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Preparation, Characterization, and Some Reactions of Cationic Hydrido-Carboxylato Complexes of Molybdenum(IV), $[MoH_2(O_2CR)(dppe)_2]^+$

Takashi Ito,* Akihiko Takahashi, and Shigeyoshi Tamura
Department of Materials Chemistry, Faculty of Engineering, Yokohama National University,
Tokiwadai, Hodogaya-ku, Yokohama 240

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Cationic carboxylatodihydridomolybdenum(IV) complexes, $[MoH_2(O_2CR)(dppe)_2]BPh_4$ ($R=CH_3$, C_2H_5, $CH_2=CH$, and $CH_2=C(CH_3)$; $dppe=Ph_2PCH_2CH_2PPh_2$), were prepared by treating $[MoH_4(dppe)_2]$ with RCOOH followed by anion exchange with $NaBPh_4$, and characterized spectroscopically. A possible pathway of the reaction is discussed on the basis of the experiment using CH_3COOD. Light irradiation of the EtOH solution of the cationic acetato complex in the presence and absence of CO afforded the known *cis*-$[Mo(CO)_2(dppe)_2]$ and the neutral hydridoacetato complex, $[MoH(O_2CCH_3)(dppe)_2]$, respectively.

Although molybdenum complexes with the carboxylato ligands bridging singly or multiply bonded two metal centers have been extensively studied,[1] only a few well defined mononuclear carboxylato complexes of molybdenum have been reported.[2–7] Furthermore a very limited number of the carboxylato complexes of molybdenum containing tertiary phosphine ligands have been reported, i.e., $[MoH_2(O_2CCF_3)_2(PMePh_2)_3]$,[3] $[MoH(O_2CR)(PMe_3)_4]$ ($R=H$, CH_3, and CF_3),[6] $[Mo(O_2CCF_3)_2(dppe)_2]$,[2] and the cationic $[Mo(O_2CCF_3)(dppe)_2]BPh_4$.[2] As an extension of our continuing studies on the preparation of group 6a metal complexes possessing functionally substituted ligands,[7,8] reactions of carboxylic acids, including unsaturated carboxylic acids, with tetrahydridomolybdenum(IV) complex, $[MoH_4(dppe)_2]$ (**1**), are investigated in this study. The analogous Mo(IV) complex with unidentate phosphine ligands, $[MoH_4(PMePh_2)_4]$, has been known to be protonated with some protonic acids such as CF_3COOH and *p*-$CH_3C_6H_4SO_3H$ to give products in which some of the phosphine ligands were dissociated.[3] Recently Caulton et al. have shown that the acidolysis of $[MoH_4(PMe_2Ph)_4]$ with HBF_4 in MeCN yielded dicationic $[MoH_2(PMe_2Ph)_4(MeCN)_2]^{2+}$,[9] whereas the similar reaction in THF (tetrahydrofuran) yielded fluorine-bridged dinuclear cation $[\{(PMePh_2)_3H_2Mo\}_2(\mu\text{-}F)_3]^+$.[10] Here we found that **1** was easily protonated with carboxylic acid RCOOH to give carboxylatodihydridomolybdenum cation of the type $[MoH_2(O_2CR)(dppe)_2]^+$ and H_2.

Results and Discussion

Preparation of the Complexes. On stirring the mixture of yellow crystals of $[MoH_4(dppe)_2]$ (**1**) and acetic acid in vacuo at room temperature for several hours, a purple homogeneous solution resulted with accompanying release of two molar equivalents of H_2. Evaporating the solvent off from the solution left deep purple oil, which was solidified into red powder (**2a**) by triturating it in hexane. The product **2a** turned purple powder on treatment it with $NaBPh_4$ in ethanol and vermilion needles (**3a**) were obtained by recrystallization of the purple powder from acetone. The products **2a** and **3a** were characterized as $[MoH_2(O_2CCH_3)(dppe)_2]CH_3CO_2$ and its anion-exchanged compound, $[MoH_2(O_2CCH_3)(dppe)_2]BPh_4\cdot 0.5(CH_3)_2CO$, respectively, on the basis of analytical (for **3a**) and spectral evidence (vide infra). The analogous carboxylatodihydridomolybdenum cations, $[MoH_2(O_2CR)(dppe)_2]A$ [$A=RCO_2$ (**2**) and BPh_4 (**3**)], were obtained similarly for propionic, acrylic, and methacrylic acids (Table 1).

$$\underset{(\mathbf{1})}{[MoH_4(dppe)_2]} + 2RCOOH \longrightarrow \underset{(\mathbf{2})}{[MoH_2(O_2CR)(dppe)_2]RCO_2} + 2H_2 \qquad (1)$$

