yield quantitatively. γ-Lactone was not detected in the reaction mixture, indicating the reluctance of **4a** to undergo CO insertion into its Mo–C bond. The residual solid of the reaction showed intense IR bands around 1930–1700 cm^{-1}, including that at 1885 cm^{-1} assignable to $Cp_2Mo(CO)$[29] (eq 5).

The oxygen atom of the oxametallacycle **4** was found to be susceptible to attack by electrophiles such as proton and alkyl halides. Treatment of **4b** and **4c** with an equimolar amount of TsOH in Et_2O reverted them to the parent cyclic (γ-hydroxyalkyl)molybdenum cations **3b** and **3c**, respectively, in almost quantitative yield (eq 1).



(5)

When **4a** or **4c** was stirred in alkyl halide such as CH_3I or C_2H_5I at room temperature for 25 h, a purple precipitate came out, which was, after being recrystallized from ethanol, characterized by IR and NMR spectra (Table I) as well as by elemental analyses as the oxygen-coordinated γ-alkoxypropyl derivative **6** (eq 6).

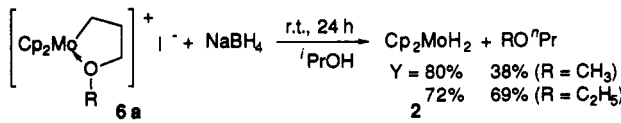


4a (R^1 = H) **6a** (R^1 = H)
4c (R^1 = CH_3) R = CH_3 (m), C_2H_5 (e) **6c** (R^1 = CH_3)

(6)

In IR spectra of **6**, a characteristic absorption appeared at 1260 cm^{-1}, which may be assignable to the C–O stretching of the coordinated ether group. ^{1}H NMR spectra of **6a** are again consistent with a symmetrical structure with regard to the plane consisting of the MoCCCO ring, whereas those of **6c** are complicated due to lack of such symmetry.

Treatment of the cationic alkoxy complexes **6a** with $NaBH_4$ afforded the dihydridomolybdenum complex **2** together with the corresponding *n*-propyl alkyl ether (eq 7).



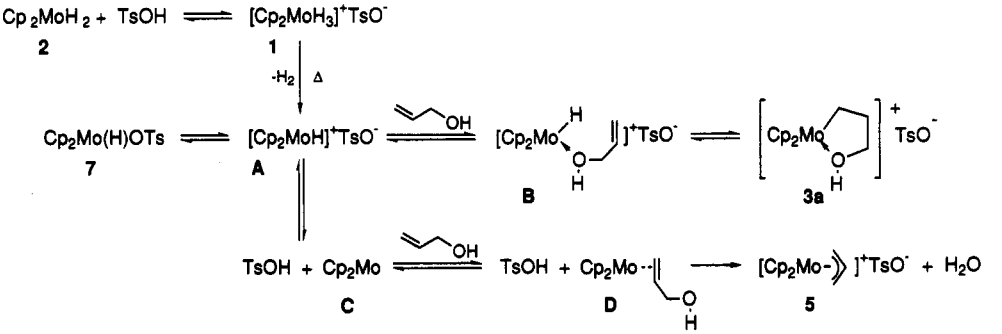
(7)

Discussion on the Possible Reaction Pathways for (γ-Hydroxypropyl)molybdenum Cations 3 and (η^3-Allyl)molybdenum Cation 5. The reaction pathway for the formation of cyclic (γ-hydroxypropyl)molybdenum cation **3** and (η^3-allyl)molybdenum cation **5** from dihydride **2** and allyl alcohol in the presence of TsOH, which is compatible with the observed evidence, is shown in Scheme II.

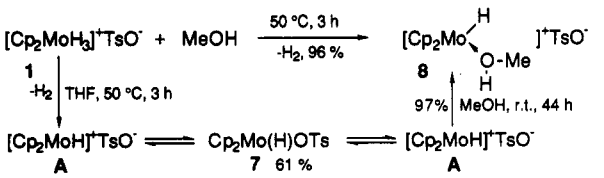
The trihydrido cation **1** formed initially by protonation of **2** may release hydrogen to give the reactive monohydrido cation **A**, which has been known to be in equilibrium with its isolable neutral isomer **7**.[24,28] The conversion of **A** to

(27) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1974**, 208.
(28) Ito, T.; Tokunaga, T.; Minato, M.; Nakamura, T. *Chem. Lett.* **1991**, 1893.
(29) Thomas, J. L.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1386.

