Synthesis and Some Reactions of Molybdenocene Derivatives Coordinated with the Chiral Carboxylato Ligands

Takashi Ito,* Lin-Ming Wan, and Makoto Minato

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

(Received August 31, 1995)

Molybdenocene derivatives with some chiral carboxylato ligand of the types, $Cp_2MoH(OCOR^*)$, $Cp_2Mo(OCOR^*)_2$, $Cp_2MoH(OCO\text{-}E^*\text{-}OCO)MoHCp_2$, $[Cp_2Mo(OCOR^*)]^+R^*CO_2^-$, are prepared by the reaction of Cp_2MoH_2 with chiral 2-methylbutanoic acid, mandelic acid, *O*-acetylmandelic acid, tartaric acid, and *O*,*O*′-diacetyltartaric acid in the presence of ketone and are characterized spectroscopically. Enantioselectivity in the reduction of the prochiral ketones using some of these hydridocarboxylato derivatives is examined.

Utilization of the organometallics in the selective synthesis of organic molecules is a matter of continuing interest. In this regard a variety of stoichiometric and/or catalytic systems comprising molecules which contain transition metals have been developed for the regio-, diastereo-, and/or enantioselective organic syntheses.[1] We have previously shown that molybdenum hydride Cp_2MoH_2 (**1**, $Cp = \eta^5\text{-}C_5H_5$) efficiently reduces ketones,[2] aldehydes,[2] and imines[3] in the presence of protonic acid such as carboxylic acid or TsOH ($Ts = p\text{-}CH_3(C_6H_4)SO_3$). Noteworthy was an extremely high diastereoselectivity of the system, which resulted in a 100% diastereoselectivity in the reduction of 4-*t*-butylcyclohexanone to yield *cis*-4-*t*-butylcyclohexanol.[2]

Enantioselective reductions of prochiral ketones have been hitherto reported as either catalytic by the use of transition metal hydrides coordinated with chiral phosphines or as stoichiometric by using inorganic hydrides such as $LiAlH_4$ or $NaBH_4$ in the presence of chiral auxiliaries.[4] In view of the fact that the system consisting of the dihydride **1** and protonic acid reduces ketones in high diastereoselectivity, we are interested in examining the enantioselectivity of the system when the prochiral ketones are reduced by using derivatives of **1** containing chiral anionic ligand. In this report, the preparation of such derivatives with chiral carboxylato ligand and the results of their application to the reduction of the prochiral ketones are described.

Results and Discussion

Preparation of the Mononuclear Molybdenocene Derivatives with Chiral Carboxylato Ligands. On the basis of our findings that monohydridotosylato complex $Cp_2MoH(OTs)$, which is sterically more demanding than the dihydride **1**, reduces cyclic ketone in the presence of TsOH in highly diastereoselective fashion, we aimed at preparing such monohydrido complexes possessing chiral anionic ligand in place of OTs, i.e. $Cp_2MoH(A^*)$. The preliminary results, in which (+)-10-camphorsulfonic acid is employed in place of TsOH, $Cp_2MoH(OCs^*)$ (OCs^* = (+)-10-camphorsulfonato), did not show any remarkable enantioselectivity when it was used in the reduction of acetophenone either in the presence or in the absence of Cs^*OH.[5]

Subsequently we aimed at preparing a monohydridocarboxylato derivative of **1** in which carboxylato ligand contains a chiral center, $Cp_2MoH(OCOR^*)$ (**2**). For the preparation of type **2** complex starting from **1**, there are three possible routes:

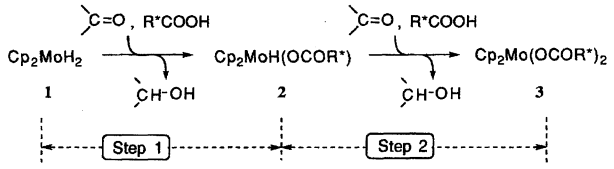
$$\text{(a)}\ Cp_2MoH_2 \xrightarrow[-H_2]{h\nu} \{Cp_2Mo\} \xrightarrow{R^*COOH} Cp_2MoH(OCOR^*) \qquad (1)^{6}$$

$$\text{(b)}\ Cp_2MoH_2 \xrightarrow[80\ ^\circ C]{TsOH} Cp_2Mo(OTs) \xrightarrow{R^*COONa} Cp_2MoH(OCOR^*) \qquad (2)^{6}$$

$$\text{(c)}\ Cp_2MoH_2 \xrightarrow[-RR'CHOH]{R^*COOH \quad RR'C=O} Cp_2MoH(OCOR^*) \qquad (3)^{2}$$

In the viewpoint of the preparation of chiral complex without inducing racemization, it would be desirable to avoid the use of the photoreaction, hence pathway (a) should be omitted. In the preliminary experiment, the second step of pathway (b), the anion metathesis reaction, was not found to be a clean reaction and the isolation of **2** from the reaction mixture was quite difficult. Thus, pathway (c), in which ketone plays a role of dehydrogenation agent, was employed in the following preparations.