Table 1. Reactions of $[MoH_4(dppe)_2]$ (**1**) with Carboxylic Acids, RCOOH.[a)]

$$[MoH_4(dppe)_2]\ (\mathbf{1}) + 2RCOOH \longrightarrow [MoH_2(O_2CR)(dppe)_2]RCOO\ (\mathbf{2}) + 2H_2$$

$$[MoH_2(O_2CR)(dppe)_2]RCOO\ (\mathbf{2}) + NaBPh_4 \longrightarrow [MoH_2(O_2CR)(dppe)_2]BPh_4\ (\mathbf{3}) + RCOONa$$

	RCOOH		**1**	Time	$NaBPh_4$	Products (mol/mol of **1**)		
	R	ml	mmol	h	mmol	H_2	**2**[b)]	**3**
(**a**)	CH_3	20	1.62	3	3.63	1.89	0.85[c)]	0.72
(**b**)	CH_3CH_2	20	0.65	20	0.85	1.69	0.82	0.38
(**c**)	CH_2=CH	10	0.86	4	1.41	1.95	d)	0.76
(**d**)	$CH_2=C(CH_3)$	10	1.05	120	1.53	1.83	d)	0.73

a) At room temperature. b) Crude yield. c) Yield estimated in a separate run. d) Not measured.

$$\mathbf{2} + \mathrm{NaBPh_4} \xrightarrow{\mathrm{EtOH}} [\mathrm{MoH_2(O_2CR)(dppe)_2}]\mathrm{BPh_4}\ (\mathbf{3}) + \mathrm{RCOONa} \qquad (2)$$

$$\mathrm{R} = \mathrm{CH_3}(\mathbf{a}),\ \mathrm{CH_2CH_3}(\mathbf{b}),\ \mathrm{CH_2{=}CH}(\mathbf{c}),\ \mathrm{CH_2{=}C(CH_3)}(\mathbf{d})$$

Since purification of the carboxylate derivatives **2** is usually more difficult as compared with that of **3** due to their poor tendencies to be crystallized, their characterizations were achieved mainly spectroscopically, although the latter have been fully analyzed as shown in Table 2. Considerable low values of the observed molecular weight in acetone as compared with the calculated values and the conductivity measurements of their acetone solution (Λ, these values are compared with the observed value of 92.5 S cm^2 mol^{-1} for $NaBPh_4$ under similar conditions) as shown in Table 2 strongly support their proposed ionic formulation.

In order to obtain some mechanistic information of the reaction (1), the similar reaction of **1** with acetic acid-*d* was examined and the formation of dideuteride analogue of **2a** with the accompanying evolution of H_2 and D_2 (molar ratio of 1.0/4.2, total amount 2.1 mol/mol of **1**) was observed. The mechanistic aspect will be discussed in the later section.

$$\underset{(\mathbf{1})}{[\mathrm{MoH_4(dppe)_2}]} + 2\mathrm{CH_3COOD} \longrightarrow \underset{(\mathbf{2a}\text{-}d_2)}{[\mathrm{MoD_2(O_2CCH_3)(dppe)_2}]\mathrm{CH_3CO_2}} + 0.4\mathrm{H_2} + 1.7\mathrm{D_2} \qquad (3)$$

Identification of the dideuteride **2a**-d_2 was achieved by confirming the disappearance of the Mo–H signals in the ^{1}H NMR spectrum of the isolated tetraphenylborate derivative, $[MoD_2(O_2CCH_3)(dppe)_2]BPh_4$ (**3a**-d_2), in $CDCl_3$. Furthermore, the absence of an H–D exchange process between the cationic acetatodihydrido complex **2a** and acetic acid-*d* was suggested by confirming that there was no difference in the ^{1}H NMR spectra taken in $CDCl_3$ before and after treatment of **2a** with excess CH_3COOD at room temperature for 3 days.

IR Spectra of the Complexes. Carboxylatodihydridomolybdenum cations **2** showed weak Mo–H stretching absorption bands at around 1880 cm^{-1}. In addition, moderately strong absorptions at around 1460 cm^{-1} and fairly weak ones at around 1380 cm^{-1} were observed, which were assigned to asymmetric and symmetric CO_2 stretchings, respectively, of the coordinated carboxylato ligand.[11] The relatively low

Table 2. Analytical Data for Complexes $[MoH_2(O_2CR)(dppe)_2]BPh_4\cdot n(CH_3)_2CO$ (**3**)

R		*n*	Analysis[a)] C/%	Analysis[a)] H/%	mol wt[a,b)]	Conductivity, Λ[c)] S cm^2 mol^{-1}
(**3a**)	CH_3-	0.5	73.1 (73.6)	6.0 (5.8)	900 (1273)	102
(**3b**)	CH_3CH_2-	1.0	72.8 (73.2)	6.1 (6.1)	d)	d)
(**3c**)	$CH_2{=}CH$-	0.5	73.1 (73.6)	6.0 (5.8)	816 (1314)	78
(**3d**)	$CH_2{=}C(CH_3)$-	0.5	73.4 (73.7)	6.0 (5.9)	867 (1328)	79

a) Calculated values are given in parentheses. b) Measured by vapor pressure osmometry in acetone at 25 °C. c) Measured in acetone at 18 °C. d) Not measured.