Scheme II. Possible Reaction Pathway for the Formation of γ-Hydroxypropyl Complex 3a and η³-Allyl Complex 5



the allyl alcohol adduct B is supported by the isolation of methanol adduct 8 as brown crystals by either heating 1 in methanol or treating the neutral monohydride 7 with methanol at room temperature (eq 8).

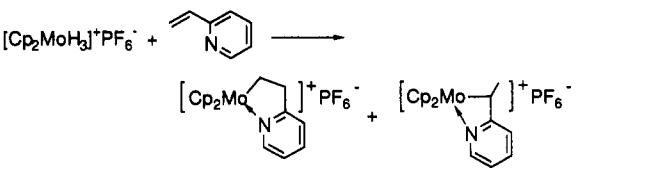


(8)

The cationic adduct 8 showed ν(Mo–H) at 1840 cm^{-1} and ν(O–H) for the coordinated hydroxy group at 2400–2800 cm^{-1} in its IR spectrum. A considerable red shift as compared with the ordinary alcoholic ν(O–H) region may be ascribed to the hydrogen bonding between the OH group and the counteranion TsO$^-$.

For verification of the subsequent intramolecular insertion process (B → 3 in Scheme II), a label experiment was employed. By a reaction analogous to eq 8, dissolution of trihydrido cation 1 in a large excess of C_2H_5OD at first gave the trideuterido cation $[Cp_2MoD_3]^+TsO^-$ (3 (d_3)).[30] When the C_2H_5OD solution of 3(d_3) was heated at 50 °C for 10 h, evolution of gas in 99% yield on the basis of 1 was observed. Mass spectral analysis of the gas revealed that its composition is D_2 (87%), HD (13%), and no H_2. To the resulting solution, which is thought to contain $[Cp_2Mo(D)(EtOD)]^+TsO^-$, was added an excess amount of β-methallyl alcohol, and the mixture was stirred at 50 °C for 20 h. The γ-hydroxypropyl complex 3c(d_1) isolated from the solution showed a weak IR absorption at 2150 cm^{-1} assignable to ν(C–D). In comparison of its ^{1}H NMR spectrum in CD_3OD with that of 3c, a significant decrease in the intensity of the multiplet at 1.56 ppm assignable to the β-methine proton and a change of signal pattern of the β-methyl group at 0.98 ppm from doublet to apparent singlet were especially characteristic, and both features are consistent with the β-deuteriated structure of 3c(d_1), $[Cp_2MoCH_2CD(CH_3)CH_2OD]^+TsO^-$. The degree of deuteriation at the β-carbon in 3c(d_1) was estimated as ca. 60% on the basis of the signal intensity of the β-methine proton, indicating that a part of the Mo–D in $[Cp_2Mo(D)(EtOD)]^+$ has been exchanged with the alcoholic proton of β-methallyl alcohol during the reaction. The absence of H–D exchange between solvent CD_3OD and complex 3c was evidenced by the ^{1}H NMR measurement of 3c in CD_3OD, which did not show any sign of the line broadening at room temperature except the signal assignable to the alcoholic hydrogen in 3c.

A reaction closely related to the formation of γ-hydroxypropyl complexes 3 has been reported for 2-vinylpyridine, where four- and five-membered cyclic products are produced (eq 9).[31-33] It is noteworthy that the four-membered isomer was not detected in the present study, possibly due to the difference of the stability between the four-membered cyclic structure and the five-membered one.



(9)

In Scheme II, η³-allyl complex 5 is thought to be formed by a route via the molybdenocene intermediate C, which is thought to be present in the system as a result of a dissociation equilibrium with monohydrido cation A. As reported by Thomas,[34] allyl alcohol as an olefin coordinates to the molybdenocene intermediate D through its π-electrons. The coordinated allylic ligand may be electrophilically attacked at the oxygen atom by TsOH liberated to give 5. The latter process was reported for the formation of cationic (η³-allyl)iron complexes by acidolysis of the coordinated allyl ethers.[35]

The fact that the selectivity of the formation of (η³-allyl)molybdenum cation 5 increases as the acidity of the protonic acid increases may be rationalized by considering an equilibrium between A and C; the higher the acidity of HX, the higher the propensity for A, giving rise to the higher selectivity for the cyclic cation 3.

