Formation of an η^3-allyl and a cyclic γ-hydroxyalkyl complex of molybdenum from reaction of MoH$_2$(η^5-cyclopentadienyl)$_2$ with homoallyl alcohol [☆]

Makoto Minato [a,*], Susumu Hiratsuka [a], Ryoko Sekimizu [a],
Takashi Ito [a,*], Kohtaro Osakada [b]

[a] *Department of Materials Chemistry, Graduate School of Engineering, Yokohama National University,
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan*
[b] *Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

Abstract

The reaction of Cp$_2$MoH$_2$ (Cp = η^5-C$_5$H$_5$) with homoallyl alcohol in the presence of a protonic acid afforded a cationic η^3-crotyl molybdenum complex and a cyclic α-methyl-γ-hydroxypropyl molybdenum complex. This reaction proceeds via the stepwise formation of the cyclic complex, followed by formation of the η^3-crotyl complex.
© 2004 Published by Elsevier B.V.

Keywords: Molybdenum; Hydrido complex; Homoallyl alcohol

1. Introduction

The oxidative addition of allylic substrates such as allyl halides, allyl alcohols, allyl carbonates, and allyl acetates to low-valent metal complexes is a fundamental organometallic transformation [1]. Nucleophilic attack on the η^3-allyl ligand which is coordinated to transition metals is one of the most important reactions in organic synthesis. In contrast to the allylic substrates, their homologs, homoallylic substrates such as homoallylic alcohols have found little use in synthesis because of their lack of reactivity. Homoallylic alcohols are formed regiospecifically by a number of routes [2]. Therefore, given the useful method for activating homoallylic alcohols by metal complexes, they would be employed as the key intermediates for synthetic purposes.

We previously reported that the reactions of allyl alcohols with bis(cyclopentadienyl)-molybdenum dihydride Cp$_2$MoH$_2$ (**1**) in the presence of protonic acid HX, such as HCl, HI, CF$_3$COOH, or TsOH (TsO = p-CH$_3$(C$_6$H$_4$) SO$_3$) afford cationic η^3-allyl molybdenum complexes and cyclic γ-hydroxypropyl molybdenum complexes [3]. In this paper, we report the extension of these studies to the reaction of **1** with homoallyl alcohol (3-buten-1-ol), leading to the formation of a cationic η^3-crotyl molybdenum complex and a cyclic α-methyl-γ-hydroxypropyl molybdenum complex.

2. Results and discussion

The reaction between Cp$_2$MoH$_2$ (**1**) and homoallyl alcohol was undertaken as the extension of our previous work on the reactions of **1** with allyl alcohols. Thus the reaction was run in methanol at 50 °C (Eq. (1)).
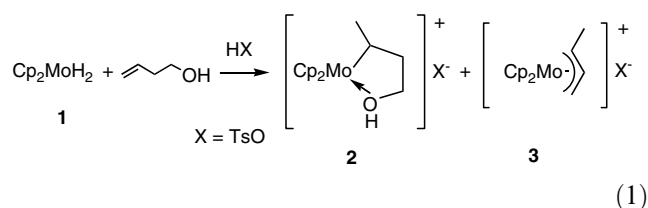
$$\tag{1}$$

^{1}H NMR analysis of the crude precipitates showed there appear to be two species present. On the basis of the similarity of this data to the ^{1}H NMR spectra for the cationic η^3-allyl molybdenum complexes and the cyclic γ-hydroxypropyl molybdenum complexes [3], the products were tentatively assigned to the cyclic α-methyl-γ-hydroxypropyl molybdenum complex (**2**) and the cationic η^3-crotyl molybdenum complex (**3**). In the present reaction, these were observed in a 2.0:1.0 ratio according to their respective Cp signals at 5.30 (**2**) and 5.42 (**3**) ppm. The solubility of **2** in THF is higher than that of **3**, which facilitates the isolation of **2**. Crystallization from THF/diethyl ether afforded **2** as dark-red crystals. Characterization of **2** was achieved by spectroscopy as well as by X-ray crystallographic analysis. Its IR spectrum displays the strong band at 2969 cm^{-1} assignable to the stretching of the O–H group coordinated to the central molybdenum atom. In the ^{1}H NMR spectrum measured in CD$_3$OD, besides the singlet signals due to Cp protons at δ 5.30 and 5.15 ppm, doublet of doublets ($\delta = 3.78$, 1H, $J = 6.5$, 7.8 Hz, OC*H*), multiplet ($\delta = 3.10$, 1H, OC*H*), multiplet ($\delta = 2.60$, 1H, MoC*H*), doublet ($\delta = 1.50$, 3H, $J = 6.5$ Hz, MoCH-(C*H*$_3$)), and multiplet ($\delta = 1.23$, 2H, MoCH(CH$_3$)C*H*$_2$) signals are, respectively, observed. The accurate structural details of **2** were determined by single-crystal X-ray crystallography [4]. The X-ray diffraction analysis reveals that **2** exists as a discrete cation and anion. The view of the molecular geometry of the cation is shown in Fig. 1.

