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Review

Molybdocenes and tungstenocenes derived from molybdenum(IV) and tungsten(IV) dihydride

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Contents

Abstract

Recent results of our studies on preparation of group 6 (Mo, W) metallocenes are reviewed. Molybdenum(IV) and tungsten(IV) dihydride Cp_2MH_2 (M = Mo, W; Cp = η-C_5H_5) have primarily been used as starting materials. Protonation with *p*-toluenesulfonic acid (TsOH) opens up a convenient route to the preparation of monohydridotosylato complexes $Cp_2MH(OTs)$, which hold potential as precursors for more sophisticated molybdocene or tungstenocene derivatives. Promising synthetic applications of them are also described.

Keywords: Molybdocenes; Tungstenocenes; Hydride complexes

1. Introduction

Group 6 (Mo, W) metallocenes have a longstanding history in the field of organometallic chemistry and have attracted attention [1]. Among these compounds, the molybdenum(IV) and tungsten(IV) dihydride Cp_2MH_2 (M = Mo (**1a**), W (**1b**);

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Cp = η-C_5H_5) play a major role in molybdocene and tungstenocene chemistry, because they show versatile reactivities towards various substrates, such as alkenes, alkynes, halogens, silanes, SO_2, CS_2, and CO. These reactions include, e.g. insertion of the carbon–carbon double or triple bond into the M–H bond to give hydride–alkyl derivatives [2] and the chemical, photochemical, or thermal generation of highly reactive tungstenocene, which can be trapped with benzene to give the hydride–phenyl derivative as a result of aromatic C–H activation [3–6]. Since the first preparation of the dihydride complexes by Green et al. [7], the complexes have proved to be useful precursors to a variety of molybdocene or tungstenocene derivatives [8]. In addition, these dihydrides have been the subject of a number of structural studies, both experimental and theoretical [9]. It is well known that these complexes are able to act as a Lewis base and are easily protonated with strong acids, such as HCl and CF_3COOH, to give cationic trihydrides $[Cp_2MH_3]^+$ [7]. This type of trihydride complexes is currently having a considerable impact on organometallic chemistry. Of particular note among the structural features of these complexes is the issue of whether the cations are characterized as a classical trihydride $[Cp_2MH_3]^+$ or as a nonclassical dihydrogen–hydride $[Cp_2M(\eta^2\text{-}H_2)(H)]^+$ [10]. Parkin et al. studied the influence of cyclopentadienyl substituents on the equilibrium between nonclassical dihydrogen–hydride and classical trihydride complexes in the molybdocene system. They found that the most stable form for the ansa molybdocene trihydride is a dihydrogen–hydride isomer, whereas the stable forms for the non-ansa complexes are trihydrides [10a]. In contrast to the molybdocene system, the tungsten counterpart exists as a classical trihydride [10c]. Consequently, different nature of these cationic hydrides for molybdenum and tungsten complexes would be closely related to their observed reactivity towards various substances.

This review highlights the reactions of the dihydride complexes Cp_2MH_2 under acidic conditions. Our primary interest in these compounds came from their intriguing reactivities and potential relevance to preparation of new types of molybdocene or tungstenocene derivatives and synthetic applications. This article is not intended to be comprehensive; instead, we describe some results obtained from our laboratory and also highlight some of the more unusual aspects of this work.

2. Syntheses and reactivities of monohydridetosylato complexes

2.1. Preparation of monohydridetosylato complexes $Cp_2MH(OTs)$

As described above, the molybdenum and tungsten dihydride are capable of acting as a Lewis base; they are easily protonated with strong acids. Such trihydride compounds have proved difficult to isolate as a result of their inherent instability [1,11]. Whereas we have found that the trihydride species can be successfully isolated as tosylates, when the dihydrides are protonated with *p*-toluenesulfonic acid (TsOH) in non-aqueous solvents (Eq. (1)) [12].

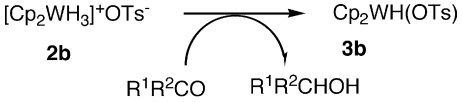
$$\underset{\substack{\mathbf{1a}:\,M=Mo\\ \mathbf{1b}:M=W}}{Cp_2MH_2} + TsOH \rightarrow \underset{\substack{\mathbf{2a}:\,M=Mo\\ \mathbf{2b}:M=W}}{[Cp_2MH_3]} + OTs^- \quad (1)$$

Addition of EtOH to an equimolar mixture of Cp_2WH_2 (**1b**) and TsOH in vacuo afforded a colorless solution. After being stirred at room temperature for 0.5 h, the solvent was evaporated off to leave off-white solid that was identified as the trihydride complex $[Cp_2WH_3]^+OTs^-$ (**2b**). Similarly obtained was the molybdenum analogue of $[Cp_2MoH_3]^+OTs^-$ (**2a**) by using Et_2O as solvent.

Both complexes **2a** and **2b** are colorless solids and are unstable to air even in the solid state, the former being more easily decomposed by air. Furthermore, **2a** was so reactive that it reacted with most of the common organic solvents releasing H_2. For example, it was converted into the monohydridetosylato complex $Cp_2MoH(OTs)$ (**3a**), when warmed at 50 °C in EtOH or THF (Eq. (2)) [13]. We found that **3a** was more easily obtained by simply heating the mixture of **1a** and TsOH in EtOH at 50 °C. The lability of **2a** may be attributable to the feasibility of the complex to form the nonclassical dihydrogen–hydride isomer and the tendency of the complex to eliminate H_2 [10a].

$$\underset{\mathbf{2a}}{[Cp_2MoH_3]^+OTs^-} \xrightarrow{-H_2} \underset{\mathbf{3a}}{Cp_2MoH(OTs)} \quad (2)$$

In contrast to the molybdenum complex **2a**, tungsten analogue **2b** was stable on heating in the solution, so that the above method of dehydrogenation was not applicable to the synthesis of the tungsten analogue **3b**. This greater stability of **2b**, compared to **2a**, may be readily rationalized in terms of the classical trihydride nature of the complex, as was mentioned in Section 1.



$R^1 = CH_3, C_2H_5$
$R^2 = CH_3, C_2H_5, (CH_3)_2CH$ (3)

However, when **2b** was treated with ketonic solvents, the monohydridetosylato tungsten complex **3b** was formed accompanied by the production of the corresponding alcohols and a grayish precipitate (by-product, vide infra) (Eq. (3)) [14]. It appears likely that the ketonic solvents function as a hydrogen acceptor in this case [15]. Acetone and ethyl methyl ketone were found to be superior reaction solvents for the synthesis of **3b** compared with the more bulky diethyl ketone or isopropyl methyl ketone, since they allowed isolation of the product in much higher yield. Green et al. reported that acetone served as a hydrogen acceptor in the reaction of $[Cp_2MoH_3]^+PF_6^-$ with 1,3-butadiene to give the η^3-crotyl derivative [16].

We found that the highly reactive **2a** also reduced various kinds of aldehydes and ketones to yield the corresponding alcohols under mild conditions. As will be mentioned in the latter part, this process can be applied to selective reduction of carbonyl compounds and imines [15,17]. We confirmed that the

trihydride complexes **2** or combing the dihydride complexes **1** with a protic acid results in the reduction of the carbonyl compounds. Whereas, in the absence of the acid, the carbonyl compounds could not be reduced by **1** at all. Clearly, the addition of the acid plays crucial roles in these reductions. It has been known that, in the reductions of ketones involving metal hydrides, association of the carbonyl oxygen by the metal cations or proton would aid in the hydride transfer [18]. In the present system, the similar effect of proton may facilitate the reactions.

The reddish powdery complexes **3a** and **3b** are extremely sensitive to air and moisture and are soluble in methanol, ethanol, THF, and CH_3CN. We found that, in methanol, both **3a** and **3b** suffered a considerable amount of solvolysis to give ionic species of the type $[Cp_2MH(MeOH)]^+OTs^-$ (M = Mo (**4a**), W (**4b**)). The molar conductivity of **4b** (21.40 S cm^2 mol^{-1}) is less than half that of **4a** (48.19 S cm^2 mol^{-1}), and hence the equilibrium shown in Eq. (4) appears to lie far to the left for the tungsten complex **4b**. In the case of the molybdenum complex, ionic species **4a** could be isolated, although **4b** was unable to be isolated.

$$\underset{3}{Cp_2MH(OTs)} \overset{+MeOH}{\underset{-MeOH}{\rightleftharpoons}} \underset{\substack{\mathbf{4a}: M = Mo \\ \mathbf{4b}: M = W}}{[Cp_2MH(MeOH)]^+OTs^-} \quad (4)$$

The preparation of monohydridehalogeno complexes Cp_2MHX analogous to **3** has been achieved by the partial reduction of Cp_2MX_2 with sodium borohydride [19], by the reaction of **1b** with CCl_4 (for X = Cl), $CHBr_3$ (for X = Br), or CH_3I (for X = I) [20], or by the protonolysis of $Cp_2WCl(SnMe_3)$ [21]. Since these types of monohydride–halogeno complexes are not necessarily adequate as precursors for other monohydride derivatives of molybdocene and tungstenocene [20], the exploitation of an alternate source for such derivatives is anticipated. In this regard, **3a** and **3b** are quite interesting. Thence, we carried out a systematic investigation on the reactivity of these complexes.

