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Reductions of C=O and C=N groups with the systems composed of $(\eta^5\text{-}C_5H_5)_2MoH_2$ and acids[1]

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Abstract

Selective reductions of organic compounds, such as carbonyl compounds and imines, using a system composed of Cp_2MoH_2 and acids are examined. This system can reduce the substrates under mild conditions. Extremely high diastereoselectivity was achieved in the reduction of 4-*t*-butylcyclohexanone. The reactivity of imines depends on their structure. Aromatic imines are found to be more reactive than aliphatic imines.

Keywords: Aromatic imines; Aliphatic imines; Diastereoselectivity

1. Introduction

Reduction of a carbonyl group using main group elements of hydride such as $LiAlH_4$ or $NaBH_4$ has been carried out routinely for many years in modern synthetic chemistry and there is a huge number of results in this area. However, there has been a growing demand among organic chemists for new systems which are capable of reducing a carbonyl group of broad spectrum under especially mild reaction conditions and occasionally with remarkable selectivities [1]. In order to find excellent reducing agents, considerable efforts have been made. In this respect, recently the reduction of a carbonyl group with transition metal hydrido complexes has received increasing attention since the properties of these complexes are easily 'fine-tuned' by the selection of a wide variety of supporting ligands [2].

We have been investigating molybdenum and tungsten polyhydride compounds, which have unique features and have proved to be a useful starting material for the syntheses of a number of molybdenum and tungsten complexes [3]. During the course of our detailed studies on the chemistry of the molybdenum dihydride Cp_2MoH_2 ($Cp = \eta^5\text{-}C_5H_5$) (**1**), we found that the system consisting of **1** and protonic acids (HA) such as carboxylic acids, HCl, and TsOH (Ts = *p*-$MeC_6H_4SO_2$) reduces aldehydes and ketones to yield the corresponding alcohols under mild conditions. An important feature of this reaction is that the system can reduce carbonyl compounds chemoselectively. In this paper, we report full details on this reduction system. We also report that the use of the system for imines results in facile reductions to the corresponding amines. Although much is known about the reduction of ketones and aldehydes, the analogous reduction of imines has received less attention. Some of these results have appeared in preliminary communications [4,5].

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[1] Dedicated to Professor Nakamura on the occasion of his retirement from Osaka University.

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Table 1
Reduction of organic carbonyl compounds with Cp_2MoH_2 (**1**) and protonic acid

Substrate/mmol	Cp_2MoH_2/mmol	Acid/mmol	Time/h	Product(s)	Yield/%
CH_3CHO/excess	0.470	AcOH/33	0.5	CH_3CH_2OH	167
$(CH_3)_2CO$/27.0	0.504	AcOH/26	7	$(CH_3)_2CHOH$	189
$(CH_3)_2CO$/20.3	0.370	CH_3CH_2COOH/19	20	$(CH_3)_2CHOH$	176
$(CH_3)_2CO$/26.9	0.598	$(CH_3)_2CHCOOH$/30	29	$(CH_3)_2CHOH$	173
$(CH_3)_2CO$/13.4	0.560	$(CH_3)_3CCOOH$/29	108	$(CH_3)_2CHOH$	104
$(CH_3)_2CO$/3.91	0.543	HCl/4.0	2	$(CH_3)_2CHOH$	207
$(CH_3)_2CO$/27.1	0.430	TsOH/1.0	6	$(CH_3)_2CHOH$	176
Cyclohexanone/1.45	0.501	AcOH/35	24	Cyclohexanol	157
$CH_3COCH_2CH_3$/0.662	0.331	AcOH/20	46	$CH_3CH(OH)CH_2CH_3$	152
$CH_3COC(CH_3)_3$/29.1	0.501	AcOH/26	82	$CH_3CH(OH)C(CH_3)_3$	122
$CH_3COOCH_2CH_3$/0.738	0.369	AcOH/23	62	No reaction	
CH_2=$CHCOCH_3$/1.23	0.397	AcOH/35	20	$CH_3COCH_2CH_3$, $CH_3CH(OH)CH_2CH_3$	56, 40