Previously, we have shown through the kinetic investigation that the reaction of dihydride **1** with carboxylic acid in the presence of ketone or aldehyde proceeds stepwise as shown in Eq. 4.[2]



(4)

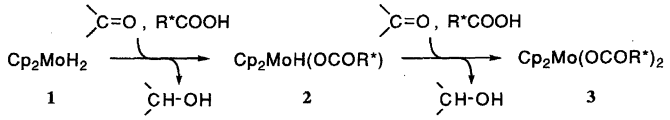
In order to obtain monohydrido derivative **2** selectively, it is necessary to promote the Step 1 reaction and suppress the Step 2 reaction. Since reaction (4) has been known to proceed via a nucleophilic attack of the molybdenum metal to the carbonyl carbon, the use of ketones with strong electron-withdrawing substituent may enhance the overall reaction rate. The higher basicity of **1** as compared with that of **2** may result in the selective formation of **2** when the electron-deficient ketone is used in an amount equimolar to **1**. In fact, the reactions of **1** in benzene at room temperature with chiral[7] (*S*)-(+)-2-methylbutanoic acid (**a**), (*S*)-(+)-mandelic acid (**b**), and (*R*)-(−)-*O*-acetylmandelic acid (**c**) in the presence of trifluoroacetophenone yielded corresponding type **2** complexes. (Table 1, Runs 1, 3, and 4) In the case of 2-methylbutanoic acid, no reaction took place with an equimolar amount of **1** even at 50 °C when acetone was employed as both hydrogen acceptor and solvent. The use of a large excess of R*COOH resulted in the formation of biscarboxylato complexes **3** (Table 1, Runs 2 and 5). The weak acid such as L-(+)-proline did not react with an equimolar amount of **1** either in benzene in the presence of trifluoroacetophenone at room temperature or in ethyl methyl ketone at 55 °C.

These results indicate that the higher the acidity of the carboxylic acid is, the higher becomes the yield of **2**; the ratio of the reaction rates for Steps 1 and 2 ($k_{\text{step 1}}/k_{\text{step 2}}$) in Eq. 4 becomes larger as the acidity of R*COOH increases.

The resulting hydridocarboxylato derivatives of molybdenocene are dark yellow (**2a**) and red crystals (**2b** and **2c**) and are unstable to air. Dicarboxylato complexes are dark purple (**3b**) and blue (**3c**) needles. Both complexes **2** and **3** are soluble in benzene, toluene, alcohols, tetrahydrofuran, and acetone and insoluble or only very slightly soluble in hexane and diethyl ether. These products were characterized by IR and ^{1}H NMR spectroscopies and elemental analyses (Table 2). The biscarboxylato derivatives of molybdenocene of the type **3** have been prepared by the metathetical reaction between Cp_2MoCl_2 and RCOONa for R=CF_3 and Ph.[8]

Preparation of the Binuclear Molybdenocene Derivatives Bridged with Chiral Carboxylato Ligands. Reaction of dihydride **1** with a half mole of L-(+)-tartaric acid (**d**) in ethanol in the presence of trifluoroaceto-

Table 1. Reactions of Cp_2MoH_2 (**1**) with R*COOH in the Presence of Ketone



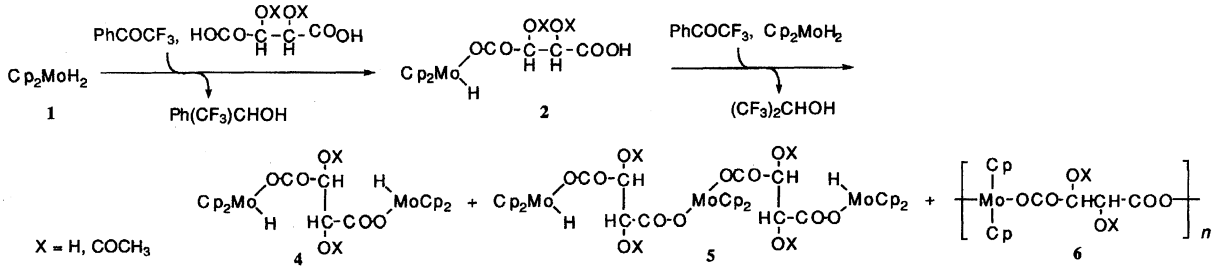
	Cp_2MoH_2(**1**)	R*COOH			$PhCOCF_3$		Temp	Time	Yield/%		
Run	mmol	R*		mmol	mmol	Solvent	°C	h	**2**	**3**	Other products
1	0.84	Me(Et)CH–	(**a**)	0.84	0.84	MeOH	20	20	11 (**2a**)	+	$PhCH(OH)CF_3$
2	0.48	Me(Et)CH–	(**a**)	23.8	—	MeCOEt	20	16	0	56 (**3a**)	MeCH(OH)Et
3	0.89	Ph(OH)CH–	(**b**)	0.90	0.89	PhH	20	5	78 (**2b**)	0	$PhCH(OH)CF_3$
4	1.35	Ph(OAc)CH–	(**c**)	1.35	1.35	PhH	20	15	49 (**2c**)	+	$PhCH(OH)CF_3$
5	0.83	Ph(OAc)CH–	(**c**)	2.49	—	Me_2CO	20	20	0	91 (**3c**)	Me_2CHOH