2.2. Reactions of monohydridetosylato complexes $Cp_2MH(OTs)$ with tertiary phosphines

$$\underset{\mathbf{3}}{Cp_2MH(OTs)} + PR_3 \rightarrow \underset{\substack{\mathbf{5} \\ R=Ph,\ Bu^n,\ OEt}}{[Cp_2MH(PR_3)]^+OTs^-} \quad (5)$$

The cationic monohydride(tertiaryphosphine) complexes $[Cp_2MH(PR_3)]^+OTs^-$ (**5**, M = Mo, W) were prepared for various phosphines by their reactions with **3** (Eq. (5)) [13,14]. Although Dias and co-workers prepared the similar cationic molybdenum complexes with halide or PF_6^- counter anion [22], they failed to obtain the tungsten analogue by the reaction of halohydrides Cp_2WHX (X = Cl, Br, and I). Our success in the tungsten complex **3b** may be ascribed to the more labile property of the TsO group as a leaving group than the halide anions. Accordingly, the present system provides us with a convenient method of preparing these types of cationic hydride(phosphine)

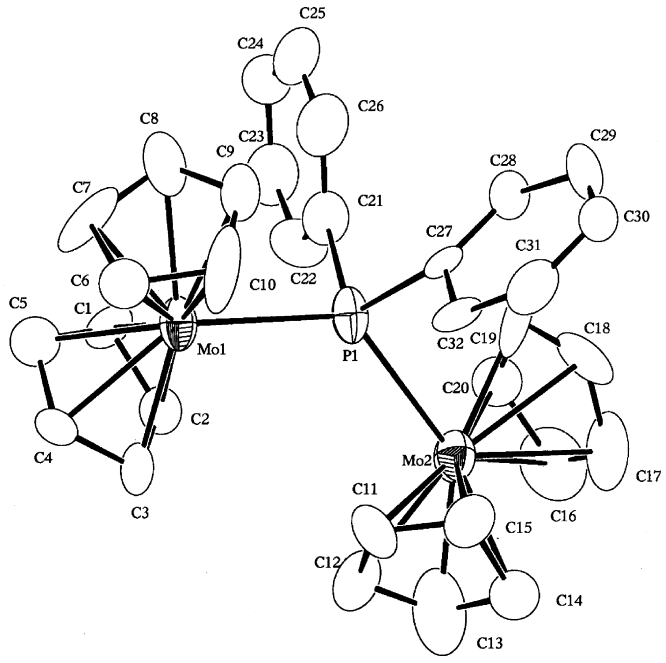
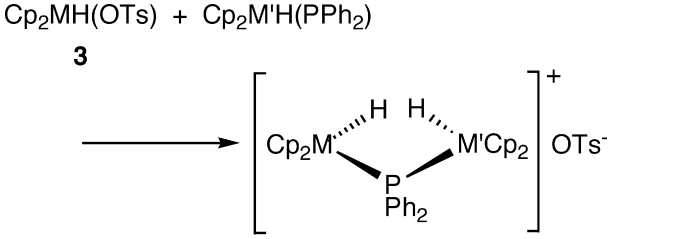


Fig. 1. Molecular structure of **6a**.

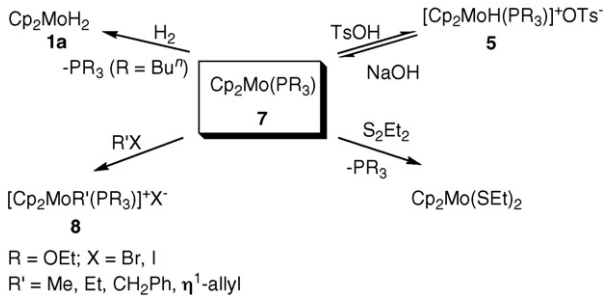
complexes of both molybdenum and tungsten.



6a: M = M' = Mo
6b: M = M' = W
6c: M = Mo; M' = W (6)

We extended the reaction successfully between **3** and phosphines to the synthesis of novel symmetric phosphido-bridged molybdenum and tungsten complexes (Eq. (6)) [23]. That is, the reactions of **3** with phosphide complexes $Cp_2M'H(PPh_2)$ (M′ = Mo, W), which were prepared by treatment of $[Cp_2M'H(PPh_2H)]^+Cl^-$ with aqueous NaOH [24], gave novel phosphido-bridged bimetallic complexes **6**. The ^{1}H NMR spectrum of molybdenum complex **6a** displayed a doublet resonance at δ −9.10 assignable to the hydride ligands. On the other hand, the hydride protons of tungsten complex **6b** appeared as doublet at δ −11.77 with ^{183}W satellites. The appearance of only a single resonance in each spectrum for the M–H groups was indicative of these complexes possessing a symmetrical structure with regard to two metal centers. Therefore, the two metal centers seemed to be electronically and structurally identical. This view was supported by the solid-state structure of **6a** (Fig. 1).

In the ^{1}H NMR spectrum of hetero–bimetallic complex **6c**, the Mo–H resonance appeared as doublet at δ −9.17, and the W–H resonance appeared also as doublet at δ −12.32 with ^{183}W



Scheme 1. Some reactions of **7**.

satellites. These resonances were obviously distinguishable, and the interchange of the hydride ligands did not take place at room temperature.

2.3. Preparation and some reactions of $Cp_2Mo(PR_3)$

$$[Cp_2MoH(PR_3)^+OTs^- \xrightarrow{NaOH} \underset{R=Ph,\ Et,\ Bu^n,\ OEt}{Cp_2Mo(PR_3)} \quad (7)$$

Treatment of **5** (M = Mo) with an equivalent NaOH in EtOH afforded phosphine-adducts of molybdocene **7**, whose structure (R = Bu^n) was determined (Eq. (7)) [13]. In the case of $PR_3 = PEt_3$, the reaction was carried out *in situ*, since isolation of the cationic complex in a pure state was difficult. Although the phosphine derivatives of molybdocene of the type **7** have been prepared for $PR_3 = PPh_3$ and PEt_3 independently by De Azevedo et al. [25] and Geoffroy and Bradley [26], our route finds an advantage over the previous ones in that it works under milder reaction conditions and, hence it is convenient for the preparation of a series of complexes with a variety of tertiary phosphines and phosphite ligands. This facile synthesis of **7** prompted us to explore the reaction chemistry of **7**.

Some reactions of $Cp_2Mo(PR_3)$ (**7**) are displayed in Scheme 1 [13]. Complex **7** reverted to the parent complex **5** on treatment with TsOH. De Azevedo et al. reported that the reaction of **7** (R = Ph) with MeI gave rise to the formation of cationic species $[Cp_2MoMe(PPh_3)]^+$, which could be isolated as a PF_6^- salt [25]. They mentioned that alkyl halides other than MeI did not work similarly and failed to obtain analogous alkyl complexes. However, we found that the phosphite complex $Cp_2Mo\{P(OEt)_3\}$ could be easily transformed to substituted alkyl complexes $[Cp_2MoR'\{P(OEt)_3\}]^+X^-$ (**8**; R′ = Me, Et, $PhCH_2$, $CH_2=CHCH_2$; X = Br, I), when $Cp_2Mo\{P(OEt)_3\}$ was allowed to react with MeI, EtI, $PhCH_2Br$, and $CH_2=CHCH_2I$. The product in the reaction of allyl iodide was found to possess η^1-allyl ligand on the basis of spectral evidence [13]. The reaction with Pr^iI afforded violet $[Cp_2MoI\{P(OEt)_3\}]^+I^-$ instead of an alkyl *i*-propyl derivative, probably via a rather unstable intermediary $[Cp_2MoPr^i\{P(OEt)_3\}]^+I^-$. The similar cationic bromo complex, $[Cp_2MoBr\{P(OEt)_3\}]^+Br^-$, was obtained as a dark colored solid by the reaction with bromine in THF at room temperature.

As reported for **7** ($PR_3 = PPh_3$) [25], the other complexes with $PR_3 = P(OEt)_3$ and PBu_3^n reacted similarly with diethyl disulfide at 50 °C to afford $Cp_2Mo(SEt)_2$ possibly via an oxidative addition involving S–S bond cleavage. Furthermore, $Cp_2Mo(PBu^n{}_3)$ was found to activate dihydrogen under fairly mild conditions; thus, it reacted with 5 atm of H_2 in benzene at 50 °C for 4 h to give the parent dihydride **1a** in 38% yield. The rest of the complexes **7**, other than $Cp_2Mo(PBu_3^n)$, failed to react with H_2. Presumably, feasibility of a dissociation of PBu_3^n due to its bulkiness may play an important role in the reaction.

Table 1
Dependence of the ratio **9a/10a** on the protic acid (HA)

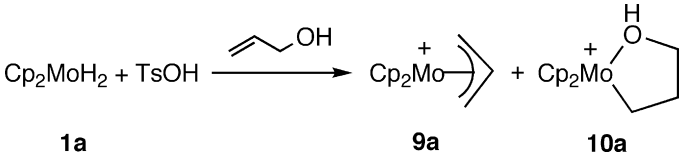
HA	pK_a	Yield (**9a** + **10a**, %)	**9a/10a**
HCl (gas)	−6.1	95	1.00/2.00
HI	−9.5	81	1.00/1.60
TsOH	1.7	97	1.00/0.45
CF_2HCOOH	1.33	77	1.00/0.55
CF_3COOH	0.50	73	1.00/0.34
CCl_3COOH	0.52	13	1.00/0.11

Reactions were performed at 50 °C for 6–8 h under an inert atmosphere of nitrogen or argon, using Schlenk techniques.

3. Syntheses and reactivities of the η^3-allyl complexes and the cyclic γ-hydroxypropyl complexes

3.1. Preparations of the η^3-allyl complexes and the cyclic γ-hydroxypropyl complexes

As noted the preceding section, the molybdenum monohydridetosylato complex **3a** reacts with methanol to give the cationic methanol adduct $[Cp_2MoH(MeOH)]^+OTs^-$ (**4a**). On the other hand, the reaction of **1a** with allyl alcohol in the presence of TsOH was found to be quite unusual. Instead of obtaining the expected allyl alcohol adduct, the reaction led to the formation of the η^3-allyl molybdenum complex **9a** and the cyclic γ-hydroxypropyl complex **10a** as a result of insertion of C=C into the Mo–H bond (Eq. (8)) [12,27].

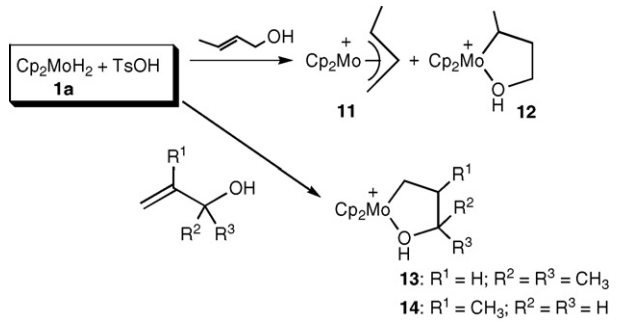


(8)

This reaction appears to proceed via the stepwise formation of the cyclic complex **10a**, followed by the formation of the η^3-allyl complex **9a** (vide infra). The sequence of the reaction not only provides a new approach to the oxametallacycle of a five-membered ring but also a possible intermediate in the transition-metal-mediated hydroxyl-directed stereoselective olefin hydrogenation [28].

