REACTIONS OF ALLYLIC COMPOUNDS WITH PHOTO-ACTIVATED MOLYBDENUM HYDRIDE

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Abstract— $[MoH_4(dppe)_2]$ (1) (dppe = Ph₂PCH₂CH₂PPh₂) reacted photochemically with allylic esters and carbonates, RCO₂CH₂CH=CH₂, to give seven-coordinate hydrido-carboxylato complexes, $[MoH(O_2CR)(dppe)_2]$ (2), together with H₂ and propene. When the esters with bulky R or carbonates were employed, the yield of propene increased significantly, while that of H₂ remained unchanged. The photoreactions of 1 with N-substituted succinic imides were also investigated.

Transition metal-assisted selective activation of the C—O bond in the unsaturated carboxylic esters and carbonates has been studied in depth for the group 8 transition elements,¹ with reference to their utilization to organic syntheses such as catalytic allyl substitution reactions.² In contrast, there have been few such studies with group 6 transition metals,³ in spite of the recent finding by Trost *et al.* of the metal-dependent chemoselectivity of allylic alkylation.⁴

A yellow suspension of the molybdenum tetrahydride, $[MoH_4(dppe)_2]$ (1) $(dppe = Ph_2PCH_2)$ CH_2PPh_2), in an excess of allyl acetate and benzene as solvent, changed to a deep red solution after irradiation with a 100 W high-pressure mercury lamp in vacuo at room temperature. Orange crystals of [MoH(O₂CCH₃)(dppe)₂] (2)[†] were isolated from the solution (yield 45%) and the accompanying formation of H_2 and propene, each in amount corresponding to the yield of 2, was confirmed by GLC. The reactions of 1 with other allylic esters and carbonates proceeded similarly, affording the corresponding carboxylato and carbonato complexes, respectively [eq. (1)]. The formato complex, 2 (R = H), has been prepared via a different route starting from 1 and carbon dioxide.⁵

$$[MoH_{4}(dppe)_{2}] + RCO_{2}CH_{2}CH \longrightarrow CH_{2} \xrightarrow{h\nu}$$
(1)

$$[MoH(O_2CR)(dppe_2] (2) + H_2 + CH_3CH = CH_2 (1)$$

 $(R = H, Me, Et, Pr^n, Bu^t,$

 $CH_2 = C(Me)$, Ph, MeO, EtO).

With the increased bulkiness of R, the yield of propene in the reaction increased significantly, whereas that of H_2 remained unchanged. Thus, when R = Bu', 1.01 mol/mol of 1 of propene was evolved together with 0.67 mol of H_2 .

The C=C double bond of an allyl group was found to affect the allyl-O bond cleavage, since the C-O bond cleavage did not take place when propyl acetate was employed as the substrate. Considering that 1 has been known to photochemically generate the coordinatively unsaturated intermediate $[MoH_2(dppe)_2]$ (A in Scheme 1),⁶ we can assume that ally acetate may coordinate to A through its C=C bond to give **B**. Reactions of 1-methylprop-2enyl acetate and but-2-enyl acetate with 1 under similar conditions, afforded 1-butene and trans-2butene, respectively, as major C₄ products. Absence of the isomerized butenes suggests that the release of olefins occurs directly from the hydrido- σ -allyl intermediate, C, without an intervening π -allyl intermediate. The reductive elimination of alkene from C yields 2 via a monodentate carboxylate, D. The less stable carboxylate, 2, with bulkier R

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[†] All new compounds including this complex which were isolated in this study showed satisfactory results in elementary analyses.



Scheme 1.

groups, may be attacked by H_2 present in the system to regenerate A, making the reaction catalytic with respect to the C—O cleavage. The proposed mechanism was supported by the fact that bubbling of H_2 into the reaction system of 1 and allyl pivalate raised the yield of propene to 2.67 mol/mol of 1, suggesting the possible catalytic hydrogenolysis of allylic esters.