Table 2. Characteristic Spectral Data and Analytical Data for Complexes **2** and **3**

Complexes		IR[a]/cm^{-1}			^{1}H NMR[b]/ppm			Elemental analyses (Calcd values)	
		ν(Mo–H)	$\nu(OCO)_{asym}$ $\nu(OCO)_{sym}$	Others	δ(Mo–*H*)	δ(Cp)	δ(COC*H*)	C/%	H/%
$Cp_2MoH\{OCOCH(Et)Me\}$	**2a**	1830	1635	—	−8.06 s	4.57 d	2.24 m	c)	c)
			1225						
$Cp_2MoH\{OCOCH(OH)Ph\}$	**2b**	1850	1620	3400	−8.52 s	4.12 d	4.84 s	56.72	4.86
			1190	ν(OH)				(57.15)	(4.80)
$Cp_2MoH\{OCOCH(OAc)Ph\}$	**2c**	1840	1650	1730	−8.22 s	4.48 d	5.88 s	56.84	4.88
			1230	$\nu(CO)_{acyl}$				(57.15)	(4.80)
$Cp_2Mo\{OCOCH(Et)Me\}_2$	**3a**	—	1605	—	—	5.10 s	2.43 m	56.04	6.56
			1230					(56.07)	(6.58)
$Cp_2Mo\{OCOCH(OAc)Ph\}_2$	**3c**	—	1610	1710	—	4.94 s	5.96 s	58.56	4.63
			1230	$\nu(CO)_{acyl}$				(58.83)	(4.61)

a) KBr. b) 270 MHz in C_6D_6. δ values downfield positive from internal $SiMe_4$ reference. c) Good analytical results were not obtainable due to contamination of **3a**.

Table 3. Reactions of Cp_2MoH_2 (**1**) with L-(+)-Tartaric Acid and (*R*,*R*)-(−)-*O*,*O*′-Diacetyltartaric Acid in the Presence of CF_3COPh



Run	Cp_2MoH_2 (**1**) mmol	$[-CH(OX)CO_2H]_2$ X		mmol	PhCOCF$_3$ mmol	Solvent	Temp °C	Time h	Yield/% **4**	**5**	**6**	Other products
6	2.30	H	(**d**)	1.15	1.15	EtOH	20	20	74 (**4d**)	0	0	**2d**, PhCH(OH)CF$_3$
7	0.81	OCH_3	(**e**)	0.41	0.81	MeOH	20	40	84[a] (**4e**)	+	0	**2e**, PhCH(OH)CF$_3$
8	2.57	OCH_3	(**e**)	1.29	2.57	PhMe	20	40	+	55[a] (**5e**)	3[a] (**6e**)	PhCH(OH)CF$_3$

a) Crude yield.

phenone afforded an orange complex which was analyzed as binuclear complex bridged with the tartarato moiety **4d** (Table 3). D-(−)-Tartaric acid reacted similarly to yield the corresponding enantiomeric counterpart. The analogous results were obtained when (2*R*,3*R*)-(−)-*O*,*O*′-diacetyltartaric acid (**e**) was employed in place of tartaric acid (**d**), although the brownish orange product **4e** was contaminated with several by-products, such as the type **2** complex $Cp_2MoH[OCOCH(OAc)CH(OAc)COOH]$ (**2e**) and the brown trimer $Cp_2MoH[OCOCH(OAc)CH(OAc)COOMo(Cp_2)OCOCH(OAc)CH(OAc)COO]HMoCp_2$ (**5e**). When the reaction with *O*,*O*′-diacetyltartaric acid was carried out in toluene, **5e** was the main product; it was contaminated with **4e** and polymeric complexes **6e**.[9] Thus, the isolation of analytically pure **4e** has so far been unsuccessful. Formation of monohydrido complexes of the type **2e** with the dibasic carboxylato ligand has been reported for tungsten analogues through the reaction of $Cp_2WH(Ph)$ with oxalic, malonic, and succinic acids.[10]

It is conceivable that the reaction of the basic Cp_2MoH_2 with carboxylic acid is so fast that the difference of the pK_a's of the tartaric acid (pK_{a_1}=2.93 and pK_{a_2}=4.23) was overcome, yielding the bridged dimer **4** instead of the hydridocarboxylato type complex **2**.