Replacement of TsOH with HCl, HI, CF_3COOH, CCl_3COOH, or CF_2HCOOH in the reaction under similar conditions resulted in the formation of complexes analogous to **9a** and **10a** with the corresponding counter anion instead of tosylate (Table 1) [27b].

It should be noted that the ratio of the resulting η^3-allyl **9a** and cyclic γ-hydroxypropyl complex **10a** changed drastically



Scheme 2. Preparations of η^3-allyl complexes and cyclic γ-hydroxypropyl complexes.

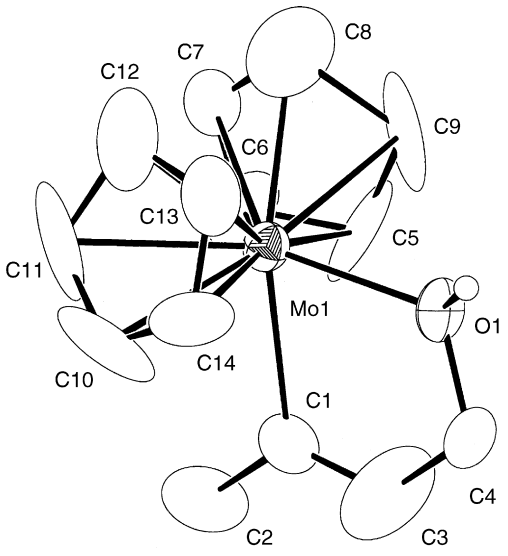
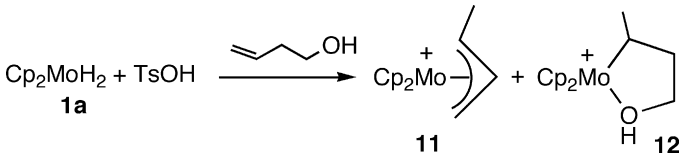


Fig. 2. Molecular structure of **12**.

depending on the nature of acids used in these reactions. Thus, preference of the formation of γ-hydroxypropyl complex to that of η^3-allyl complex increases approximately as the acidity of HX increases.

Treatment of **1a** with crotyl alcohol (2-buten-1-ol) in the presence of TsOH afforded η^3-allyl (**11**) and cyclic γ-hydroxypropyl complex (**12**) similarly (Scheme 2) [27b]. In contrast, the reactions using 2-methyl-3-buten-2-ol and β-methallyl alcohol (2-methyl-2-propen-1-ol) resulted in the exclusive formation of the oxametallacycle complexes (**13** and **14**). No η^3-allyl type complexes have been observed in these reactions.



(9)

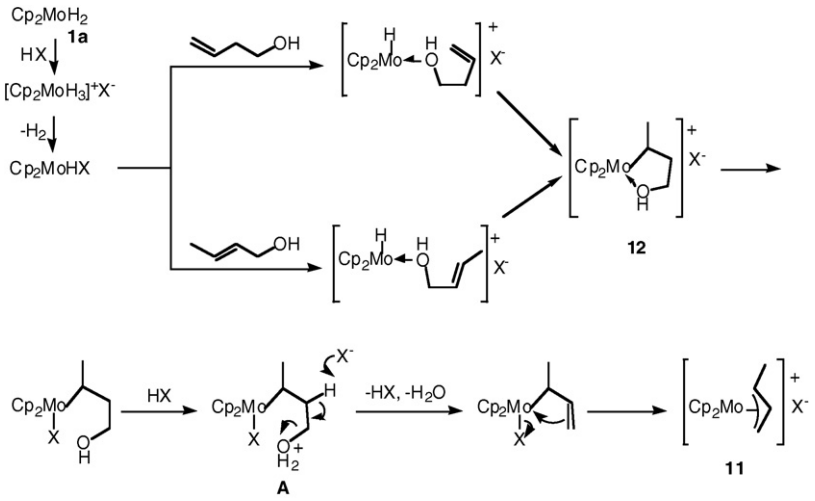
Recently, the extension of these studies to the reaction of **1a** with homoallyl alcohol (3-buten-1-ol) has been reported (Eq. (9)) [29]. Interestingly, the reaction proceeded in a similar manner as in the reaction of crotyl alcohol to give **11** and **12** whose structure was fully determined by an X-ray analysis (Fig. 2).

We found that in analogy with the allyl alcohol system, use of strong acid favored the formation of the (γ-hydroxyalkyl)molybdenum cations **12**. Although Green and co-workers reported the analogous $[Cp_2Mo(\eta^3\text{-allyl})]^+PF_6^-$ could be made by treatment of $[Cp_2MoH_3]^+PF_6^-$ with butadiene [16], to our knowledge, the formation of an η^3-allyl complex and/or a cyclic γ-hydroxypropyl complex by the reaction of a metal complex with homoallyl alcohol is entirely unprecedented. In addition, our procedure appears to be favorable for preparing the η^3-allyl type complexes, because one does not need to rely on the laborious multi-step synthesis.

The reaction mechanism that accounts for the production of **11** and **12** by reacting **1a** with homoallyl alcohol appears to be a very complex one. It is well known that transition metal hydride complexes are able to catalyze olefin rearrangement [30]. Hence, one of the plausible explanations was that homoallyl alcohol underwent rapid isomerization to give crotyl alcohol at first; then, it reacted exclusively with **1a**. However, detailed inspection of the reaction mixture using GLC and ^{1}H NMR revealed that there was no indication for the preceding formation of crotyl alcohol.

Following observations would provide insight into the reaction mechanism. Monitoring of the reaction by ^{1}H NMR spectroscopy showed that **12** was initially formed; then, it was converted to **11**. Thus, **12** was assumed to be the precursor of **11**. This hypothesis was well confirmed by the reaction between **12** and excess of TsOH in MeOH, which resulted in the quantitative formation of **11**. On the basis of this reaction profile, the plausible mechanism that would account for the formation of **11** and **12** from both crotyl alcohol and homoallyl alcohol is proposed in Scheme 3 [29]. In addition, certain general observations pertained to all reactions between **1a** and allyl alcohol includes in this study.

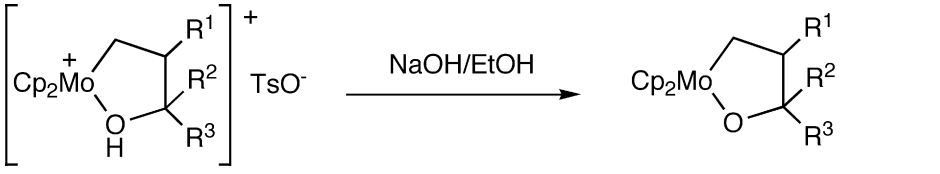
As described the preceding section, the trihydride cation initially formed by protonation of **1a** releases hydrogen to give the reactive monohydride complex. After coordination of homoallyl alcohol or crotyl alcohol to the complex, cyclization via intramolecular insertion into the Mo–H bond occurs affording **12**. In the case of homoallyl alcohol, both a five- and a six-membered ring would be formed, but the five-membered ring was exclusively preferred. This observation may be rationalized in terms of more favorable entropy factors leading to a five-membered ring [31], although the other may also be offered. Namely, five-membered ring closure seems to give the more stable cation **12** in which the molybdenum atom bearing positive charge is bound to the secondary carbon atom. As mentioned above, when **12** was treated with TsOH, it readily transformed into **11**. Furthermore, we confirmed that this reaction did not take place without acid at all. These results suggest that **12** is dehydrated with acid to give the intermediate η^1-allyl molybdenum complex; then, isomerization involving η^1-allyl to η^3-allyl interconversion takes place to yield **11**. In this dehydration step, X^- anion would act as base that removes the β-proton from the intermediate **A**. The relative basicity of the X^- anion appears to affect the rate of the reaction with stronger base reacting faster; therefore, $CF_3SO_3^-$ group would be less likely to react with **A** than $CF_3CO_2^-$ and TsO^-. These considerations are consistent



Scheme 3. Plausible mechanism for the formation of **11** and **12**.

with the experimental observations that preference of the formation of γ-hydroxypropyl complex increases as the acidity of HX increased.

3.2. Reactions of the cyclic γ-hydroxypropyl complexes and related complexes



15: $R^1 = R^2 = R^3 = H$
16: $R^1 = R^2 = H$; $R^3 = CH_3$
17: $R^1 = CH_3$; $R^2 = R^3 = H$ (10)

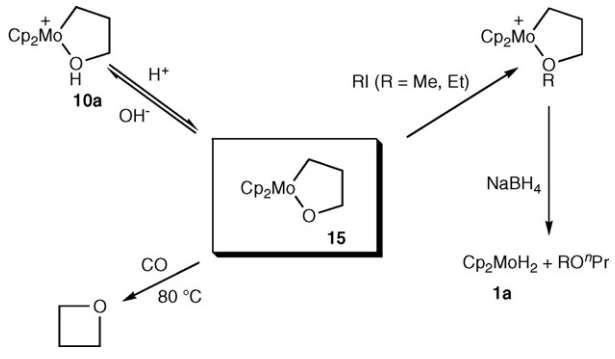
Treatment of the cyclic γ-hydroxypropyl complexes with an equimolar amount of NaOH in ethanol at room temperature gave the neutral molybdenaoxacyclopentane derivatives **15** (yield 77%), **16** (91%), and **17** (70%) (Eq. (10)) [27]. Alternatively, the reaction can be done as a one-pot synthesis starting with **1a**, allyl alcohol, and gaseous HCl, followed by addition of ethanolic NaOH.