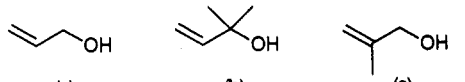
The presence of an equilibrium between 3 and D was deduced from the following evidences. (i) When the cyclic cation 3a(Cl) was heated at reflux in allyl alcohol for 4 h, a part of 3a(Cl) was converted to the η³-allyl cation 5(Cl),

(30) Although $[Cp_2MoD_3]^+TsO^-$ itself was difficult to isolate due to its high reactivity, the corresponding tungsten analog, $[Cp_2WD_3]^+TsO^-$, was isolated from the reaction between $[Cp_2WH_3]^+TsO^-$ and a large excess of CD_3OD. $[Cp_2WD_3]^+TsO^-$ showed a new IR band at 1390 cm^{-1} assignable to ν(W–D). The following equilibrium may be conceivable for the exchange reaction:

$$[Cp_2WH_3]^+TsO^- \rightleftharpoons Cp_2WH_2 + TsOH \overset{CD_3OD}{\rightleftharpoons} Cp_2WH_2 + TsOD \rightleftharpoons [Cp_2WH_2D]^+TsO^- \overset{CD_3OD}{\rightleftharpoons} \cdots \rightleftharpoons [Cp_2WD_3]^+TsO^-$$

(31) Calhorda, M. J.; Dias, A. R. *J. Organomet. Chem.* **1980**, *197*, 291.
(32) Calhorda, M. J.; Dias, A. R. *J. Organomet. Chem.* **1980**, *198*, 41.
(33) Calhorda, M. J.; Dias, A. R. *Rev. Port. Quim.* **1981**, *23*, 12.
(34) Thomas, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 1838.
(35) Eisenstadt, A. *J. Organomet. Chem.* **1972**, *38*, C32.

Chart I



		(a)	(b)	(c)
A.E.D.		6.3110	6.2971	6.3076
product selectivity	3	minor	sole product	sole product
	5	main	none	none

the ratio 5(Cl)/3a(Cl) being 7/8. (ii) The ratio of 1.00/0.55 for 5(CF_2HCO_2)/3a(CF_2HCO_2) for the reaction of 2 and allyl alcohol in the presence of CF_2HCOOH, which is shown in Table I, changed to 1.00/0.43 by extending the reaction time to 13 h. Furthermore, absence of the reverse conversion, i.e. the conversion from the η^3-allyl cation 5 to the cyclic propyl cation 3, which is evidenced by the fact that the latter was not detected after the former was heated in allyl alcohol at 50 °C for 7 h, suggests an irreversible reaction from D to the final product 5.

It may be conceivable that the steric factor also affects selectivity in the reaction path shown in Scheme II, since cyclic alkyl cation 3 is the sole product when substituted allylic alcohols are reacted in the presence of not only strong acid but also even relatively weak acids such as TsOH, CF_3COOH, CF_2COOH, and $CClH_2COOH$. In the case of these substituted allylic alcohols, the steric bulk of the alkyl substituents on the alcohol may prevent the latter from having a π-coordination to molybdenocene. That the basicity of the hydroxy oxygen in the allylic alcohols scarcely affects the reaction selectivity was confirmed by calculating its atom electron density (AED) by the MNDO method for three allylic alcohols. As shown in Chart I, there was no distinct correlation between AED and a preference for the formation of 3.

Further details of the reaction leading to cationic(η^3-allyl)molybdenum complex 5 will be reported elsewhere.

Experimental Section

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 an inert atmosphere. ^1H and ^{13}C NMR spectra were measured on the JEOL FX-90Q spectrometer. GLC was recorded on Shimadzu GC-3BT (for H_2) and GC-7A or GC-14A (for organic compounds; SDC-410, PEG-20M, Diglyserol, Gaskuropack, and capillary column of CBP20-M25-025) gas chromatographs. H_2 gas evolved through the reaction was measured by a Toepler pump and analyzed by GLC using a molecular sieve 5A column. EI/MS was measured on a Hitachi M-80 spectrometer at 70 eV.