Carboxylato and carbonato complexes, 2, were moderately air-stable in the solid state and were readily soluble in aromatic hydrocarbons to give reddish-brown air-sensitive solutions. The IR of 2 (R = Me) showed the v(Mo—H) band at 1870 cm⁻¹ and $v(CO_2)$ of the bidentate carboxylato ligand at 1540 and 1450 cm⁻¹. The ¹H NMR spectra of 2 (R = Me) in benzene- d_6 at room temperature exhibited a Mo—H signal at δ – 6.23 ppm as triplets of triplets (A₂M₂X pattern), suggesting coupling of the hydride with two pairs of magnetically inequivalent ³¹P nuclei, each consisting of two equivalent ${}^{31}P({}^{2}J(HP) = 64.8 \text{ and } 30.7 \text{ Hz}, \text{ respectively}).$ The ${}^{31}P{}^{1}H$ NMR spectrum of 2 (R = Me) in xylene at room temperature, which showed a pair of triplets at δ 75.4 and 101.0 ppm (with reference to external PPh₃; ${}^{2}J(PP) = 17.7$ Hz), was consistent with the 'H NMR results. The spectral characteristics of the other carboxylato and carbonato complexes were very similar to those found for the acetato complex and suggest the pentagonal bipyramidal coordination geometry of the seven-coordinate complex, 2, at room temperature, which is fluxional in the solution as revealed by the temperature ¹H and ³¹P{¹H} NMR spectra.

The preliminary X-ray molecular structural analysis of the single crystal of the carbonato complex, 2 (R = OEt), shows that it possess essentially the same geometry as in solution, although it is considerably distorted from the pentagonal bipyramidal framework.

Reaction of 1 with N-allyloxysuccinic imide in benzene under irradiation resulted in the allyl–O bond cleavage to give a hydrido–oxyimido complex, 3, together with propene and H_2 [eq. (2)]. Treatment of 3 with CO released N-hydoroxysuccinic imide with the accompanying formation of known $Mo(CO)_2(dppe)_2$:

$$[MoH_{4}(dppe)_{2}]$$
(1)
+C(O)CH_{2}CH_{2}C(O)NOCH_{2}CH=:CH_{2} \xrightarrow{hv} (M_{0}OH_{2}OH_{2}CH_{2}CH_{2}CH_{2}CH_{2})]
(3)
+H_{2}+CH_{3}CH=:CH_{2}. (2)

Acknowledgements—This work was supported by a Grant-in-Aid for Scientific Research (No. 63550640) and for Special Project Research (Nos 62215013 and 63106004) from the Ministry of Education, Science and Culture, Japan. T.I. thanks the General Sekiyu Research & Development Encouragement & Assistance Foundation for financial support. The authors thank Dr K. Osakada of Tokyo Institute of Technology, for the single crystal X-ray structural analysis.

REFERENCES

- See for example, (a) Y. Hayashi, T. Yamamoto, A. Yamamoto, S. Komiya and Y. Kushi, J. Am. Chem. Soc. 1986, 108, 385; (b) T. Yamamoto, M. Akimoto, O. Saito and A. Yamamoto, Organometallics 1986, 5, 1559 and refs cited therein.
- 2. J. Tsuji, Organic Synthesis by Means of Transition Metal Complexes. Springer, Berlin (1975).
- 3. See for example, B. M. Trost, Chem. Ber. 1984, 315.
- T. Tatsumi, H. Tominaga, M. Hidai and Y. Uchida, J. Organomet. Chem. 1981, 215, 67; T. Tatsumi, H. Tominaga, M. Hidai and Y. Uchida, J. Organomet. Chem. 1981, 218, 177.
- 5. T. Ito and T. Matsubara, J. Chem. Soc., Dalton Trans. 1988, 2241.
- J. L. Graff, T. J. Sobieralski, M. S. Wrighton and G. L. Geoffroy, J. Am. Chem. Soc. 1982, 104, 7526; M. S. Wrighton, J. L. Graff, R. J. Kazlauskas, J. C. Mitchner and C. L. Reichel, Pure Appl. Chem. 1984, 54, 161.