2. Results and discussion

2.1. Reduction of carbonyl compounds with *1* and protonic acids

The molybdenum dihydride Cp_2MoH_2 (**1**) was first synthesized by Green and co-workers [6]. It has long been known that this complex has basic character and is easily protonated to give cationic trihydride $[Cp_2MoH_3]^+$ [7]. However, its property has scarcely been studied, partly because of the difficulty in its isolation in analytically pure form. Recently we have found that the trihydride cation can be successfully isolated as tosylate when the hydride is protonated with TsOH in non-aqueous solvent [8]. The trihydride complex $[Cp_2MoH_3]^+OTs^-$ was labile and was easily converted to monohydridotosylato complex $Cp_2MoH(OTs)$ (**2**), which behaves as a highly reactive molybdenocene precursor, with accompanying evolution of 1 mol of H_2 when warmed in ethanol. We also found that **2** can be successfully obtained in the presence of hydrogen acceptor such as acetone, that was hydrogenated to afford 2-propanol quantitatively. This result indicates a contrast with that of Nakamura and Otsuka [9]. Reactivity of **1** toward various olefins and acetylenes was investigated by them in detail [10]. They showed catalytic hydrogenation of 1,3-and 1,4-dienes, methyl acrylate, methyl crotonate, crotonaldehyde, or mesityl oxide using **1** as catalyst at 140–150°C under 160 atm of hydrogen without solvent. In this case, the carbonyl groups were found to survive the reduction and **1** was active only for the carbon–carbon double bond. Accordingly, the addition of acid alters the chemoselectivities of this reduction system. We were much interested in reducing carbonyl group using **1** and protonic acids, and tried the hydrogenation of several carbonyl compounds.

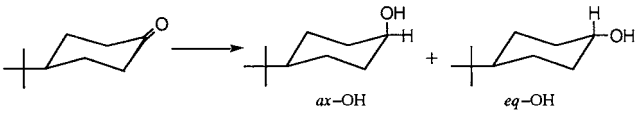
At first we carried out the reduction in the presence of large excess of substrates and acids at room temperature. Yields were determined by GLC and were based on the complex used. The results are shown in Table 1.

$$Cp_2\underset{1}{MoH_2} + 2RCOR' \xrightarrow{2HA} Cp_2MoA_2 + 2RCHOHR';$$

HA = protonic acid

Acetaldehyde, acetone methylethylketone, and cyclohexanone were reduced by this system easily at room temperature, while ethyl acetate was not reduced at all. When one equivalent of acetic acid (AcOH) was used, reduction without solvent was too slow at room temperature to give reasonable yields of the alcohols. However, the use of methanol as solvent resulted in a surprising enhancement of the rate so that high yields of the product resulted from reactions at 50°C. It is noteworthy that **1** reacts with two equivalents of substrate, indicating two hydrido ligands were consumed for the reaction. Bulky acids such as pivalic acid require prolonged stirring. On the other hand, in the presence of strong acid, such as HCl or TsOH, the reaction was completed within 6 h in good yield and two equivalents of acid sufficed for the reduction. The sterically hindered pinacolone was hydrogenated smoothly to give the corresponding alcohol in good yield. α,β-Unsaturated ketones were found to be reduced to yield saturated ketones and alcohols indicating that 1,4-reduction takes place. We confirmed that simple unactivated alkenes, such as ethylene, 1-heptene, and cyclohexene could not be reduced by this system, although **1** reacted with allylic alcohols to give cationic cyclic γ-hydroxypropylmolybdenum derivatives and π-allyl complexes [11].

The stereochemical behavior of this reduction system was examined by using 4-*t*-butylcyclohexanone.