Complex **4d** was soluble in methanol, ethanol, tetrahydrofuran, and acetonitrile and insoluble in benzene, toluene, acetone, diethyl ether, and hexane; it was able to be purified analytically pure. Solubility of the complexes **4e** and **5e** was similar to that of **4d** except that they are soluble in acetone and toluene. Such similarity in the solubility of **4e** and **5e** hindered their isolation. Grayish polymeric **6e** was soluble only in methanol and was stable to air for several days. Some spectral data for these complexes are listed in Table 4.

Preparation of the Cationic Molybdenocene Derivatives with the Chelate Carboxylato Ligand. We have already shown that the hydridocarboxylato complex of the type **2** further reacts with carboxylic acid in the presence of ketone to yield dicarboxylato derivatives of molybdenocene **3** (Step 2 of Eq. 4). Because of this, it is inevitable that the complexes **2** prepared according to Eq. 4 are usually contaminated with the dicarboxylates **3**. It is noteworthy, however, that no dimandelato by-product was detected in the reaction mixture when hydridomandelato derivative was prepared according to Eq. 4 (Table 1, Run 3). In order to get further insight into this peculiar behavior of mandelic acid, we examined the reaction of **2b** with mandelic acid in the

Table 4. Characteristic Spectral Data for Complexes **4**—**6**

Complexes		IR[a]/cm^{-1} ν(Mo–H)	$\nu(OCO)_{asym}$ $\nu(OCO)_{sym}$	Others	^{1}H NMR[b]/ppm δ(Mo–*H*)	δ(Cp)	δ(COC*H*)
$[Cp_2Mo(H)OCOCH(OH)–]_2$	**4d**	1810	1630	3400	−8.69 s	5.11 s	3.69 d
			1310	ν(OH)			
$[Cp_2Mo(H)OCOCH(OAc)–]_2$	**4e**	1790	1640	1730	c)		
			1220	$\nu(CO)_{acyl}$			
$[Cp_2Mo(H)OCOCH(OAc)CH(OAc)COO–]_2MoCp_2$	**5e**	1810	1640	1730	c)		
			1220	$\nu(CO)_{acyl}$			
$[–MoCp_2–OCOCH(OAc)CH(OAc)COO–]_n$	**6e**	—	1630	1730		5.70 m	5.10 d
			1220	$\nu(CO)_{acyl}$			

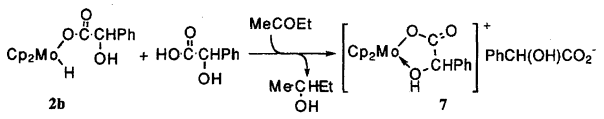
a) KBr. b) 270 MHz in CD_3OD. δ values downfield positive from internal $SiMe_4$ reference. c) Contamination of the by-products prevented from full assignment of the ^{1}H NMR signals.

Table 5. Preparation of the Cationic Monomandelato Derivatives of Molybdenocene, **7** and **8**

Run	Complexes	mmol	R*COOH R*	mmol	Solvent	ml	Temp °C	Time h	Products	Yield/%
9	**2b**	0.41	Ph(OH)CH– (**b**)	0.41	MeCOEt	3.5	20	44	**7**	84
10	**1**	1.45	Ph(OH)CH– (**b**)	3.62	Me_2CO	8.0	20	144	**7**	80
11	**2b**	0.68	—	—	MeCOEt	7.0	20	143	**8**	48
12	**7**	0.15	a)	—	—	—	20	5.5	**8**	45

a) Treated with 0.21 mmol of NaOH in MeOH.

presence of ethyl methyl ketone (Table 5, Run 9) (Eq. 5).



(5)

Unlike the other carboxylic acid, this reaction did not afford a blue-to-purple colored complex which is characteristic of dicarboxylato complex of type **3** but resulted in the formation of red crystals in 84% yield. The reaction was accompanied by the formation of 2-butanol in 90% yield. The red crystals thus formed were assigned to the novel cationic monocarboxylato derivative of molybdenocene **7**, based on the spectral evidence (vide infra), in which a hydroxyl group coordinates to the metal center giving rise to the chelate coordination of the α-hydroxycarboxylato ligand. The same complex **7** was obtained in 80% yield when dihydride **1** was allowed to react with excess mandelic acid (2.5 mole/mole of **1**) in acetone (Table 5, Run 10).

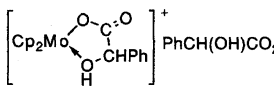
When **2b** was stirred at room temperature in ethyl methyl ketone in the absence of mandelic acid, a slow reaction took place, and, after 143 h, a brown complex assignable to **8** was obtained in 48% yield together with 2-butanol in 63% yield (Table 5, Run 11).