Some reactions of complex **15** are displayed in Scheme 4 [27b]. The oxygen atom of the complex was found to be susceptible to attack by electrophiles, such as proton or alkyl halides. Thus, treatment with an equimolar amount of TsOH in Et_2O reverted it to the parent cyclic complex **10a** in almost quantitative yield. On the other hand, when **15** was stirred in alkyl halide, such as CH_3I or C_2H_5I, at room temperature for 25 h, the oxygen-coordinated γ-alkoxypropyl derivatives were formed. Treatment of the resulting cationic complexes with $NaBH_4$ gave rise to the formation of the corresponding *n*-propyl alkyl ether accompanied by the reproduction of the dihydride molybdenum complex **1a**.

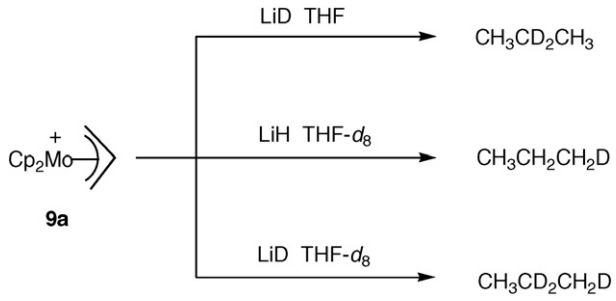
Thermolysis of **15** in toluene at 80 °C afforded a trace amount of oxetane as detected by GLC. Its yield increased by purging the system with CO (3 atm). Expected γ-lactone was not detected in the reaction mixture at all, indicating the reluctance of **15** to undergo CO insertion into its Mo–C bond.

3.3. Reactions of the η^3-allyl molybdenum complex with alkali metal hydride

As noted above, we have shown that $[Cp_2Mo(\eta^3\text{-allyl})]^+$ complexes are conveniently prepared by treatment of **1a** with



Scheme 4. Some reactions of **15**.

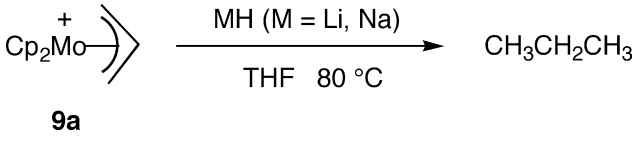


Scheme 5. Reduction of **9a** using deuterium-labeled reagents.

an excess of allyl alcohol in the presence of protic acids. The cationic η^3-allyl type complexes, thus generated, appeared as an interesting target for further reaction with nucleophiles. The Mo-catalyzed nucleophilic alkylation reactions that involve η^3-allyl molybdenum intermediates have already developed into a powerful synthetic procedure complementary to the Pd-catalyzed process in that, in contrast to the situation with Pd, the reaction takes place mostly at the more substituted carbon atom when unsymmetrical substrates are used [32].

Significant catalytic developments involving η^3-allyl molybdenum complexes would surely benefit from a better understanding of the reactivity of the complexes toward nucleophiles. There have been many reports related to this area; some of the most intriguing results have been obtained. Notable in this regard is the work of Green and co-workers [16]. They have found that the reactions of $[Cp_2Mo(\eta^3\text{-allyl})]^+$ complexes with $NaBH_4$ to form a metallacyclobutane, $[MoCp_2(CH_2CH_2CH_2)]$, in which the nucleophilic attack occurs on the central carbon of the η^3-allylic group. Common allyl ligands are known to be prone to nucleophilic attack at the terminal carbon (C-1 or C-3), although theoretical investigation has pointed out that the central carbon is more reactive than the terminal ones toward nucleophiles [33]. Thus, it is of interest to extend the chemistry of the complexes $[Cp_2Mo(\eta^3\text{-allyl})]^+$ by studying their interactions with a wide range of Lewis bases or nucleophiles.

We found that treatment of **9a** with alkali metal hydride MH (M = Li, Na) in refluxing THF resulted only in reduction of the allyl ligand to give propane (Eq. (11)) [34].



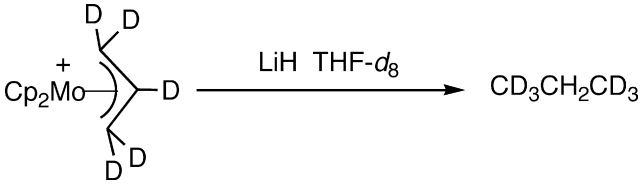
(11)

Both ^{1}H NMR and GC analyses of the volatile product did not show evidence of the presence of propene, suggesting that the reaction did not proceed by common nucleophilic substitution at an allylic carbon. The formation of propane may be somewhat anomalous in that alkali metal hydrides are generally regarded as Lewis base, and they are seldom utilized as a reducing agent. To elucidate the reaction mechanism, studies with deuterium-labeled reagents were performed (Scheme 5).

$CH_3CH_2CH_2D$ was obtained using THF-d_8 as the reaction solvent, while the reaction of **9a** with LiD in THF produced $CH_3CD_2CH_3$. Furthermore, treatment of **9a** in THF-d_8 with LiD gave $CH_3CD_2CH_2D$. Hence, salient features of the reduction may be summarized as follows:

(i) The nucleophilic attack occurs twice at the central carbon of the η^3-allyl ligand.
(ii) Only one deuterium unit from the solvent is incorporated into one of the methyl groups in the resulting propane.

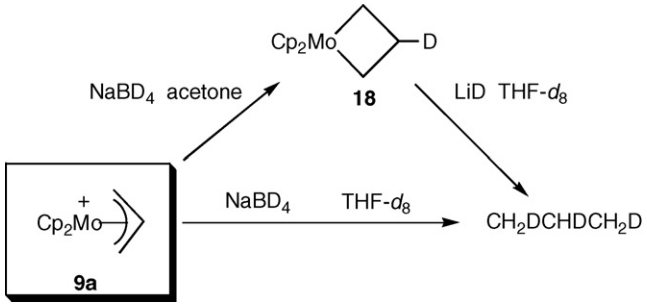
Consequently, questions about the source of the hydrogen of another methyl group and the fate of the hydrogen atom at the central carbon of the allyl ligand were raised. A more plausible scenario involves 1,2-hydrogen migration from the central to the terminal carbon. In order to prove this hypothesis, a study with a fully deuteriated η^3-allyl complex, which was prepared from readily available pentadeuterioallyl alcohol [35], was performed. Reduction of the complex with LiH in refluxing THF-d_8 gave expected $CD_3CH_2CD_3$; thus, the 1,2-deuterium migration took place (Eq. (12)).



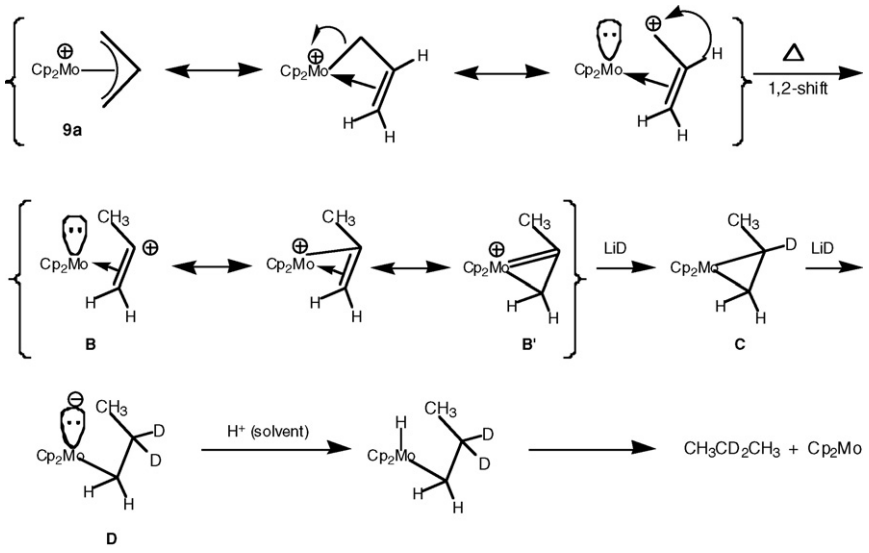
(12)

As noted above, in $[Cp_2Mo(\eta^3\text{-allyl})]^+$ complexes, nucleophilic reactions proceed via metallacyclobutane derivatives. However, in the present case, support for the formation of an intermediate metallacyclobutane species was not obtained. Accordingly, to establish whether or not this pathway was operative here, a study with a deuterium-labeled metallacyclobutane compound $[MoCp_2(CH_2CHDCH_2)]$ (**18**), which was obtained from the reaction of **9a** with $NaBD_4$ [16], was performed (Scheme 6).

Reduction of **18** was achieved by reaction with LiD in THF-d_8. Detailed analysis of GC–MS and the ^{1}H NMR spectrum revealed the formation of $CH_2DCHDCH_2D$. Thus, this reaction did not involve the 1,2-hydrogen migration from the central to the terminal carbon. In addition, unlike the reaction between **9a** and MH, a substantial amount of propene was formed, which



Scheme 6. Formation of propane via the metallocyclobutane.



Scheme 7. Proposed mechanism for the formation of propane from **9a** and LiD.

was consistent with the previous results [16]. Furthermore, the same product, $CH_2DCHDCH_2D$, was also obtained, when **9a** was directly reduced by $NaBD_4$. We thus concluded that the reduction of **9a** with MH did not proceed via the usual metallacyclobutane process.

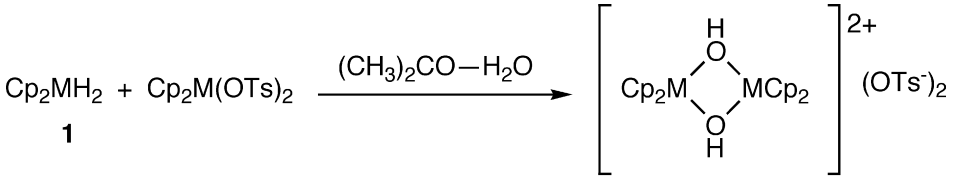
A mechanism accounting for the reaction pathways is proposed in Scheme 7 on the basis of the reaction profile. The thermal reaction would induce the 1,2-shift of the hydrogen atom giving the intermediate olefin complex **B**, which would exist in several canonical forms. The reaction of **B** with LiD results in the formation of the metallacyclopropane complex **C** [36]; it subsequently undergoes a second attack by LiD to give the σ-alkyl anionic complex **D**. Proton abstraction from THF, followed by reductive elimination, would lead to the formation of propane and an unstable molybdocene. Support for this hypothesis was provided by the reaction in the presence of PPh_3, which gave a phosphine adduct, $Cp_2Mo(PPh_3)$ (**7**).