Its reduction afforded *cis*-4-*t*-butylcyclohexanol (*ax*-OH) as the main product when more than two equivalents of acid, e.g. RCO_2H (R = CF_3, Me, Et, or Bu^t), HCl, or TsOH, were used. The diastereoselectivity was found to decrease with increasing bulk of the alkyl group in carboxylic acids and by reducing the amount

Table 2
Reduction of 4-*t*-butylcyclohexanone with Cp_2MoH_2 (**1**) and protonic acid

Entry	Cp_2MoH_2/mmol	Acid/mmol	Time/h	Products/%	
				ax-OH	*eq*-OH
1	0.341	AcOH/17	25	122	29
2	0.437	CH_3CH_2COOH/24	51	111	33
3	0.363	$(CH_3)_3CCOOH$/20	96	20	18
4	0.412	CF_3COOH/0.82	30	99	37
5	0.483	CF_3COOH/0.48	30	61	43
6	0.366	HCl/0.84	17	138	17
7	0.370	HCl/0.38	22	49	17
8	0.392	TsOH/1.0	72	128	18
9	0.403	TsOH/0.40	72	47	79
10	$Cp_2MoH(OTs)$/1.46	TsOH/1.5	24	68	0

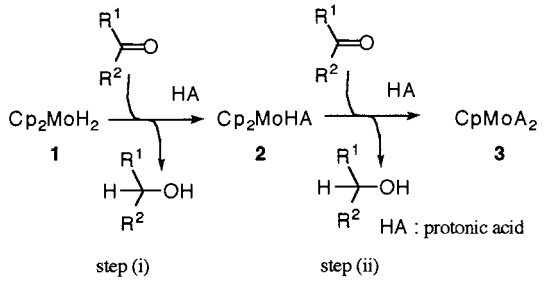
of acid. In particular, use of one equivalent of TsOH resulted in inversion of the diastereoselectivity from excess of the *cis*-isomer (*ax*-OH) to excess of the *trans*-isomer (*eq*-OH) as shown in Table 2. Similar results were obtained when 4-*t*-butylcyclohexanone was reduced with **1** and acetic acid in methanol at 50°C.

These stereochemical studies suggest that the reaction proceeds via two successive pathways, in which monohydrido complex Cp_2MoHA (**2**) is a key intermediate. Thus, in step (i) in Scheme 1, the starting dihydride **1** reacts with the acid and the substrate to give 1 mol each of alcohol and the monohydrido complex **2**. In the next step (ii), another mole of the substrate interacts with **2** to give a second mole of product together with the disubstituted molybdenum complex **3**.

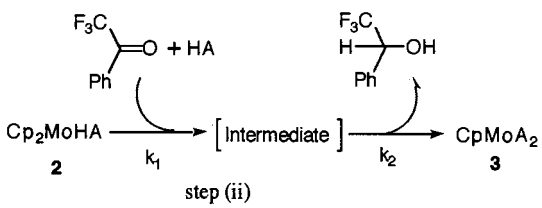
The existence of these two successive pathways was further substantiated by following ^{1}H-NMR spectroscopy of the reduction of 2,2,2-trifluoroacetophenone with **1** and acetic acid in benzene-d_6. Cp signals of each compound (**1**, **2**, and **3**) were found to be a reliable indication in estimating the reaction path. The signal assignable to the Cp protons of the monohydrido **2** and the diacetato **3** were observed at δ 4.77 and 5.07 ppm, respectively. The signal of **1** disappeared immediately indicating step (i) is very fast and step (ii) is a rate-determining stage in this reaction sequence. The intensity of the signal of **2** increased during the first stage and decreased as **3** was formed. The detailed study showed the existence of an unidentified intermediate, which is gradually increased with decreasing concentration of **2** and is decreased as **3** was formed, in step (ii) (Scheme 2). Assuming that the reaction obeys a successive pseudo first order kinetics, we obtained the experimental rate constants k_1(0.042 min^{-1}) and k_2(0.101 min^{-1}) for step (ii) by means of the Runge–Kutta procedure.