The molecular structure contains the five-membered ring consisting of Mo–C–C–C–O atoms: the ring is roughly planar, having a sum of internal angles 536.08°. The most unusual feature of the structure is the C1–C3 bond distance (1.28 Å). It is abnormally shorter than the

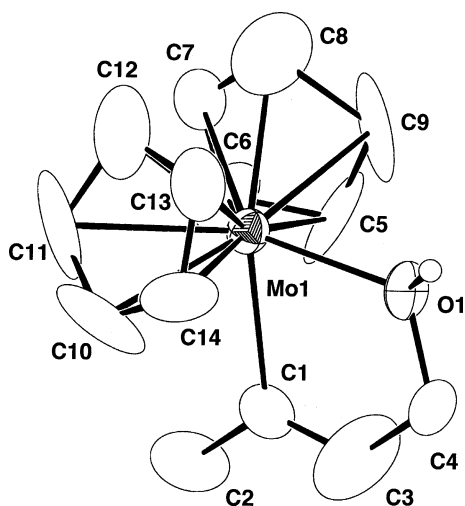Fig. 1. Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Mo1–O1 2.18(1), Mo1–C1 2.27(3), C1–C2 1.49(3), C1–C3 1.28(4), C3–C4 1.39(4), O1–C4 1.45(2); O1–Mo1–C1 74.0(8), Mo1–C1–C3 112(2), C1–C3–C4 124(3), O1–C4–C3 111(2), Mo1–O1–C4 115(1).

value expected for a C–C single bond (1.54 Å) and is rather close to a full double bond (1.34 Å). Approximate sp^2 hybridization at C1 is also reflected in the C2–C1–C3 bond angle of 125°. Furthermore, the C1–C2 distance is 1.49 Å, as expected for a single C(sp^2)–C(sp^3) bond. However, ^{13}C NMR data for **2** poses a rather puzzling situation. The ^{13}C resonances for the C1 and C3 carbon atoms appear at δ 31.9 and 41.8 ppm, respectively; these values seem to be close to a C–C saturated system. Therefore, we interpret this to mean that the canonical form **A** shown in Eq. (2) makes a nontrivial contribution. The C4–O1 bond length (1.45 Å) is appropriate for a C(sp^3)–O single bond.

(2)
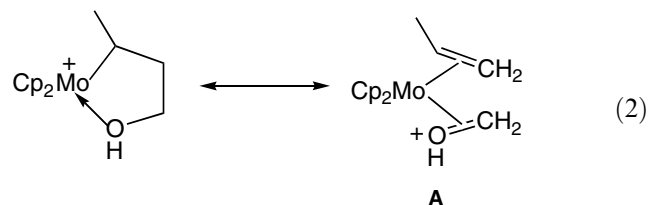
The η^3-crotyl complex (**3**) was characterized by NMR and IR spectrum. The IR spectrum of **3** shows the characteristic medium-intensity absorption at 3081 cm^{-1} assignable to the stretching of the C–H bonds of the Cp ligands. The ^{1}H and ^{13}C NMR signals were identified by comparing the spectrum data with those reported for the related η^3-crotyl molybdenum complex [5]. In the ^{1}H NMR spectrum, **3** exhibits two sharp Cp singlets at δ 5.42 and 5.19 ppm. The CH$_3$ doublet of the crotyl ligand appears at δ 1.87 ppm (3H, $J = 9.1$ Hz). The η^3-allyl protons resonate at δ 4.23 (central, m, 1H), 3.22–3.05 (internal and terminal-*syn*, m, 2H), and 1.72 (terminal-*anti*, m, 1H). The ^{13}C NMR spectrum shows the η^3-crotyl resonances at δ 92.6 (central), 64.8 (terminal), 33.5 (internal), and 21.0 (CH$_3$) ppm.