In conclusion, the most significant result of this study is the demonstration that the propane obtained from **9a** and alkali metal hydride occurs by the 1,2-hydrogen migration process followed by double nucleophilic addition of the hydride at the central carbon and a different mechanism than the reduction using $NaBH_4$. This difference in reactivity appears to stem from the difference of hardness of these hydride anions [34].

4. Syntheses and reactions of di-μ-hydroxo dinuclear complexes of molybdenum and tungsten

4.1. Preparations of the di-μ-hydroxo dinuclear complexes of molybdenum and tungsten

As noted the preceding section, during our studies on the preparation of $Cp_2WH(OTs)$ **3b**, we isolated accidentally a di-μ-hydroxo dinuclear complex, $[Cp_2W(\mu\text{-}OH)_2WCp_2]^{2+}(OTs^-)_2$ **19b**, as a by-product though only in low yield. Afterwards, this peculiar complex was most conveniently prepared in high yield via the direct reaction of Cp_2WH_2 with $Cp_2W(OTs)_2$ in aqueous acetone (Eq. (13)) [37]. In addition, the analogous molybdenum complex **19a** was also prepared in a similar fashion to **19b**.



19a: M = Mo
19b: M = W (13)

The molecular structure, as determined by an X-ray crystallographic analysis, consists of binuclear metal units where each metal atom is tetrahedrally coordinated by two η^5-cyclopentadienyl ligands and two μ-hydroxide bridges which link the metals together (Fig. 3).

Much attention has long been focused on the compounds of this type in terms of a precursor for the di-μ-oxo complexes, which are particularly interesting in view of their ability to activate molecular oxygen as well as biological aspects [38]. Although μ-hydroxo dinuclear molybdenum or tungsten complexes containing H_2O [39] or CO [40] as a co-ligand are well known, the analogous complexes with cyclopentadienyl ligand are relatively rare. Evidently, introduction of a cyclopentadienyl

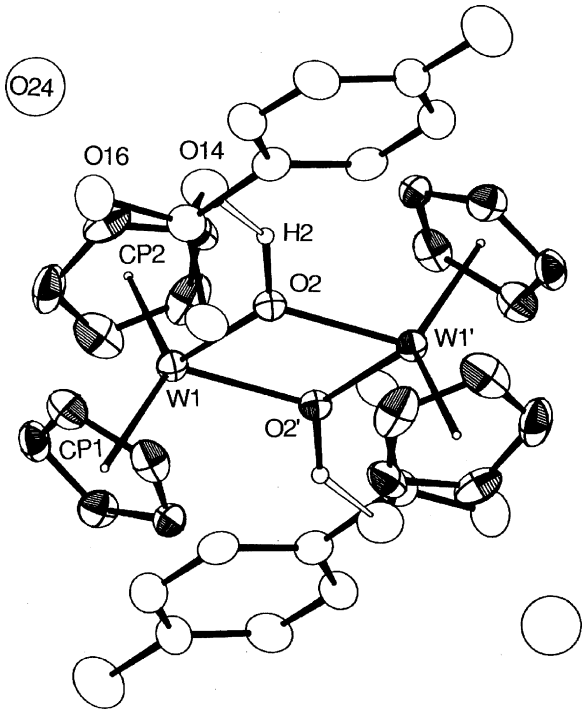


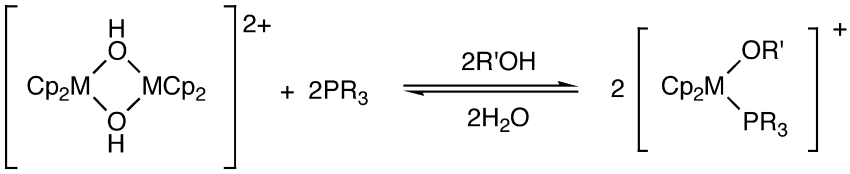
Fig. 3. Molecular structure of **19b**.

ligand into a μ-hydroxo dinuclear metal structure lends new versatility to the reaction chemistry of this class of compounds [41].

It is of interest to consider the route by which the products **19** are formed in the reactions between Cp_2MH_2 and $Cp_2M(OTs)_2$. We confirmed that both Cp_2MH_2 and $Cp_2M(OTs)_2$ were essential for the formation of complexes **19** in good yields. Furthermore, no formation of complex **19a** was observed when the reaction was carried out under rigorously anhydrous conditions, implying that water takes part in the reaction significantly. These results can be rationalized in terms of the mechanism shown in Scheme 8.

The initial stage of this reaction is replacement of one OTs^- group in ditosylato complex $Cp_2M(OTs)_2$ by OH^-. Trapping of *p*-toluenesulfonic acid formed by basic Cp_2MH_2 (**1**) would facilitate the reaction. The resulting hydroxy complex is dimerized into the dinuclear complex **19**, accompanied by the migration of OTs^- group from the inner sphere to the outer. Apparently, the greater tendency of the OH^- group, as compared with halide anions, such as Cl^- or I^-, to act as a bridging ligand would be responsible for the formation of the dimeric species **19** [42]. As shown in the preceding section, the resulting trihydride complex $[Cp_2MH_3]^+OTs^-$ (**2**) is easily converted into the monohydridetosylato complex $Cp_2MH(OTs)$ (**3**), which would react with the additional acid to afford ditosylato complex $Cp_2M(OTs)_2$. Accordingly, Cp_2MH_2 plays an important role not only as a stimulator of the whole process but also as a source for the starting material $Cp_2M(OTs)_2$.

4.2. Reactions of the di-μ-hydroxo dinuclear complexes with tertiary phosphines

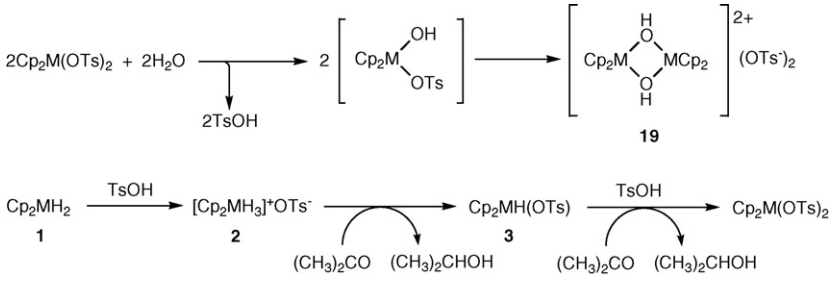


19 **20**

R = Et, Bu^n, Ph

R' = Me, Et, Pr^i, CF_3CH_2, Ph (14)

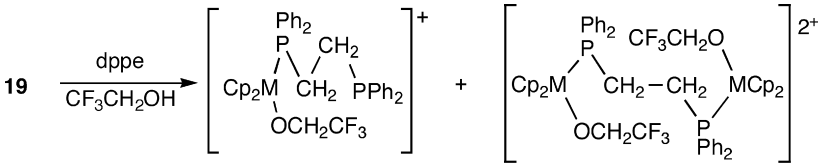
The hydroxo groups in the complexes **19** are sufficiently labile to undergo displacement by a wide variety of substrates. We found that reactions between complexes **19** and monodentate tertiary phosphines always proceeded with concomitant incorporation of coexisting alcohols to yield novel alkoxo phosphine complexes $[Cp_2M(PR_3)(R'O)]^+OTs^-$ (**20**, R = Et, Bu^n, and Ph; R′ = Me, Et, Pr^i, CF_3CH_2, and Ph) (Eq. (14)) [37]. The resulting complexes **20** were readily and quantitatively reverted to the original complexes **19** on dissolving the former in benzene containing a small quantity of water with liberation of



Scheme 8. Plausible mechanism for the formation of **19**.

the phosphine ligands, which suggests the reversibility of the reactions.

The reactions between complexes **19** and tertiary phosphines showed the following remarkable trends. In methanol, ethanol, or 2-propanol, only basic phosphines, such as triethylphosphine or tributylphosphine, reacted with **19**; no substitution of the hydroxo bridging groups by less basic triphenylphosphine was observed in these solvents. However, in moderately acidic alcohol, such as trifluoroethanol, or in the presence of phenol, the reaction of less reactive triphenylphosphine took place smoothly to afford the corresponding phosphine complexes in good yields. Therefore, the outcome of the reactions appears to be dependent on the nucleophilicity of tertiary phosphines and the acidity of coexisting alcohols. In addition, it was of particular interest in the reactions that no compounds resulting from incorporation of two phosphine ligands were formed; the labile alkoxo ligand bound to the central metals of **20** was not displaced by a second phosphine ligand, even in the presence of the excess tertiary phosphine.



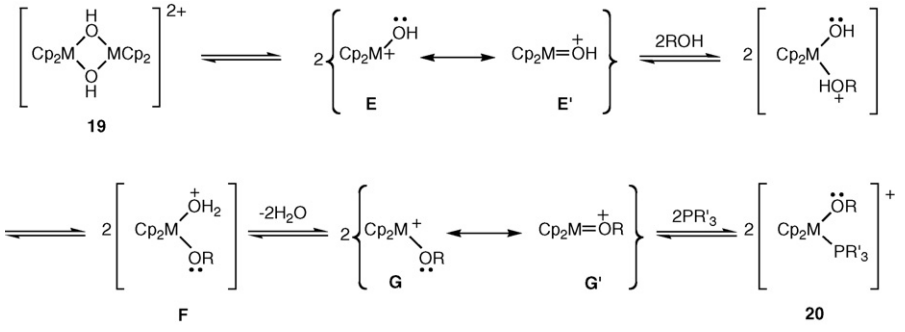
M = Mo (**21a**), W (**21b**) M = Mo (**22a**), W (**22b**) (15)

The reactions of **19** with bidentate ligand dppe (where dppe represents 1,2-bis(diphenylphosphino)etane) are similar to the reactions with monodentate phosphines, in that they also result in the formation of alkoxo phosphine complexes $[Cp_2M(\eta^1\text{-dppe})(CF_3CH_2O)]^+$ (**21**) and $[Cp_2(CF_3CH_2O)M(\mu\text{-dppe})MCp_2(CF_3CH_2O)]^{2+}$ (**22**) (Eq. (15)) [43]. It was ascertained that the amount of dppe added to the reaction mixture could influence the product distribution. Thus, the good yields of **21** can be obtained, if a large excess of dppe is added to **19** in solution. On the other hand, the reactions of **19** with dppe in a molar ratio of 1:1 give **22** as major product. In these reactions, complexes containing chelating dppe ligand have not been observed at all; that is, dppe does not yield chelated complexes.