The diastereoselectivity of this reducing system may be rationalized by assuming that there is no stereoselectivity in step (i), whereas step (ii) proceeds with remarkable selectivity. In accordance with this assumption, 100% selectivity (*cis*-isomer) was achieved when 4-*t*-butylcyclohexanone was reduced using the independently prepared monohydrido complex $Cp_2MoH(OTs)$. The isolated yield of pure *cis*-*t*-butylcyclohexanol was 68% based on the ketone. Furthermore, we observed that the chiral monohydridocarboxylato complex, obtained by the reaction of **1** with tartaric acid, reduced prochiral ketones to give the corresponding enantiomerically enriched alcohols [12].

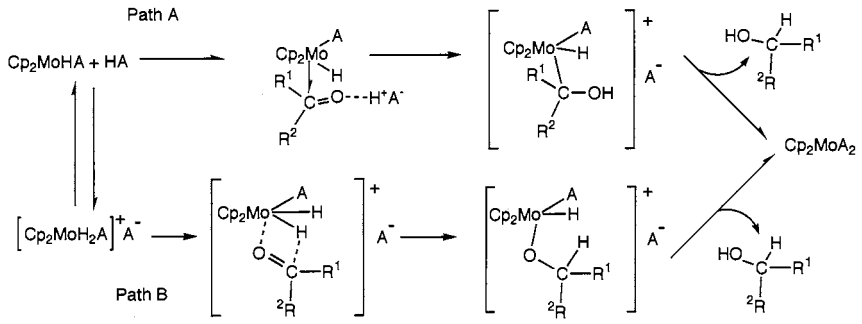
Two pathways are possible for both steps (i) and (ii) as shown in Scheme 3. One involves nucleophilic attack of the metal on the carbonyl carbon, where the electrophilicity is enhanced by protonation at the neighboring carbonyl oxygen atom, then the hydride migrates from the metal to the carbon (Path A). An alternative path involves initial protonation of the basic complex **1**, then the carbonyl group inserts into the Mo–H bond giving an alkoxo intermediate, which decomposes with the acid (Path B). The former pathway, which is similar



Scheme 1.



Scheme 2.



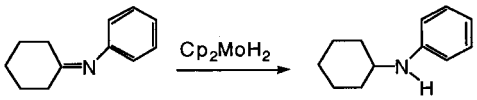
Scheme 3.

to those proposed for ketone and aldehyde reduction with $[Mo(CO)_5]^-$, seems to be more plausible than the latter [13]. We observed that the rate of reduction of 2,2,2-trifluoroacetophenone was much faster than that of acetophenone suggesting the initial nucleophilic attack of the molybdenum on the positive carbonyl carbon because the trifluoromethyl is a powerful electron-withdrawing group, and in 2,2,2-trifluoroacetophenone this attack seems to be more favorable.

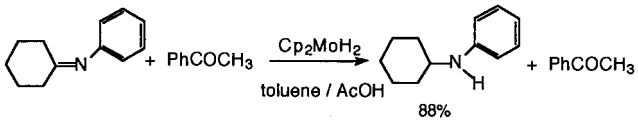
2.2. Reduction of imines with **1** and protonic acids

As shown above, significant success has been achieved in the reduction of ketones and aldehydes through use of **1** and protonic acid system, and then we tried the reduction of imines using this system.

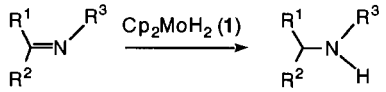
At first we carried out the reduction of *N*-cycldohexylideneaniline to *N*-cyclohexylaniline at room temperature under various conditions in order to obtain the optimum conditions. Three different types of solvents, namely methanol, THF, and toluene were tested. The results are shown in Table 3.



The reactions proceeded in satisfactory yields and all solvents tested were suited to this process. The reductions were completed within 70 h at room temperature in all cases. It was noted that, in contrast to the reduction of ketones and aldehydes, the imine was reduced in methanol without protonic acid. In toluene or in THF, no product was obtained in the absence of protonic acid. Since the imines are known to be more susceptible to the nucleophilic attack than ketones or aldehydes, it is conceivable to consider that methanol played a role of protonic acid in this case. As *N*-cyclohexylaniline seems to be more reactive than ketones, we examined the reduction of this imine in the presence of acetophenone in our system and confirmed that the imine was reduced selectively and acetophenone was recovered unreacted.