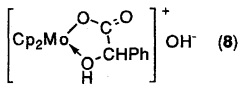
In the absence of carboxylic acid, the fairly acidic hydroxyl proton in the mandelato ligand may play the role of acid and the water molecule contaminated in the solvent seems to have cleaved the cyclic intermediate. Formation of more than 50% of 2-butanol suggests the presence of an extra proton source other than α-hydroxyl proton. Cationic complex **8** with the hydroxide anion as a counter cation was also obtained by treatment of **7** with an equimolar amount of NaOH in methanol in 45% yield (Table 5, Run 12).

Essentially the analogous results were obtained when tartaric acid was employed in place of mandelic acid. In this case, carboxylato-bridged dimeric cations corresponding to **7** and **8**, respectively, were obtained, although they were hard to purify.

Red crystals of the cationic complexes **7** and **8** are fairly stable to air in the solid state and are soluble only in the alcoholic solvents, tetrahydrofuran, and dimethyl sulfoxide (DMSO). As shown in Table 6, complex **7** exhibits strong IR absorption assignable to the free carboxylate anion at 1720 cm^{-1} in addition to the asymmetric and symmetric OCO stretchings around 1620 and 1300 cm^{-1}, respectively, which are characteristics of a carboxylato ligand coordinated in a monodentate fashion.[11]

Table 6. Characteristic Spectral and Electric Conductivity Data for Complexes **7** and **8**





Complexes	IR[a]/cm^{-1} ν(OCO)$_{asym}$	ν(OCO)$_{sym}$	ν(OCO)$_{free}$	ν(OH)	^{1}H NMR[b]/ppm δ(Cp)	δ(COC*H*)	δ(COC*H*)$_{free}$	Mole conductivity[c] ms cm^2 mol^{-1}
7	1620	1300	1720	3400	5.66 s	4.27 s	4.99 s	0.9
8	1630	1295	—	3300	5.66 d	4.27 s	4.40 s	66

a) KBr. b) 270 MHz in DMSO-d_6. δ values downfield positive from internal $SiMe_4$ reference. c) Mole conductivities in MeOH solution.

Table 7. Recovery of Carboxylic Acids from Complexes **3a**, **3c**, and **7** and the Comparison of their Specific Rotatory Power

Run	Complexes X		mmol	HCl aq (35%)[a] ml	Products R*COOH	Yield/%	[α]	Starting acid [α]
13	$Cp_2Mo\{OCOCH(Et)Me\}_2$	(**3a**)	0.49	4.8	Me(Et)CHCOOH	97	b)	b)
14	$Cp_2Mo\{OCOCH(OAc)Ph\}_2$	(**3c**)	0.16	1.6	Ph(OAc)CHCOOH	85	−123.8	−117.5
15	$[Cp_2Mo\{OCOCH(OH)Ph\}]^+$ $[OCOCH(OH)Ph]^-$	(**7**)	0.43	4.8	Ph(OH)CHCOOH	88	−135.7	−132.9

a) Reactions are carried out in acetone at room temperature for 3 h. b) Not measured.

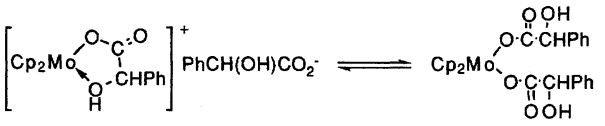
Table 8. Reduction of Acetophenone with the System Composed of Binuclear and Trinuclear Complexes **4** and **5**

Run	Complexes	mmol	Dibasic Carboxylic Acids	mmol	MeCOPh mmol	Solvent	Temp °C	Time h	MeCH(OH)Ph Yield/%	[α]	ee%[b]	
16	**4d-L**	0.92	L-Tartaric acid	0.55	8.6	MeOH	20	90	73	−9.8	24	(*S*)[c]
17	**4d-L**	0.66	L-Tartaric acid	—	8.6	MeOH	5–20	180	38	−15.1	37	(*S*)[c]
18	**4d-L**	0.83	L-Tartaric acid[a]	0.53	13	MeOH	20	180	43	−13.0	31	(*S*)[c]
19	**4d-D**	0.73	D-Tartaric acid	0.43	13	MeOH	20	90	54	13.5	25	(*R*)[d]
20	**4d-D**	0.50	D-Tartaric acid	3.00	13	MeOH	0–10	180	99	8.4	16	(*R*)[d]
21	**4d-D**	0.80	D-Tartaric acid	3.33	13	MeOH	−20—−10	180	32	7.3	14	(*R*)[d]
22	**4e-*RR***	0.59	(*R,R*)-(−)-*O,O'*-Diacetyltartaric acid	0.88	13	MeOH	20	96	138	3.4	8	(*R*)[c]
23	**4e-*RR***	0.39	(*R,R*)-(−)-*O,O'*-Diacetyltartaric acid	0.68	13	PhMe	20	72	47	5.5	11	(*R*)[d]

a) Molecular Sieve 4A (0.7 g) was added. b) Asymmetric yields were determined by an automatic polarimeter in 1 dm tube. c) Based on maximum value of $[\alpha]_D$ −40.6 (MeOH). d) Based on maximum value of $[\alpha]_D$ 52.5 (CH_2Cl_2).