A mechanism accounting for the reaction pathways is proposed in Scheme 9, on the basis of literature precedents and the reaction profile. The first step, in the sequence leading to formation of **20**, would be dissociation of **19** into the monomeric 16-electron complexes **E**. In this case, it is possible that a resonance limiting form **E′**, which may be formally viewed as a protonated oxo-complex [44]. Taking into account the fact that the reaction between **19** and a tertiary phosphine is very susceptible to a coexisting alcohol as noted above, it seems likely that the next step consists of nucleophilic attack of the alcohol on the metal center. Then, proton transfer to the hydroxy group occurs to give alkoxo complex **F**; this process is quite similar to the reported hydrolysis of **19** [45]. Subsequent elimination of water from **F** produces an unsaturated species **G**. This dehydration step would be a facile process, since π-donation by an alkoxo ligand is well established toward early transition metals [46], and so the canonical form **G′** would make a greater contribution to the hybrid. Inevitably, the final step in the mechanism is nucleophilic attack of a tertiary phosphine on the central metal to afford the product **20**.

4.3. Reactions of the di-μ-hydroxo dinuclear complexes with tropolone

It was subsequently found that complexes **19** reacted with tropolone to afford cationic molybdocene and tungstenocene complexes containing tropolonato ligand ($C_7H_5O_2^-$, trop) [47]. Tropolonato ligand, which is known to form a series of chelate complexes with metal ions, is the seven-membered ring analogue of the benzenoid catecholato ligand [48]. Tropolonato complexes are also broadly similar to analogous β-diketonato complexes, although there are often very significant differences [49]. In comparison with catecholato or β-diketonato complexes, relatively little information is available regarding the chemistry of the tropolonato complexes.



Scheme 9. Plausible mechanism for the formation of **20**.

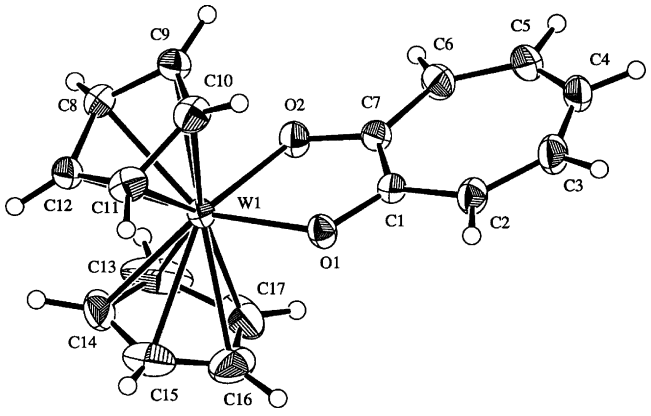
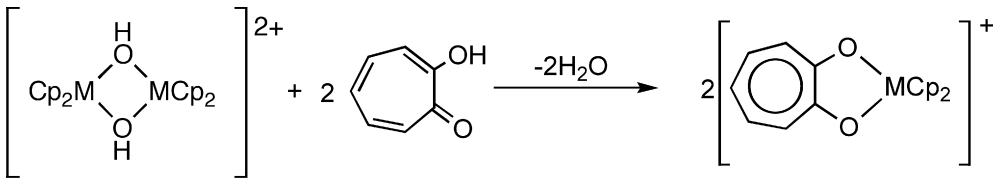


Fig. 4. Molecular structure of **23b**.

The W–O bond lengths are nearly equivalent, and the tropolonato ligand exhibits an essentially planar seven-membered ring. That is, the complex possesses a bidentate chelate mode of coordination. These results indicate that the coordination mode of the tropolonato ligand in **23** is different from that of the dppe ligand in **22**.

4.4. Synthesis of the tropolonato complex containing photosensitive calix[4]arene moiety

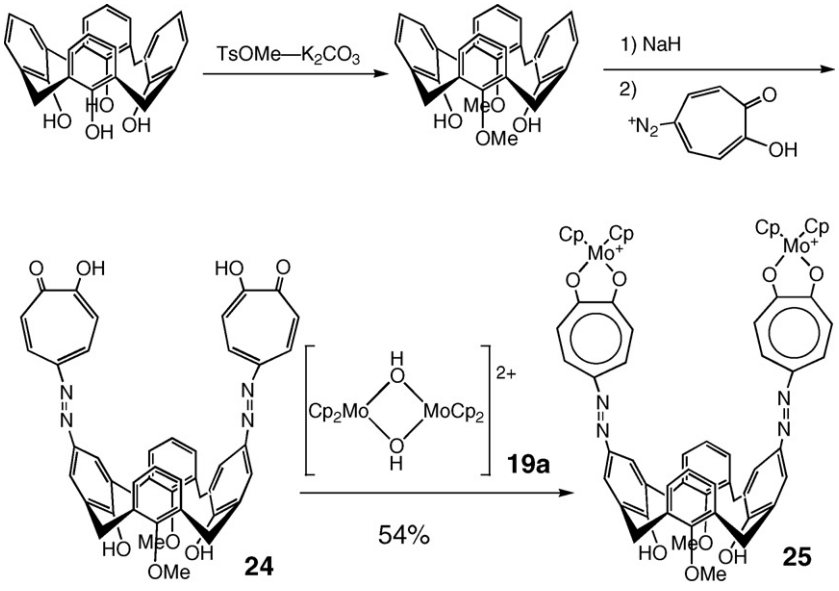
It appeared reasonable to expect that the $Cp_2M(trop)^+$ groups would act as a good electron-acceptor. Hence, it occurred to us that the cationic center of the tropolonato complexes might interact with anions or neutral electron-rich molecules. We envisioned that the complexes **23** would be assembled to create new hybrid materials, when properly functionalized. Accordingly, we decided to incorporate this cationic component into a calix[4]arene framework and designed a new calix[4]arene derivative, in which the molybdocene–tropolonato groups are linked to the upper rim via photoactive azo spacers in order to change the properties of the resulting calixarene in response to light.



19 M = Mo (**23a**), W (**23b**) (16)

Treatment of **19** with tropolone under argon in methanol at 50 °C for 5 h afforded the tropolonato complexes (M = Mo (**23a**), W (**23b**)) in almost quantitative yields (Eq. (16)). The resulting complexes were not soluble in a non-polar solvent, such as benzene or toluene but soluble in methanol and DMSO. They were found to be stable to air both in the solid state and in solution. The molecular structure of **23b**, which was fully confirmed by an X-ray analysis (Fig. 4), shows that the central metal is surrounded by a distorted tetrahedral array of the two centers of cyclopentadienyl rings and the two oxygen atoms of tropolonato ligand.

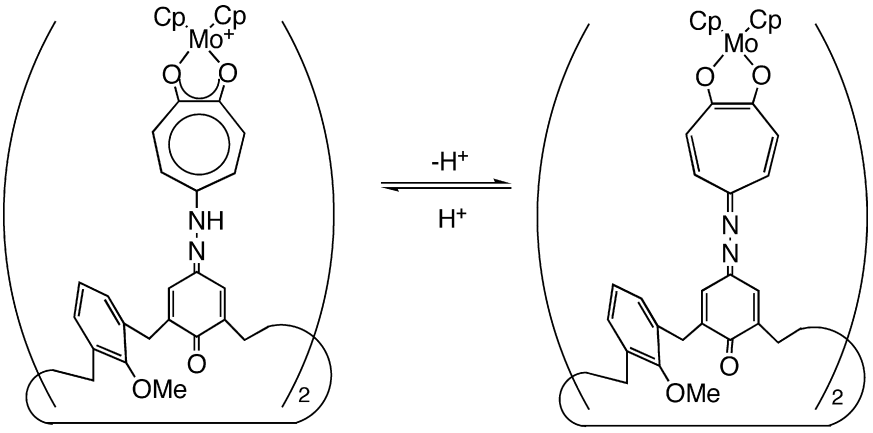
A number of calix[4]arenas, carrying a wide variety of groups on the upper and lower rims, have been prepared in the last decade. When appropriately modified, they provide attractive platform to which to attach ligating moieties for transition metal



Scheme 10. Preparation of the tropolonato complex containing photosensitive calix[4]arene moiety.

centers [50]. The scope of calix[4]arenes chemistry is expected to be extended dramatically by incorporation of metallic centers into the peripheral sites [51,52].

The calixarene-tropolonato ligand **24** was obtained in three steps from 4-*tert*-butyl-calix[4]arene (Scheme 10) [47]. The reaction of **24** with **19a** proceeded in similar fashion as tropolone and resulted in the formation of the desired compound **25**. Detailed UV–vis analyses of **24** and **25** have established that complexation with cationic molybdocene leads to a large change in the absorption spectra. The most dramatic spectroscopic change in pyridine was observed in the band at 420 nm, which decreased considerably and shifted to 470 nm upon coordination. In addition, a new peak at longer wavelength (720 nm) appeared. These results indicate that, in the solution, the hydrazone form **25a** and the diimine form **25b** are in equilibrium (Eq. (17)) [53]. Evidently, cationic molybdocene moiety acts as an electron-acceptor that extends the π-conjugated system in this case. Consequently, it is expected that the tropolonato–molybdocene group can function as a novel type transition metal acceptor.



25a **25b** (17)

Nakamura and Otsuka have hypothesized that their reduction system proceeds by a radical chain mechanism. On the other hand, we believe that our reduction system occurs by transfer of a hydride ion to a carbonyl carbon with prior or concurrent protonation of the carbonyl oxygen atom, as is the case of $NaBH_4$.