Guaranteed grade commercial allylic alcohols and alkyl halides were degassed prior to use. Guaranteed grade commercial *p*-toluenesulfonic acid hydrate was dried in vacuo and stored under argon. Cp_2MoH_2 (2) was prepared by the published method.[36]

Preparation of Bis(η^5-cyclopentadienyl)trihydridomolybdenum(VI) *p*-Toluenesulfonate (1). To the flask containing Cp_2MoH_2 (2; 0.694 g, 3.04 mmol) and *p*-toluenesulfonic acid hydrate (0.578 g, 3.04 mmol) was added freshly purified diethyl ether (20 mL) by the trap-to-trap method. When the mixture was stirred at room temperature for 2 h, a colorless precipitate came out, which was filtered off, washed with diethyl ether, and dried in vacuo to give a white powder of the cationic complex $[Cp_2MoH_3]^+TsO^-$ (1; 1.13 g, 92%). Since 1 is so reactive that there is no suitable solvent for recrystallization, every effort to obtain it analytically pure was unsuccessful. However, the tungsten analog of 1, $[Cp_2WH_3]^+TsO^-$, which was obtained by a similar reaction between Cp_2WH_2 and *p*-toluenesulfonic acid in ethanol, was able to be purified by recrystallization from ethanol. (Anal. Calcd for $C_{17}H_{20}SO_3W$: c, 41.82; H, 4.13; S, 6.57. Found: C, 41.58; H, 4.18; S, 6.57.) On the basis of the close resemblance between it and 1 in IR spectra, the purity of the latter was assessed.

Preparation of Bis(η^5-cyclopentadienyl)(3-hydroxypropyl-*C*^{1},*O*)molybdenum(IV) *p*-Toluenesulfonate (3a). To the flask containing Cp_2MoH_2 (2; 2.585 g, 11.3 mmol) and *p*-toluenesulfonic acid hydrate (2.16 g, 11.3 mmol) was added 15 mL of allyl alcohol. When the solution was stirred at 50 °C for 11 h, the original yellow color changed to reddish brown. From the solution, volatile liquid was removed by evaporation in vacuo. The residual solid was extracted with ethanol (70 mL), and the solvent was evaporated off from the extract. The residual brownish solid was extracted with acetone to remove the byproduct, $[Cp_2Mo(\eta^3\text{-}C_3H_5)]^+TsO^-$ (5). Evaporating off the solvent from the extract and drying the residual solid in vacuo gave reddish orange crystals of 3a (0.387 g, 7.5%). Anal. Calcd for $C_{20}H_{24}SO_4Mo$: C, 52.63; H, 5.30; S, 7.02. Found: C, 52.72; H, 5.39; S, 7.10.

Preparation of Bis(η^5-cyclopentadienyl)(3-hydroxypropyl-*C*^{1},*O*)molybdenum(IV) Chloride (3a(Cl)). To Cp_2MoH_2 (2; 0.141 g, 0.620 mmol) was added gaseous HCl (0.614 mmol) and allyl alcohol (2 mL) by the trap-to-trap method. The mixture was heated at 50 °C in vacuo for 6 h. Solvent was evaporated off from the mixture, and the residue was dried in vacuo. The ^1H NMR spectrum of the residual solid measured in CD_3OD showed the mixture to consist of 3a(Cl) and 5 and their ratio (2.0/1.0) was calculated from the relative intensities of the signals assignable to each compound's Cp protons. The total yield of products was 95.3%. 3a(Cl) was isolated from the mixture by extracting it with acetone. Anal. Calcd for $C_{13}H_{17}OClMo$: C, 48.69; H, 5.34. Found: C, 49.43; H, 5.36.

Preparation of Bis(η^5-cyclopentadienyl)(3-hydroxy-3-methylbutyl-*C*^{1},*O*)molybdenum(IV) *p*-Toluenesulfonate (3b). Method 1 (Starting from 2). To the flask containing Cp_2MoH_2 (2; 0.111 g, 0.485 mmol) and *p*-toluenesulfonic acid hydrate (0.0951 g, 0.500 mmol) was added 2-methyl-3-buten-2-ol (2 mL) by the trap-to-trap method. The initial yellow solution changed through orange to red by heating at 50 °C for 10 h. The reaction was accompanied by a formation of a small amount of green precipitate. From the system, volatile liquids were removed under reduced pressure and the residue was extracted with ethanol. Concentrating and cooling to −78 °C of the solution caused the precipitation of the green solid, which was removed by filtration. Evaporating off the solvent from the filtrate, extracting the residue with acetone, concentrating the extract, and cooling the concentrate to −30 °C gave reddish orange crystals of 3b (0.105 g, 45%). We could not obtain the analytically pure product, although it was judged as spectroscopically pure. The failure in purification may probably be ascribed to the difficulty in complete removal of acetone from the crystals.