Subsequently, we carried out the reduction of several imines and the results are shown in Table 4.



imine **I** $R^1 = R^2 = CH_2CH_3$, R^3 = Ph
imine **II** $R^1 = R^2 = {}^nPr$, R^3 = Ph
imine **III** $R^1 = CH_2CH_3$ R^2 = Ph, R^3 = Ph
imine **IV** R^1, $R^2 = -(CH_2)_5-$, R^3 = cyclohexyl
imine **V** $R^1 = R^2 = CH_2CH_3$, $R^3 = CH_2Ph$
imine **VI** $R^1 = R^2 = CH_2CH_3$, $R^3 = CH_2CH_2Ph$
imine **VII** $R^1 = CH_2CH_3$, R^2 = Ph, R^3 = cyclopentyl

Table 3
Reduction of *N*-cyclohexylideneaniline with **1**

Entry	Cp_2MoH_2/mmol	Imine/mmol	Solvent	Yield/%[a]
1	0.73	1.47	Toluene	89[b]
2	0.77	0.77	Toluene	0
3	0.81	1.69	THF	81[b]
4	0.81	1.69	THF	0
5	0.72	1.44	Methanol	79

[a] Isolated yield based on the **1**.
[b] AcOH (1.71 mmol) was added.

Table 4
Reduction of imines with Cp_2MoH_2 (**1**)

Entry	Cp_2MoH_2/mmol	Imine/mmol	Time/h	Yield/%[a]
1	1.10	**I**/3.10	18	78
2	1.05	**II**/2.69	72	48
3	1.47	**III**/1.48	24	53[b]
4	0.228	**IV**/0.48	24	0[b]
5	1.06	**V**/2.26	92	125[b]
6	0.972	**VI**/1.93	92	107[b]
7	0.993	**VII**/2.03	92	103[b]

[a] Based on the **1** used.
[b] The reduction was carried out in the presence of TsOH.

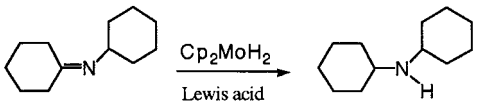
Table 5
Reduction of *N*-cyclohexylidenecyclohexylamine with **1** and Lewis acid

Entry	Cp_2MoH_2/mmol	Imine/mmol	Lewis acid/mmol	Solvent	Temperature/°C	Time/h	Yield/%[a]
1	1.74	3.44	$TiCl_4$/1.32	Toluene	r.t.	24	0
2	1.17	1.19	$TiCl_4$/1.18	Methanol	r.t.	24	20
3	2.01	2.00	$TiCl_4$/1.97	Methanol	40	24	22
4	0.838	0.847	BF_3/0.853	Methanol	40	24	19
5	0.712	0.713	$Ti(C_3H_7O)_4$/0.704	Methanol	r.t.	92	7
6	0.893	0.893	$Ti(C_2H_5O)_4$/0.880	Methanol	r.t.	92	14
7	0.738	4.30	$Yb(OTf)_3$/0.871	Methanol	50	24	90

[a] Isolated yield based on the **1** used.

The imines, other than *N*-cyclohexylidenecyclohexylamine (**IV**), were hydrogenated to the corresponding amines. It is worth pointing out that the reduction of the imines bearing phenyl group in their structure proceeds smoothly, although the aliphatic imine was not reduced at all. This result indicates a contrast with that of Bäckvall and Wang [14]. Recently they reported that ruthenium-catalyzed transfer hydrogenation of imines and they found aliphatic imines are more reactive than aromatic ones. As shown in Table 4, in the case of a reducible imine, the phenyl group may or may not be attached directly to the C=N moiety, suggesting that the phenyl group would not activate the imino group with the aid of an electronic effect. Although the mechanism of this reduction is not known with certainty, it seems likely that the complex **1** or the trihydrido complex $[Cp_2MoH_3]^+$ interacts with the phenyl group of the imine at the beginning, then it attacks the C=N moiety. Intuitively, if the complex and the aliphatic imine are initially held together, the reduction will proceed. It is well known that **1** reacts with a Lewis acid to form a 1:1 adduct which can be expected to bind further to an imine [15]. Therefore we decided to study the reduction in association with Lewis acids.