Reduction of a carbonyl group using main group element hydride reagents, such as $LiAlH_4$ or $NaBH_4$, has been carried out routinely for many years in modern synthetic chemistry [55]. However, there has been a growing demand among organic chemist for new systems that are capable of reducing a carbonyl group of broad spectrum under especially mild reaction conditions and occasionally with remarkable selectivities [56].

$$\underset{\mathbf{1a}}{Cp_2MoH_2} + 2RCOR' \xrightarrow{2HA} Cp_2MoA_2 + 2RCHOHR' \qquad (18)$$

At first, we carried out the reduction in the presence of large excess of substrates and protic acids at room temperature (Eq. (18)) [15,17b]. As shown in Table 2, trihydride complex $[Cp_2MoH_3]^+$ (**2a**) would be utilized as a mild reducing reagent for the reduction of carbonyl groups; acetaldehyde, acetone, cyclohexanone, and sterically hindered pinacolone were reduced by this system easily at room temperature to afford the corresponding alcohols. Ethyl acetate is not reduced at all; thus, this system will reduce ketones and aldehydes selectively without affecting ester group. The yield, which was based on the complex used, was found to be at least >120% in each case, indicating that two molecules of ketone or aldehyde can be reduced by one molecule of complex **1a**. Clearly, two hydride ligands of **1a** were consumed for the reaction. α, β-Unsaturated ketone (3-buten-2-one) was reduced to yield the saturated ketone and alcohol, suggesting that 1,4-reduction takes place predominantly. The present result is different from that obtained with a main group element hydride reagent, such as $LiAlH_4$, in that it reduces the conjugated system in 1,2-manner. This difference is readily rationalized by invoking HSAB principle. In terms of the HSAB considerations, it is obvious that complex **2a** is substantially softer than $LiAlH_4$ [57]. We confirmed simple unactivated alkenes, such as ethylene, 1-heptene, and cyclohexene could not be reduced by this system, although **2a** reacted with allylic alco-

5. Reduction of ketones, aldehydes, and imines with the systems composed of Cp_2MoH_2 and acids

5.1. Selective reduction of carbonyl groups

This chapter is concerned with selected applications of Cp_2MoH_2 (**1a**) as a reducing reagent for carbonyl compounds and imines [15,17]. As noted in the preceding section, in ketonic solvents, the trihydride complex $[Cp_2MoH_3]^+OTs^-$ (**2a**) is easily converted to the monohydridetosylato complex $Cp_2MoH(OTs)$ (**3a**) with accompanying reduction of the solvents. However, this result indicates a contrast with that of Nakamura and Otsuka, who investigated the reactivity of **1a** toward various olefins, acetylenes, and alkyl halides [2,54]. They found that **1a** was active only for carbon–carbon multiple bonds and carbon–halogen bond. For example, **1a** can reduce α-bromo ketones to the corresponding ketones without affecting carbonyl group. Accordingly, the addition of acid alters the substrate selectivities of this reduction system.

Table 2
Reduction of organic carbonyl compounds with Cp_2MoH_2 (**1a**) and protic acid

RCOR′	HA	Product(s)	Yield (%)[a]
CH_3CHO	AcOH	CH_3CH_2OH	167
$(CH_3)_2CO$	AcOH	$(CH_3)_2CHOH$	189
$(CH_3)_2CO$	TsOH	$(CH_3)_2CHOH$	176
$(CH_3)_2CO$	HCl	$(CH_3)_2CHOH$	207
Cyclohexanone	AcOH	Cyclohexanol	157
$CH_3COC(CH_3)_3$	AcOH	$CH_3CH(OH)C(CH_3)_3$	122
$CH_3COOCH_2CH_3$	AcOH	No reaction	
$CH_2=CHCOCH_3$	AcOH	$CH_3COCH_2CH_3$, $CH_3CH(OH)CH_2CH_3$	56, 40

[a] Based on the complex used.

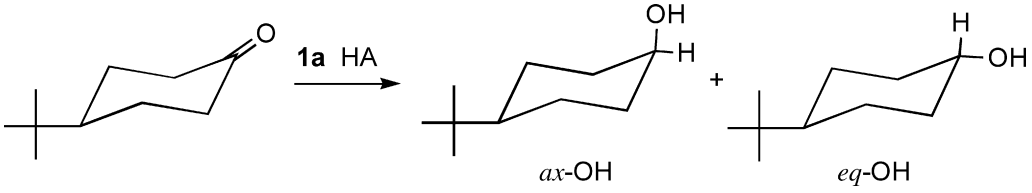
Table 3
Reduction of 4-*t*-butylcyclohexanone with Cp_2MoH_2 (**1a**) and protic acid

	Entry	HA	Cp_2MoH_2/HA	Yield (%)
			ax-OH	*eq*-OH
1	AcOH	1/50	122	29
2	CH_3CH_2COOH	1/55	111	33
3	$(CH_3)_3CCOOH$	1/55	20	18
4	CF_3COOH	1/2	99	37
5	CF_3COOH	1/1	61	43
6	HCl	1/2	138	17
7	HCl	1/1	49	17
8	TsOH	1/3	128	18
9	TsOH	1/1	47	79
10	TsOH	1[a]/1	68	0

[a] $Cp_2MoH(OTs)$ was used instead of Cp_2MoH_2.

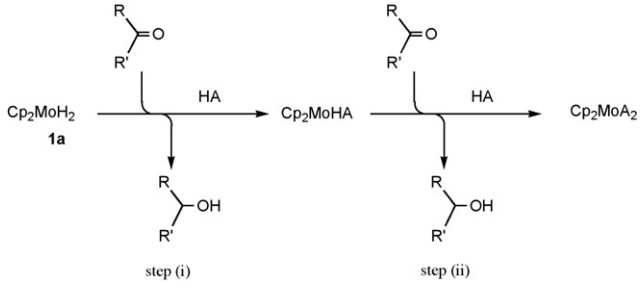
hols to give cationic γ-hydroxypropyl molybdenum derivatives and π-allyl complexes, as mentioned in the preceding section.

The stereochemical behavior of this reduction system was examined by using 4-*t*-butylcyclohexanone (Eq. (19), Table 3) [15]. Its reduction afforded *cis*-4-*t*-butylcyclohexanol (axial alcohol, *ax*-OH) as the major product, when more than two equivalents of acid, e.g. RCOOH (R = CF_3, Me, Et, or Bu^t), HCl, or TsOH, were used. These results are contrasted with that derived from the reaction with $LiAlH_4$ in which the major reduction product is *trans*-4-*t*-butylcyclohexanol (equatorial alcohol, *eq*-OH) [58]. On the other hand, the analogous stereochemical result is obtained with a reduction system composed of iridium salt and phosphorous acid [59].



(19)

As shown in Table 3, the diastereoselectivity was found to decrease with increasing bulk of the alkyl group in carboxylic acids and by reducing the amount of acid used (Entries 3 and 5). In particular, use of one equivalent of TsOH (Entry 9) resulted in inversion of the diastereoselectivity from excess of axial alcohol (Entry 8) to excess of equatorial alcohol. A similar result was obtained, when 4-*t*-butylcyclohexanone was reduced with **1a** and acetic acid in methanol at 50 °C [15].



Scheme 11. Reduction of carbonyl compounds using **1a** and protic acids.

These stereochemical studies suggest that the reduction proceeds via two successive pathways, in which monohydride complex Cp_2MoHA is a key intermediate. Thus, in step (i) in Scheme 11, the starting dihydride **1a** reacts with an acid and a carbonyl compound to give 1 mol each of alcohol and the monohydride complex. In the next step (ii), the monohydride complex reduces another mole of the substrate with the aid of the acid to give a second mole of product together with the disubstituted molybdenum complex Cp_2MoA_2. The existence of these two successive pathways was further substantiated by ^1H NMR studies [17].

The diastereoselectivity of this reducing system may be rationalized by assuming that step (i) gives poor stereoselectivity, whereas step (ii) proceeds with remarkable selectivity. In accordance with this assumption, 100% selectivity (axial alcohol) was achieved, when 4-*t*-butylcyclohexanone was reduced using the independently prepared monohydride complex $Cp_2MoH(OTs)$ (Table 3, Entry 10).

5.2. Reduction of imines

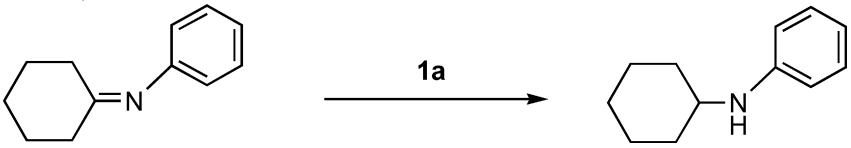
As shown above, significant success has been achieved in the reduction of ketones and aldehydes, through use of **1a** and

Table 4
Reduction of *N*-cyclohexylideneaniline with **1a**

Entry	HA	**1a**/HA	Solvent	Yield (%)[a]
1	AcOH	1/2	Toluene	89
2	–	1/0	Toluene	0
3	AcOH	1/2	THF	81
4	–	1/0	THF	0
5	–	1/0	Methanol	79

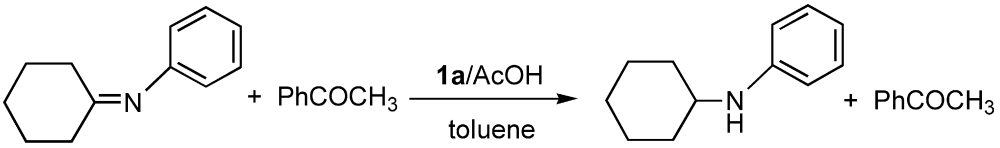
[a] Based on the complex used.

protic acid system. Next, we tried the reduction of imines using this system [17]. At first, we carried out the reduction of *N*-cyclohexylideneaniline to *N*-cyclohexylaniline under various conditions in order to obtain the optimum conditions (Eq. (20), Table 4).