Absence of the band at 1720 cm^{-1} in **8** and the low frequency shift of ν(OH) going from **7** to **8** by 100 cm^{-1} strongly suggest the anion exchange from carboxylate in **7** to hydroxyl in **8**. The presence of two kinds of carboxylate group, coordinated and free, in **7** was also evidenced by ^{1}H NMR spectra where two sets of signals assignable to carboxylato groups were observed.

Interestingly, electric conductance of the methanol solution of **7** was found to be significantly lower than that of **8**, as shown in Table 6. This result may be rationalized by considering the contribution of the neutral dicarboxylato isomer which is in equilibrium with the ionic **7** as shown below (Eq. 6).

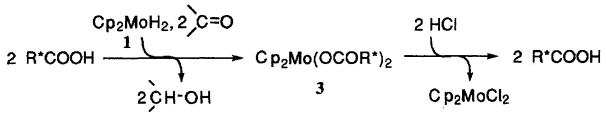


7 (6)

Examination of the Retention of the Chirality of the Carboxylic Acids. Since the dihydrido complex **1** has been known to be a strong base whose basicity corresponds to that of ammonia,[12] there is a possibility that racemization of the chiral acid might have taken place during the reaction represented in Eq. 4. In order to examine this, recovery of the carboxylic acid from some of the isolated carboxylato complexes and the measurement of the optical purity of the recovered carboxylic acid were attempted.

Treatment of the carboxylato complexes **3a**, **3c**, and **7** with dil hydrochloric acid in acetone at room temperature released corresponding carboxylic acid almost quantitatively, accompanied by the formation of Cp_2MoCl_2 (Table 7). Comparison of the specific rotatory power of the carboxylic acids thus recovered with those of the corresponding starting carboxylic acids revealed that racemization was not induced by this sequence of the reactions (Table 7).

These results, in which the chirality of the carboxylic acids has been retained throughout the reaction, suggest that the complex Cp_2MoH_2 (**1**) may be utilized as a protecting agent for the various chiral carboxylic acids. As shown in Eq. 7, **1** reacts with carboxylic acids in the presence of ketone under mild conditions to give, in most cases, dicarboxylato complexes **3**, from which carboxylic acids are easily recovered quantitatively by treatment with dilute HCl in acetone.



(7)

Reduction of Prochiral Ketones with Hydridomolybdenocene Derivatives Coordinated with the Chiral Carboxylato Ligands. In order to inspect the possibility of the asymmetric induction in the reduction of the prochiral ketones to the chiral alcohols, reactions of prochiral ketones such as ethyl methyl ketone and acetophenone with hydridomolybdenocene derivatives **2**, **4**, and **5** in the presence or absence of acid are examined.

When ethyl methyl ketone or acetophenone was reduced with mononuclear hydridocarboxylato complexes **2a**, **2b**, and **2c** either in the presence or absence of the corresponding chiral carboxylic acids, the enantioselectivity of the produced 2-butanol or 1-phenylethanol, respectively, was trivial with the ee values of only 0.7—3.5%. These results are in accord with that obtained previously for the (hydrido)-camphorsulphonato complex.[5]

A significant improvement in the enantioselectivity was observed when acetophenone was reduced with the dibasic acid-bridged binuclear hydrido complex **4d** (Table 8). Thus, use of the binuclear complex prepared from the L- or (2*R*, 3*R*)-isomer of tartaric acid (**4d-L**) in methanol in the presence of L-tartaric acid at room temperature in the reduction of acetophenone resulted in the formation of *S*-isomer of 1-phenylethanol in 73% yield with 24% ee (Table 8, Run 16). When binuclear complex **4d-D** which was prepared from D- or (2*S*,3*S*)-isomer of tartaric acid was used, (*R*)-1-phenylethanol was yielded (Run 19). Such enantioselectivity was not observed by binuclear and trinuclear hydrido complexes **4e** and **5e** which are prepared from *O,O'*-diacetyltartaric acid (Runs 7 and 8).

A slight increase of the selectivity was observed when

the reaction was conducted in the absence of added chiral carboxylic acid though the yield of alcohol was lowered considerably (Run 17). Increase of the amount of acid tended to increase the reactivity with a concomitant decrease of the enantioselectivity (Runs 19 and 20). Addition of molecular sieve 4A in the reaction mixture improved the selectivity a little (Run 18). Change of reaction temperature to −20 °C did not improve but rather lowered the selectivity (Runs 20 and 21).

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 NMR spectra were measured on a JNM-EX270 spectrometer. GLC was recorded on Shimadzu GC-7A and GC-14A gas chromatographs using PEG-20M column. The specific rotatory power was measured in a quartz cell using Horiba SEPA-200 rotatory meter. Electric conductivity of the solution was measured by Toa CM-20S conductivity meter.