Method 2 (Starting from 1). To $[Cp_2MoH_3]^+TsO^-$ (1; 0.178 g, 0.445 mmol) was added 2-methyl-3-buten-2-ol (3 mL), and the mixture was heated at 80 °C in vacuo for 15 h. The system changed from a yellow solution through a green solution/brown precipitate and then finally to a brown solution/green precipitate. Evolution of H_2 (72%) was observed in the reaction. Evaporating off the alcohol, washing the residue with diethyl ether, extracting from the residue with ethanol, and recrystallizing from acetone afforded reddish brown crystals of 3b (0.0949 g, 44%).

Preparation of Bis(η^5-cyclopentadienyl)(3-hydroxy-2-methylpropyl-*C*^{1},*O*)molybdenum(IV) *p*-Toluenesulfonate (3c). Methods analogous to those described above for 3b (methods 1 and 2) were applicable to the preparation of 3c using β-methallyl alcohol in place of 2-methyl-3-buten-2-ol: yield 74%

(36) Green, M. L. H.; McCleverty, J. A.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 4854.

(method 1) and 79% (method 2). Anal. Calcd for $C_{21}H_{28}SO_4Mo$: C, 53.62; H, 5.57; S, 6.81. Found: C, 53.48; H, 5.57; S, 6.82.

Preparation of 2,2-Bis(η^5-cyclopentadienyl)-1-oxa-2-molybdenacyclopentane (4a). Method 1 (from 3a/NaOH). To the ethanol (10 mL) solution of cyclic γ-hydroxypropyl complex **3a** (0.189 g, 0.413 mmol) was added 5.62 mL of the ethanol solution of NaOH (0.0735 mmol/mL), and the mixture was stirred at room temperature for a night. Solvent was removed in vacuo to leave a dark brown solid, which was extracted with toluene. Concentrating the extract, adding hexane to the concentrate, and cooling to −78 °C gave reddish brown crystals of oxametallacycle **4a**, which were filtered off and dried in vacuo (0.090 g, 77%). Anal. Calcd for $C_{13}H_{16}OMo$: C, 54.94; H, 5.67. Found: C, 54.79; H, 5.89.

Method 2 (from 2/HCl/Allyl Alcohol). To Cp_2MoH_2 (**2**; 0.463 g, 2.03 mmol) were added gaseous HCl (2.03 mmol) and allyl alcohol (2 mL) by the trap-to-trap method. When the mixture was stirred in vacuo at 50 °C for 6 h, the solution changed from yellow to reddish brown. From the solution, excess allyl alcohol was evaporated off to leave a reddish brown solid, which was washed well with diethyl ether. The solid was dissolved in ethanol (25 mL). NaOH in ethanol (2.69 mmol/mL, 7.6 mL) was added to the solution, and the mixture was stirred at room temperature for 13 h. Working up the solution as above yielded **4a** (0.294 g, 51% based on **2** used).

Preparation of 2,2-Bis(η^5-cyclopentadienyl)-5,5-dimethyl-1-oxa-2-molybdenacyclopentane (4b). Treatment of **3b** (0.164 g, 0.339 mmol) with NaOH in ethanol by a method analogous to that described above (method 1) gave an orange powder of oxametallacycle **4b** (91%). Anal. Calcd for $C_{15}H_{20}OMo$: C, 57.70; H, 6.46. Found: C, 57.47; H, 6.43. Mp (under vacuum): 140–142 °C dec. Similarly obtained was orange powder of 2,2-bis(η^5-cyclopentadienyl)-4-methyl-1-oxa-2-molybdenacyclopentane (**4c**) from **3c** (0.171 g, 0.364 mmol) in 70% yield. Anal. Calcd for $C_{14}H_{18}OMo$: C, 56.38; H, 6.08. Found: C, 57.10; H, 6.20. Mp (under vacuum): 163–165 °C dec. The sodium salt of tosylate, NaOTs, was isolated as a byproduct in 99% yield, which was identified by IR and flame reaction.

Reaction of 4a with CO. The toluene (10 mL) solution of molybdenaoxacyclopentane **4a** (0.0686 g, 0.214 mmol) was allowed to react with carbon monoxide (3.4 atm) at 80 °C for 10 h in an autoclave. After the reaction, the volatile portion was separated from the solution by the trap-to-trap method and submitted for GLC analysis to observe formation of oxetane. The residual solid was washed with hexane and dried in vacuo to give 0.0184 g of crude product, which showed strong IR absorptions at 1885, 1770, and 1755 cm^{-1}.