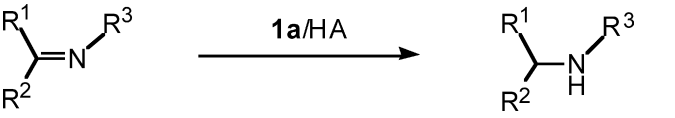
(20)

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 appears surprising that, in contrast to the reduction of ketones and aldehyde, the imine was reduced in methanol without adding protic acid (Entry 5), although in toluene and in THF, no product was obtained in the absence of acid (Entries 2 and 4). Since imines are generally basic, so that methanol may be a strong enough acid to transfer a proton to this weak base.



(21)

As *N*-cyclohexylideneaniline looks more reactive than ketones, we examined the reduction of *N*-cyclohexylaniline in the presence of acetophenone using the present system (Eq. (21)) [17]. We confirmed, then, that the imine was reduced selectively in good yield, and acetophenone was recovered unreacted.



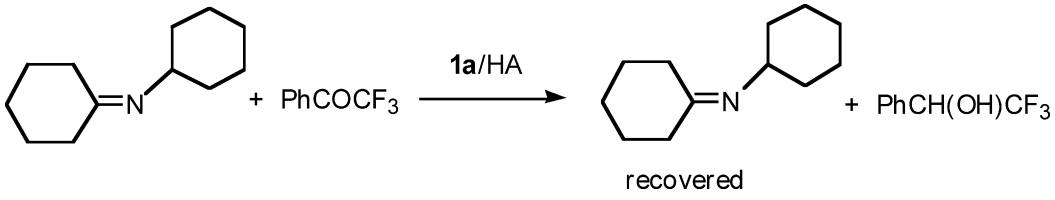
(22)

Table 5
Reduction of imines with **1a**

Entry	Imine			HA	Yield (%)[a]
	R^1	R^2	R^3		
1	CH_2CH_3	CH_2CH_3	Ph	AcOH	78
2	Pr^n	Pr^n	Ph	AcOH	48
3	CH_2CH_3	Ph	Ph	TsOH	53
4	$-(CH_2)_5-$		Cyclohexyl	TsOH	0
5	CH_2CH_3	CH_2CH_3	CH_2Ph	TsOH	125
6	CH_2CH_3	CH_2CH_3	CH_2CH_2Ph	TsOH	107
7	CH_2CH_3	Ph	Cyclopentyl	TsOH	103

[a] Based on the complex used.

Subsequently, a series of imines was subjected to reduction in the same manner as *N*-cyclohexylideneaniline (Eq. (22), Table 5). It is worth pointing out that the reduction of the imines bearing phenyl group in their structure proceeds smoothly, although the aliphatic imine (*N*-cyclohexylidenecyclohexylamine) is not reduced at all (Entry 4). This interesting substrate selectivity allows for the preferential hydrogenation of the following ketone in the presence of the aliphatic imine (Eq. (23)).



(23)

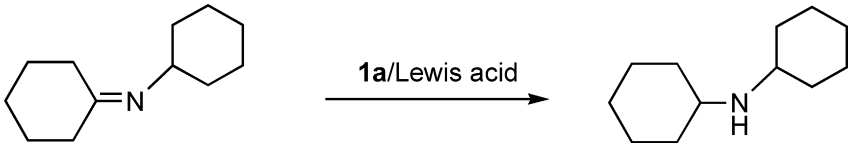
In the case of a reducible imine, the phenyl group may or may not be attached directly to the C=N moiety, suggesting that the phenyl group would not activate the imino group with the aid of an electronic effect. This characteristic selectivity indicates a contrast with the result of Wang and Bäckvall, who reported that ruthenium-catalyzed transfer hydrogenation of imines and found aliphatic imines are more reactive than aromatic ones [60]. Thus, our process is complementary to the Bäckvall's method.

Table 6
Reduction of *N*-cyclohexylidenecyclohexylamine with **1a** and Lewis acid

Entry	Lewis acid	Solvent	Temperature (°C)	Yield (%)[a]
1	$TiCl_4$	Toluene	r.t.	0
2	$TiCl_4$	Methanol	r.t.	24
3	$TiCl_4$	Methanol	40	22
4	BF_3	Methanol	40	19
5	$Ti(OCH_2CH_3)_4$	Methanol	r.t.	14
6	$Ti[OCH(CH_3)_2]_4$	Methanol	r.t.	7
7	$Yb(OTf)_3$	Methanol	50	90

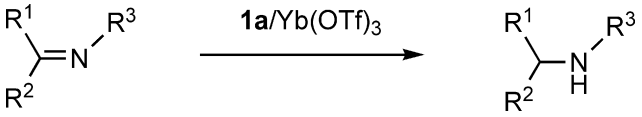
[a] Based on the complex used.

Although the mechanism of the present reduction process is not known with certainty, it seems likely that complex **1a** interacts with the phenyl group of an imine at the beginning, then it attacks the C=N moiety. Intuitively, if complex **1a** and an aliphatic imine are initially held together, the reduction may proceed. It is well known that **1a** reacts with a Lewis acid to form a 1:1 adduct [61]. One might expect that the Lewis acid would bind further to the imine. To test the hypothesis, we examined into the reduction of *N*-cyclohexylidenecyclohexylamine in association with Lewis acids (Eq. (24)) [17b].



(24)

Several Lewis acids were tested, and the results are summarized in Table 6. Expectedly, the Lewis acids were found to be efficient in the reduction. Especially, the reaction using $Yb(OTf)_3$ in methanol gave a high product yield (90%). This compound has been utilized as a promising Lewis acid in organic synthesis, since Kobayashi's pioneering works demonstrating it to be a good catalyst in the Diels–Alder reaction [62]. $Yb(OTf)_3$ is known to have a specific coordination number and to be a stable Lewis acid in protic media such as water [63]. These unique properties may be responsible for the best result in the present reduction system.



(25)

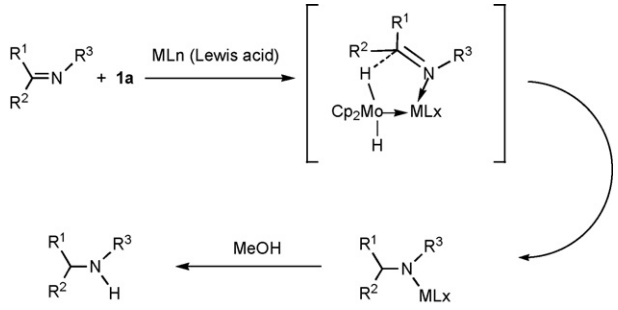
Then we carried out the reduction of several aliphatic imines using Cp_2MoH_2–$Yb(OTf)_3$ system (Eq. (25)), and the results are shown in Table 7. The reduction proceeded smoothly in all cases. The success in the reduction of the aliphatic imines using Lewis acid may be the result of a favorable five-membered cyclic transition state, where complex **1a** is effectively linked by the Lewis acid to the imines, for hydrogen transfer as shown in Scheme 12. A similar 'bidentate effect' would not be expected for protic acids.

We conclude from the results presented above that combination of Cp_2MoH_2 (**1a**) with acids is a valuable tool for reductions

Table 7
Reduction of aliphatic imines with **1a** and $Yb(OTf)_3$

Entry	Imine			Yield (%)[a]
	R^1	R^2	R^3	
1	$-(CH_2)_5-$		n-C_8H_{17}	40
2	CH_2CH_3	CH_2CH_3	Cyclohexyl	35
3	CH_2CH_3	CH_2CH_3	n-CH_8CH_{17}	49

[a] Based on the complex used.



Scheme 12. Reduction of aliphatic imines using **1a** and Lewis acids.

of C=O and C=N groups, because it provides different substrate-, regio-, or diastereoselectivity to conventional reductions using main group element hydride reagents.

6. Summary and conclusion

The coordination chemistry and organometallic chemistry of molybdocene and tungstenocene derivatives have been investigated extensively over the past 40 years. Consequently, an enormous number of both molybdocene and tungstenocene complexes have been prepared, and their reaction chemistry has been applied in a variety of areas. Among these compounds, the molybdenum(IV) and tungsten(IV) dihydride Cp_2MH_2 have been especially intriguing, because they show versatile reactivities towards various substrates. This review highlights the reactions of the dihydride complexes Cp_2MH_2 under acidic conditions.

Protonation with TsOH leads to the isolation of the cationic trihydride complexes $[Cp_2MH_3]^+OTs^-$, which, in turn, convert to the monohydridetosylato complexes $Cp_2MH(OTs)$. These complexes have an extensive reactivity towards common Lewis bases and nucleophiles; thus, they provide new pathways to more sophisticated molybdocene and tungstenocene derivatives. Of critical interest is the formation of olefin insertion products, cyclic (γ-hydroxyalkyl) complexes, upon reaction of allylic or homoallylic alcohols. The oxametallacyclopentane complexes, thus obtained, are easily dehydrated with acid to give η^3-allyl

complexes. Especially noteworthy is the reaction occurring between the resulting $Cp_2Mo(\eta^3\text{-allyl})^+$ complex and alkali metal hydride to produce propane. The formation of propane has been shown to take place via unprecedented double nucleophilic addition of the hydride at the central carbon of the η^3-allyl ligand.

In addition to the monohydridetosylato complexes, the reactions occurring between Cp_2MH_2 and TsOH provide the cationic di-μ-hydroxo dinuclear complexes, $[Cp_2M(\mu\text{-}OH)_2MCp_2]^{2+}(OTs^-)_2$, that are another class of potential precursors to new molybdocene and tungstenocene derivatives. The reactions of tertiary phosphines PR_3, for example always proceed with concomitant incorporation of coexisting alcohols to afford novel alkoxo phosphine complexes $[Cp_2M(PR_3)(R'O)]^+OTs^-$.

A remarkable addendum to the foregoing results is that the system composed of Cp_2MH_2 and acid is able to reduce carbonyl compounds and imines. This reduction process appears to be a useful tool in organic synthesis. The advantages of the process lie in the mild conditions employed and different stereoselectivities compared to other conventional reductions.

We conclude that the unique system composed of Cp_2MH_2 and acid opens an easy access to various kinds of molybdocene and tungstenocene derivatives which prove to have a rich chemistry and represent valuable new precursors for the exploration of the organometallic chemistry of the group 6 elements.

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