Guaranteed grade commercial chiral carboxylic acids were used as purchased. Cp_2MoH_2 (**1**) was prepared according to the literature method.[12)]

Preparation of the Complexes 2—5. Since the procedures for the preparation of complexes **2**—**5** are similar to one another, the preparation of bis(η^5-cyclopentadienyl)hydrido[(*S*)-2-mandelato]-molybdenum(IV) (**2b**) is described below as a typical example. The reaction conditions and yields for each preparation are shown in the corresponding Tables.

To the flask containing Cp_2MoH_2 (**1**) (0.203 g, 0.890 mmol) and (*S*)-(+)-mandelic acid (0.137 g, 0.900 mmol) were added trifluoroacetophenone (0.125 cm^3, 0.89 mmol) and benzene (6 cm^3) by a trap-to-trap method and the mixture was stirred in vacuo at room temperature for 5 h. From the solution, the solvent was removed by evaporation in vacuo and the residue was washed with diethyl ether to give yellow powder of **2b** (0.264 g, yield 78%). Red microcrystalline **2b** was obtained on leaving its saturated solution in a mixture of Et_2O/EtOH (10/1) at −28 °C for a week.

In the preparation of 2-methylbutanoato complexes **2a** and **3a**, isolation of the products from unreacted 2-methylbutanoic acid was somewhat difficult and it was necessary to remove traces of carboxylic acid as the toluene azeotrope in vacuo. These additional procedures rendered the yield of **2a** fairly low.

Elemental analyses for complex μ-L-tartrat-bis[bis(η^5-cyclopentadienyl)hydridomolybdenum(IV)] (**4d-L**) (not cited in the Table). Found: C, 47.43; H, 4.51%. Calcd for $C_{24}H_{26}O_6Mo_2$: C, 47.86; H, 4.35%.

Preparation of Polynuclear Complex [–MoCp$_2$–OCOCH(OAc)CH(OAc)COO–]$_n$ (6e). The mixture of trinuclear complex (**5e**) (0.448 g, 0.392 mmol), (2*R*,3*R*)-(−)-*O*,*O*′-diacetyltartaric acid (0.159 g, 0.679 mmol), and acetophenone (1.5 cm^3, 13 mmol) in 20 cm^3 of toluene was stirred at room temperature for 72 h, while a gray precipitate accumulated in solution gradually. After the reaction, the solvent was evaporated off in vacuo to leave a gray solid, which was washed with diethyl ether and dried in vacuo to yield 0.517 g of a gray powder of **6e**.

Preparation of Bis(η^5-cyclopentadienyl)[(hydroxy-$\varkappa O$)phenylacetato-$\varkappa O$]molybdenum(IV) Mandelate (7). The mixture of Cp_2MoH_2 (**1**) (0.330 g, 1.45 mmol) and (*S*)-(+)-mandelic acid (0.543 g, 3.62 mmol) in 8 cm^3 of acetone was stirred at room temperature for 144 h, while the solution changed at first to red and then gradually deposited a red precipitate. The precipitate was collected by filtration, washed with acetone and dried in vacuo to yield red powder of **7** in 80% yield (0.610 g). Red prisms of **7** were obtained by recrystallization from a solvent of 50 : 50 (v/v) acetone/ethanol at −28 °C. Found: C, 56.72; H, 4.28%. Calcd for $C_{26}H_{23}O_6Mo\cdot H_2O$: C, 57.26; H, 4.62%.

Preparation of Bis(η^5-cyclopentadienyl)[(hydroxy-$\varkappa O$)phenylacetato-$\varkappa O$]molybdenum(IV) Hydroxide (8). Method a: Hydridomandelato complex **2b** (0.268 g, 0.708 mmol) in 7 cm^3 of ethyl methyl ketone was stirred at room temperature for 143 h, while a brown precipitate gradually came out. From the solution, the solvent was removed by a trap-to-trap method. Formation of 2-butanol in 81% yield was observed by a GLC analysis of the recovered liquid phase. The residue was washed with diethyl ether and benzene and dried in vacuo to yield red powder of **8** in 44% yield (0.123 g).

Method b: To the cationic complex **7** (0.081 g, 0.15 mmol) in methanol (4 cm^3) was added 2.5 M ethanol solution of NaOH (0.085 cm^3, 0.21 mmol, M=mol dm^{-3}); the mixture was stirred at room temperature for 5.5 h. Standing the solution at −28 °C for 2 d afforded red plates. These were filtered off and washed with hexane and dried in vacuo to yield red crystals of **8** in 45% yield (0.0272 g).