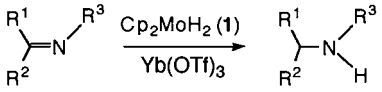
2.3. Reduction of *N*-cyclohexylidenecyclohexylamine with **1** and Lewis acids



Several Lewis acids were tested and the results are shown in Table 5. Expectedly, the Lewis acids were found to be efficient in the reduction of *N*-cyclohexylidenecyclohexylamine to dicyclohexylamine. Especially, the reaction using $Yb(OTf)_3$ gave a high product yield (90%). This compound has been utilized as a promising Lewis acid in organic synthesis since Kobayashi's pioneering work demonstrating $Yb(OTf)_3$ to be a good catalyst in the Diels–Alder reaction [16]. It has the specific coordination number and is a stable Lewis acid in aqueous media [17]. These unique properties may be responsible for the best result in the present system. In our system, methanol was used as a solvent, and the Lewis acidity of $Yb(OTf)_3$ seems to be not influenced by this protic media In contrast with the protonic acid system, **1** reacts with one equivalent of the substrate indicating only one hydrido ligand was consumed for the reduction.

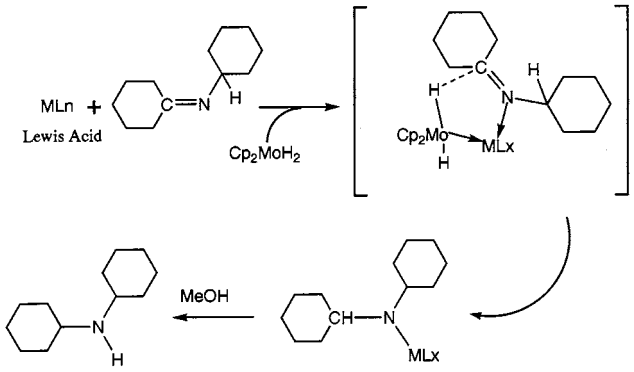
2.4. Reduction of aliphatic imines with **1** and $Yb(OTf)_3$

Then we carried out the reduction of several aliphatic imines using Cp_2MoH_2–$Yb(OTf)_3$ system and the results are shown in Table 6.



imine **VIII** $R^1, R^2 = -(CH_2)_5-$, R^3 = n-C_8H_{17}
imine **IX** $R^1, R^2 = CH_2CH_3$, R^3 = cyclohexyl
imine **X** $R^1, R^2 = CH_2CH_3$, R^3 = n-C_8H_{17}

The reduction proceeded smoothly in all cases. The success in the reduction of the aliphatic imine using Lewis acid may be the result of a favorable five-membered cyclic transition state, where the complex **1** is effectively linked by a Lewis acid to an imine, for hydrogen transfer as shown in Scheme 4. A similar 'bidentate effect' can not be expected for protonic acids.



Scheme 4.

Table 6
Reduction of aliphatic imines with Cp_2MoH_2 (**1**) and $Yb(OTf)_3$

Entry	Cp_2MoH_2/mmol	Imine/mmol	$Yb(OTf)_3$/mmol	Time/h	Yield/%[a]
1	0.791	**VIII**/1.71	0.846	92	40
2	1.11	**IX**/2.25	1.48	48	35
3	0.678	**X**/1.39	0.808	48	49

[a] Based on the **1** used.