In the reactions of allyl alcohols with **1**, the ratio of the resultant η^3-allyl and the cyclic γ-hydroxypropyl molybdenum complexes was found to change drastically depending on the nature of acids used. Hence the reactions of **1** with homoallyl alcohol in the presence of other acids were examined. The dependence of the ratio **2/3** on the kind of protonic acid HX in the reaction was examined by monitoring the ^{1}H NMR signal intensities of the Cp resonances of the crude reaction products and the results are summarized in Table 1. As noted, preference of the formation of **2** to **3** increases as the acidity of HX increases; this tendency is compatible with the results for the allyl alcohol system.

Table 1
Dependence of the ratio **2/3** on the protonic acid

HX	Reaction conditions	Yield (**2 + 3**) (%)	**2/3**
CF$_3$COOH	50 °C, 6 h	98	1.3/1.0
TsOH	50 °C, 6 h	91	2.0/1.0
CF$_3$SO$_3$H	50 °C, 6 h	95	24.5/1.0

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. The present results show the course of the reaction of **1** with homoallyl alcohol is quite similar to that with the allyl alcohol system. In fact, we found that the compounds **2** and **3** are also synthesized independently from **1** and crotyl alcohol (2-buten-1-ol). Hence, one of the plausible explanation for the formation of **2** and **3** from homoallyl alcohol is that homoallyl alcohol undergoes rapid isomerization to give crotyl alcohol; then it reacts exclusively with **1**. It is well known that transition metal hydride complexes are able to catalyze olefin rearrangement [6]. However, detailed inspection of the reaction mixture using GLC and ^{1}H NMR revealed that there is no indication for the formation of crotyl alcohol.

Following observations provide insight into the mechanism of this reaction. Monitoring of the reaction by ^{1}H NMR spectroscopy showed that **2** is first formed; then it is converted to **3**. Thus, **2** is assumed to be the intermediate species in the formation of **3**. To prove the feasibility of this path, the reaction of **2** with excess of TsOH in MeOH was examined. We found that compound **2** is completely converted into **3** at room temperature within 10 h. Based on these observations and the previous results concerning the allyl alcohol system, the plausible mechanism for the reaction between **1** and homoallyl alcohol is proposed in Scheme 1.

The trihydrido cation formed initially by protonation of **1** releases hydrogen to give the reactive monohydrido complex **4** [3]. After coordination of homoallyl alcohol to the complex, cyclization via intramolecular insertion into the Mo–H bond occurs affording **2**. These pathways are quite similar to those observed in the allyl alcohol system. In the case of homoallyl alcohol, both a five- and a six-membered ring will be formed, but the five-membered ring is only preferred. This phenomenon would be explained by more favorable entropy factors leading to a five-membered ring [7], although other explanation would also be offered. Five-membered ring closure seems to give the more stable cation **2** in which the molybdenum atom bearing positive charge is bound to the secondary carbon atom. As mentioned above, when **2** was treated with TsOH, it readily transformed into **3**. Moreover, we confirmed that this reaction does not proceed without acid at all. Thus, **2** is dehydrated with acid to give the intermediate η^1-allyl molybdenum complex; then isomerization involving η^1-allyl to η^3-allyl interconversion occurs to yield **3**. In this dehydration step, X^- group of the acid HX would act as a base which removes the β-proton from the intermediate **5**. The relative basicity of the X^- group seems to affect the rate of the reaction with stronger base reacting faster. Therefore, $CF_3SO_3^-$ group will be less likely to react with **5** than $CF_3CO_2^-$ and TsO^-. These considerations are consistent with the experimental observations that preference of the formation of **2** to **3** increases as the acidity of HX increases.