Reaction of 4b with TsOH·H_2O. Molybdenaoxacyclopentane **4b** (0.0285 g, 0.0913 mmol) and *p*-toluenesulfonic acid hydrate (0.0204 g, 0.107 mmol) were stirred in diethyl ether at room temperature for 30 min to give a brown precipitate. After the solvent was evaporated off, the residue was washed with diethyl ether and recrystallized from acetone to give brown crystals of the cationic cyclic (γ-hydroxypropyl)molybdenum derivative **3b** in 58% yield.

The similar reaction of **4c** (0.0304 g, 0.102 mmol) and *p*-toluenesulfonic acid hydrate (0.0203 g, 0.106 mmol) yielded the corresponding cation **3c** in 69% yield.

Reaction of 4a and 4c with Alkyl Halides. To the flask containing 2,2-bis(η^5-cyclopentadienyl)-1-oxa-2-molybdenacyclopentane (**4a**; 0.095 g, 0.347 mmol) was added methyl iodide (2 mL) by the trap-to-trap method, and the mixture was stirred at room temperature for 25 h. From the resulting reddish violet solution, the volatile portion was removed in vacuo and the residue was extracted with ethanol. The extract was concentrated, and when the concentrate was cooled to −78 °C, purple crystals of $[Cp_2\overset{\curvearrowright}{Mo}(CH_2)_3\overset{\curvearrowleft}{O}CH_3]^+I^-$ (**6a$_m$**; 0.0949 g, 64%) were obtained. Anal. Calcd for $C_{14}H_{19}OIMo$: C, 39.46; H, 4.49. Found: C, 39.52; H, 4.63.

By a similar reaction of **4a** with ethyl iodide, the corresponding ethoxy complex $[Cp_2\overset{\curvearrowright}{Mo}(CH_2)_3\overset{\curvearrowleft}{O}C_2H_5]^+I^-$ (**6a$_e$**) was obtained in 59% yield. Anal. Calcd for $C_{15}H_{21}OIMo$: C, 40.93; H, 4.81; I, 28.83. Found: C, 40.91; H, 4.72; I, 28.45.

Similarly obtained were the γ-alkoxy-2-methylpropyl derivatives starting from **4c**. $[Cp_2\overset{\curvearrowright}{Mo}CH_2CH(CH_3)CH_2\overset{\curvearrowleft}{O}CH_3]^+I^-$ (**6c$_m$**): yield 80%. Anal. Calcd for $C_{15}H_{21}OIMo$: C, 40.93; H, 4.81; I, 28.83. Found: C, 40.98; H, 4.25; I, 28.56. $[Cp_2\overset{\curvearrowright}{Mo}CH_2CH(CH_3)CH_2\overset{\curvearrowleft}{O}C_2H_5]^+I^-$ (**6c$_e$**): yield 75%. Anal. Calcd for $C_{16}H_{23}OIMo$: C, 42.31; H, 5.10; I, 27.94. Found: C, 42.15; H, 4.92; I, 27.55.

Reaction of 6a$_m$ and 6a$_e$ with $NaBH_4$. Cyclic γ-methoxypropyl complex **6a$_m$** (0.0808 g, 0.190 mmol) and $NaBH_4$ (0.0717 g, 1.90 mmol) were mixed in 2-propanol (5 mL). When the mixture was stirred at room temperature for 24 h, the solution changed from violet to yellow. Formation of methyl propyl ether (38%) was observed by GLC analysis of the distillate of the reaction mixture. Benzene extraction of the residue, evaporation of the solvent, and recrystallization of the residual solid from ethanol yielded yellow needles of Cp_2MoH_2 (**2**; 0.0344 g, 80%).

A similar reaction of cyclic γ-ethoxypropyl complex **6a$_e$** with $NaBH_4$ yielded ethyl propyl ether (69%) and Cp_2MoH_2 (**2**; 0.0137 g, 72%).

Preparation of MeOH Adduct 8. $[Cp_2MoH_3]^+TsO^-$ (**1**; 0.109 g, 0.273 mmol) in methanol (3 mL) was heated at 50 °C in vacuo for 3.5 h to give a clear brown solution. Evolution of H_2 in 96% yield was observed by a Toepler pump and GLC. The solution was filtered, and addition of diethyl ether to the filtrate yielded $[Cp_2Mo(H)(CH_3OH)]^+TsO^-$ (**8**) in 89% yield.

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