Table 3. Selected IR and ^{1}H NMR Data for Complexes $[MoH_2(O_2CR)(dppe)_2]BPh_4$ (**3**)

Complex		IR[a)]			^{1}H NMR[b)]	
	R	ν(Mo–H)	$\nu(OCO)_a$	$\nu(OCO)_s$	δ(Mo–H)[c)]	δ(RCOO)[d)]
(**3a**)	Me	1880 w, br	1470 m	1410 w	−4.08 (pq, 40.5, **2**)	0.03 (t, [1.4], **3**, CH_3)
(**3b**)	$MeCH_2$	1880 w, br	1475 s	1375 w	−4.04 (pq, 43.0, **2**)	0.01 (t, 6.15, **3**, CH_3), 0.20 (m, **2**, CH_2)
(**3c**)	$CH_2{=}CH$	1880 w, br	1455 m	1370 w	−3.94 (pq, 40.5, **2**)	ca. 4.8 (m, **3**, $CH_2{=}CH$)
(**3d**)	$CH_2{=}CMe$	1885 w, br	1455 m	1370 w	−3.84 (pq, 40.5, **2**)	0.78 (s, **3**, CH_3), 4.59 (s, **1**, $=CH_2$), 4.85 (s, **1**, $=CH_2$)

a) Measured as KBr disk; values in cm^{-1}. b) 90 MHz in $CDCl_3$. Given as chemical shift δ in ppm, downfield positive from tetramethylsilane as an internal reference. Signals due to dppe ligand, BPh_4 anion and solvated acetone are omitted for brevity. Multiplicity abbreviations are: pq = pseudo quintet, t = triplet, m = multiplet. c) In parentheses are multiplicity, ^2J(P–H) in Hz, and **relative intensity**. d) In parentheses are multiplicity, *J*(H–H), [*J*(P–H)] in Hz, **relative intensity**, and assignment where necessary.

values of the separation between these two ν(OCO) bands (60—100 cm^{-1}) suggest that the carboxylato ligands in these complexes coordinate to the metal bidentately.[11,12]

NMR Spectra of the Complexes. As shown in Table 3 and Fig. 1, ^{1}H NMR spectra of carboxylato complexes **3** showed a characteristic pseudo quintet signal [apparent J(PH)=ca. 40 Hz] assignable to hydride protons at around δ −4, which is not so much different from the parent neutral tetrahydride **1** [δ(Mo–H)=−3.64 in chlorobenzene].[13] The pseudo quintet pattern of the signal may be analyzed as $A_2M_2X_2$ spin system where A_2 are hydride protons, and M_2 and X_2 are pairs of two equivalent phosphorus atoms. The deviation of the signal pattern from the typical 1:4:6:4:1 quintet suggests that the values of J(AX) and J(AM) differ slightly each other. Methyl protons of the acetato ligand in **3a** resonated at δ 0.03 as a triplet which was higher than the corresponding free acetic acid by δ 2.1.[14] The similar trends were observed for the protons attached to α-carbon of the propionato ligand of the complex **3b** in accordance with the reported results for hydridocarboxylato complexes of ruthenium.[15] Measurement of the phosphorus-decoupled ^{1}H NMR for complexes **3a** and **3b** revealed that both the pseudo quintet signals of Mo–H and the triplet signals of the protons attached to the α-carbon changed to singlets (Fig. 1), indicating that these splittings originated from the coordinated phosphines.

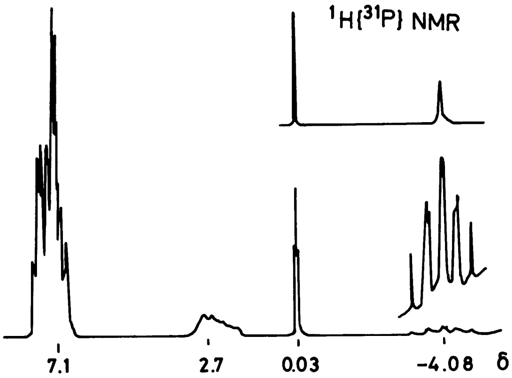


Fig. 1. ^{1}H NMR spectra of $[MoH_2(O_2CCH_3)(dppe)_2]BPh_4$ (**3a**), (100 MHz in $CDCl_3$ at room temperature).