3. Experimental

Unless otherwise noted, all manipulations were conducted using standard Schlenk techniques under purified argon or nitrogen. Commercially available reagent grade chemicals were used as such without any further
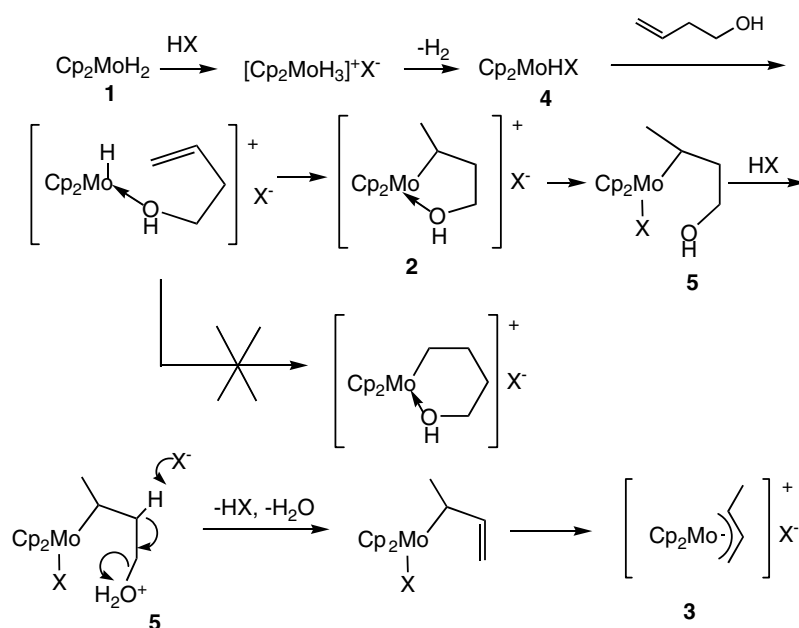
Scheme 1.

purification. All solvents were dried by standard methods and were stored under argon.

An equimolar amount of Cp_2MoH_2 (**1**) (0.186 g, 0.815 mmol) and unhydrated TsOH (0.139 g, 0.807 mmol) were loaded in a Schlenk tube. An excess of homoallyl alcohol (2 ml) was vacuum-transferred into the tube. The reaction mixture was cooled to −78 °C and was degassed. The resultant solution was kept at 50 °C with stirring for 6 h. As the reaction proceeded, the color of the solution changed from yellow to dark-red. After removal of the volatile components under vacuum, the residue was extracted with methanol. The extract was filtered, then concentrated in vacuo. The resulting residue was dissolved in acetone. The red-brown precipitates were formed on cooling the solution in a refrigerator. The present precipitates (0.341 g) contained the cyclic α-methyl- γ-hydroxypropyl molybdenum complex (**2**) and the cationic η^3-crotyl molybdenum complex (**3**) (see Table 1). Recrystallization from THF/diethyl ether affords **2** as dark-red crystals. Isolation of **3** was carried out following a procedure. After removal of the volatile components from the reaction mixture, the residue was washed with several portions of ethanol and hexane to remove **2**. High vacuum drying afforded **3** as dark-red powders (30%).

The reactions of **1** with homoallyl alcohol in the presence of other acids (CF_3COOH and CF_3SO_3H) were carried out under essentially the same conditions. The results are summarized in Table 1.

References

[1] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Book, Mill Valley, CA, 1987, p. 175.
[2] A. Manual, Organometallics in Synthesis, Wiley, New York, 1994, p. 496.
[3] (a) T. Igarashi, T. Ito, Chem. Lett. (1985) 1699;
(b) T. Ito, T. Igarashi, Organometallics 6 (1987) 199;
(c) T. Ito, K. Haji, F. Suzuki, T. Igarashi, Organometallics 12 (1993) 2325;
(d) M. Minato, J. Ren, H. Tomita, T. Tokunaga, F. Suzuki, T. Igarashi, T. Ito, J. Organomet. Chem. 473 (1994) 149.
[4] Crystal data for **2**: dark-red prism; $C_{21}H_{26}O_4SMo$, F.W. 470.43; orthorhombic, space group *Pna*21 (#33); $a = 19.16(2)$ Å, $b = 7.760(5)$ Å, $c = 13.77(2)$ Å, $V = 2046(7)$ Å^3, $Z = 4$; $D_{calc} = 1.526$ g/cm^3; Rigaku AFC5R diffractometer; 298 K; Mo Kα radiation ($\lambda = 0.71069$ Å); $R_1 = 0.073$ for 1549 observed reflections.
[5] M.P.T. Sjögren, H. Frisell, B. Åkermark, P. Norrby, L. Eriksson, A. Vitagliano, Organometallics 16 (1997) 942.
[6] R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, Wiley, New York, 1988, p. 188.
[7] M.B. Smith, J. March, March's Advanced Organic Chemistry, Wiley, New York, 2001, p. 984.