3. Experimental details

3.1. General

All manipulations were conducted under purified argon or nitrogen. Air-sensitive reagents and products were handled by standard Schlenk techniques. Solvents were dried and purified in the usual manner, and stored under an atmosphere of argon. Commercially available chemicals were used as such without any further purification. Unhydrated TsOH was prepared by refluxing the hydrate in benzene for 5 h followed by crystallization by allowing the resulting solution to stand at ambient temperature. Infrared spectra were determined on a Perkin–Elmer 1600 series spectrometer. NMR spectra were recorded on a JEOL JNMEX-270 spectrometer. ^{1}H-NMR chemical shifts were referenced to tetramethylsilane (TMS). Cp_2MoH_2 was synthesized by the published method [6]. Imines were prepared from the appropriate amine and ketone by the usual water removal procedure (Dean Stark, or using a molecular sieve 4A). The structure assignment of the products was carried out by comparison of the IR and ^{1}H-NMR spectra with those of the authentic samples. Gas chromatography (GLC) for qualitative and quantitative analyses were carried out on a Shimadzu Model GC-7A chromatograph and GC-14A chromatograph. Yields were determined using an internal standard.

3.1.1. Reduction of carbonyl compounds with **1** and protonic acids

Typical procedure is as follows. To the flask containing Cp_2MoH_2 (**1**: 0.115 g, 0.504 mmol) was added AcOH (1.5 ml, 26 mmol) and acetone (2 ml, 27 mmol) by a trap-to-trap method. The mixture was stirred at room temperature in vacuo for 7 h. From the system, volatile liquids were removed under reduced pressure and the resulting solution was analyzed by GLC. 2-Propanol so obtained was 0.95 mmol (189%). Experiments listed in Table 1 were carried out under essentially the same conditions, and the detailed reaction conditions and the results are compiled in Table 1.

3.1.2. Reduction of 4-*t*-butylcyclohexanone with **1** and protonic acids

Typical procedure is as follows. To a solution of Cp_2MoH_2 (0.110 g, 0.483 mmol) and 4-*t*-butylcyclohexanone (0.156 g, 1.01 mmol) in THF (5 ml) was added equimolar amount of CF_3COOH (37 μl, 0.483 mmol). The reaction mixture was stirred at ambient temperature for 30 h under argon. The resultant solution was concentrated to dryness under reduced pressure and the residue was extracted with hexane. The resulting solution was analyzed by GLC.

3.1.3. Reduction of *N*-cyclohexylideneaniline with **1** and protonic acid

Typical procedure is as follows. To a solution of Cp_2MoH_2 (0.165 g, 0.725 mmol) and the imine (0.255 g, 1.47 mmol) in toluene (10 ml) was added equimolar amount of acetic acid (0.103 g, 1.71 mmol). The reaction mixture was stirred at ambient temperature for 34 h under argon. The resultant solution was concentrated to dryness under reduced pressure. To this residue was added a proper quantity of 5% sodium hydrogen carbonate solution and the mixture was extracted with ether in three portions. The extracts were combined and dried over $MgSO_4$. The product was purified by medium pressure column chromatography using hexane–ethyl acetate (9:1).

3.1.4. Reduction of imines with **1** and protonic acid

The reductions of imines were carried out by the same procedures as above. The detailed reaction conditions and the results are compiled in Table 4.

3.1.5. Reduction of *N*-cyclohexylidenecyclohexylamine with **1** and Lewis acids

Typical procedure is as follows. To a solution of Cp_2MoH_2 (0.168 g, 0.738 mmol) and the imine (0.770 g, 4.30 mmol) in methanol (50 ml) was added equimolar amount of $Yb(OTf)_3$ (0.540 g, 0.871 mmol). The reaction mixture was stirred at 50°C for 24 h under argon. The resultant solution was concentrated to dryness under reduced pressure. To this residue was added a proper quantity of 5% sodium hydrogen carbonate solution and the mixture was extracted with ether in three portions. The extracts were combined and washed with brine. The resulting solution was analyzed by GLC.

*3.1.6. Reduction of aliphatic imines with **1** and $Yb(OTf)_3$*

The reductions of imines were carried out by the same procedures as above. The detailed reaction conditions and the results are compiled in Table 6.

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