Recovery of 2-Methylbutanoic Acid from Complex 3a. On adding acetone (10 cm^3) and HCl (35% aq, 0.5 cm^3, ca. 4.8 mmol) to **3a** (0.208 g, 0.486 mmol), yellow precipitate came out rapidly. After being stirred for 3 h at room temperature, the mixture was filtered. GLC analysis of the filtrate showed formation of 2-methylbutanoic acid in 97% yield. The yellow precipitate which is assignable to Cp_2MoCl_2 on the spectral basis was obtained in 73% yield.

Recovery of *O*-Acetylmandelic Acid from Complex 3c. On adding acetone (5 cm^3) and HCl (35% aq, 0.16 cm^3, ca. 1.6 mmol) to **3c** (0.0948 g, 0.155 mmol), yellow precipitate came out rapidly. After being stirred for 3 h at room temperature, the mixture was filtered. The solvent was evaporated off from the filtrate and the residue was crystallized from water at 5 °C to give a colorless solid of *O*-acetylmandelic acid in 85% yield. Specific rotatory power measured in acetone at room temperature showed the optical purity of 98% ee. Analogous results were obtained when complex **7** (0.225 g, 0.43 mmol) was treated similarly with HCl to give mandelic acid in 88% yield, the optical purity of which was 98% ee.

Reduction of Prochiral Ketones. Since the procedures are similar to one another, reduction of acetophenone with μ-tartarato complex **4d-D** is described below as a typical example (Run 19 in Table 8).

Complex **4d-D** (0.440 g, 0.730 mmol), D-(−)-tartaric acid (0.065 g, 0.43 mmol), and acetophenone (1.5 cm^3, 13 mmol) were dissolved in 10 cm^3 of methanol in the Schlenk flask and the solution was stirred at room temperature for 90 h. After the solvent was removed by evaporation in vacuo, the residue was washed four times with 13 cm^3 of ethanol. The combined washings were concentrated by a rotary evaporator and the concentrate was separated by the column chromatography with silica gel. 1-Phenylethanol was thus isolated in 54% yield on the basis of **4d-D** and the measurement of its optical purity in dichloromethane revealed the enantioselectivity of 25% ee [(*R*)-isomer].

This work was supported by Grant-in-Aid for Scientific

Research (B) No. 07455354 and Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 0523614 from the Ministry of Education, Science, Sports and Culture. We thank Dr. Masako Tanaka of Tokyo Institute of Technology for elemental analyses and Prof. Seiichi Inoue of Yokohama National University for help with the specific rotatory power measurement.

References

1) See for example: a) A. Yamamoto, "Organotransition Metal Chemistry, Fundamental Concepts and Applications," John Wiley & Sons, New York (1986); b) R. H. Crabtree, "The Organometallic Chemistry of the Transition Metals," 2nd ed, John Wiley & Sons, New York (1993); c) L. S. Hegedus, "Transition Metals in the Synthesis of Complex Organic Molecules," University Science Books, Mill Valley (1994).

2) T. Ito, M. Koga, S. Kurishima, M. Natori, N. Sekizuka, and K. Yoshioka, *J. Chem. Soc., Chem. Commun.*, **1990**, 988.

3) M. Minato, Y. Fujiwara, and T. Ito, *Chem. Lett.*, **1995**, 647.

4) a) M. Hudlicky, "Reductions in Organic Chemistry," John Wiley & Sons, New York (1984), p. 96; b) K. E. Koenig, "Asymmetric Synthesis," ed by J. D. Morrison, Academic Press Inc., Orlando (1985), Vol. 5, p. 71; c) J.-M. Brunel, O. Pardigon, B. Faure, and G. Bruno, *J. Chem. Soc., Chem. Commun.*, **1992**, 287; N. Srivastava, A. Mital, and A. Kumar, *J. Chem. Soc., Chem. Commun.*, **1992**, 49; M. Falorni, G. Giacomelli, and L. Lardicci, *Gazz. Chim. Ital.*, **120**, 765 (1990).

5) K. Yoshioka and T. Ito, unpublished results.

6) N. Sekizuka, T. Igarashi, L.-M. Wan, and T. Ito, unpublished results.

7) Hereafter, all chiral carboxylic acids employed in this study will be described, unless otherwise stated, without denotation of the chirality, such as (*S*)-(+)- etc., for clarity except when it is appeared in the text for the first time.

8) M. G. Harriss, M. L. H. Green, and W. E. Lindsell, *J. Chem. Soc. A*, **1969**, 1453.

9) C. E. Carraher, Jr., *J. Polym. Sci., Part A-1*, **9**, 3661 (1971).

10) T. Ito, S. Sugimoto, T. Ohki, T. Nakano, and K. Osakada, *J. Organomet. Chem.*, **426**, 69 (1992).

11) S. D. Robinson and N. F. Utley, *J. Chem. Soc., Dalton Trans.*, **1973**, 1912.

12) M. L. H. Green, J. A. McCleverty, I. Pratt, and G. Wilkinson, *J. Chem. Soc.*, **1961**, 4854.