In the ^{13}C NMR spectra of complexes **3**, carbonyl carbon of the carboxylato ligand resonated at δ 181—191 (Table 4). The signals due to carboxylato ligands were observed at the reasonable positions as judged from their corresponding ^{1}H NMR signals.

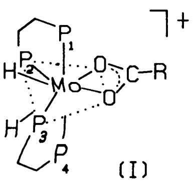
^{31}P{^{1}H} NMR spectra of the complexes **3a**—**d** (Table 4) consisted of double triplets appearing at about δ 81 and 61, respectively, downfield from the external PPh_3 reference, which suggests that there are two pairs of magnetically unequivalent phosphorus nuclei, each consisting of two equivalent phosphori. The ^{31}P NMR spectra did not show any change at the temperature range from 20 to 70 °C.

Structure of the Complexes. On the basis of the spectral evidences described above, the bicapped octahedral structure, either I or II, seems to be most conceivable for the present octacoordinate cationic complexes **3**, although a square antiprism and a dodecahedron arrangements have been known to occur most commonly in the octacoordinate complexes.[16] The $A_2M_2X_2$ pattern of the hydride signal of the ^{1}H NMR spectra is elucidated by assigning A to the hydrides, M to the equatorial phosphori P_2 and P_3, and X to the axial P_1 and P_4, respectively. Of the two triplets of ^{31}P NMR signals, the signals at 61 ppm may be assigned to the mutual trans axial phosphorus atoms P_1 and P_4, and those at 81 ppm to equatorial P_2 and P_3.[15b] Of the two possible structures, structure I in which two hydride caps are directed toward the side occupied with phosphine ligands seems to be more preferable to II in view of the steric congestion around the hydrogen atoms. The pentagonal bipyramidal structure has been determined recently for the related

Table 4. ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR Data for $[MoH_2(O_2CR)(dppe)_2]BPh_4$ (**3**)

Complex		^{13}C NMR[a]			^{31}P NMR[b]		
	R	MoO_2C	α-C	β-C	P_E	P_A	J(P-P)/Hz[c]
(**3a**)	Me	188.73	23.35		80.88	61.61	5.86
(**3b**)	$MeCH_2$	191.54	29.88	6.74	81.12	61.24	6.35, 6.31
(**3c**)	CH_2=CH	181.02	d)	d)	81.24	61.81	5.86
(**3d**)	CH_2=CMe	182.24	d) 15.08 (α-*Me*)	d)	81.08	61.45	5.86

a) 22.5 MHz in $CDCl_3$. Given as chemical shift δ in ppm, downfield positive from tetramethylsilane as an internal reference. Signals due to dppe ligand, BPh_4 anion and solvated acetone which appeared at the ordinary region are omitted for brevity. All signals listed appeared as a singlet unless stated otherwise. b) 36.2 MHz in $CDCl_3$. Given as chemical shift δ in ppm, downfield positive from triphenylphosphine in CH_2Cl_2/C_6D_6 as an external reference. All signals are observed as triplet. c) For those there are two figures each of which corresponds to P_E and P_A respectively, and these differences may be originated from the second order couplings between various phosphori. d) Obscured due to overlapping with dppe and BPh_4 signals.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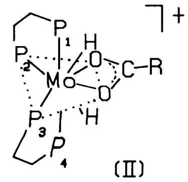

(II)

neutral, seven-coordinate, hydridocarboxylatomolybdenum complex in which the hydride ligand resides in a pentagonal plane flanked with two equatorial phosphorus nuclei.[6)]

Properties and Some Reactions of the Complexes. Carboxylatodihydridomolybdenum(IV) complexes **2** and **3** are moderately stable to air in the solid state and even in the solution in the dark. Furthermore, they are thermally stable: The solid acetato complex **3a** was found to be stable in vacuo up to 150 °C. The complexes bearing carboxylate anions **2** were soluble in chloroform, dichloromethane, ethanol, and acetone and slightly soluble in benzene and toluene, whereas those with BPh_4 anions **3** were soluble only in acetone and the halogenated solvents. When the solution of **3a** in $CHCl_3$ was heated at 60 °C for 2 h in the dark, 14% of CH_2Cl_2 on the basis of **3a** was formed. Subsequently, by allowing the resulting solution to leave under the exposure of the sunlight for 10 days, the formation of CH_2Cl_2 in 85% yield was observed. These results suggest that the cation which is thermally stable is easily activated by the light irradiation.

$$\mathbf{3a} + CHCl_3 \xrightarrow{h\nu} CH_2Cl_2 + \text{yellow complex} \qquad (4)$$

Although complexes **2a** and **3a** were found to be inert to CO, alkenes (e.g. 1-heptene), alcohols (e.g. 2-propanol), and phenol even heating at 60 °C, complex **2a** released one mole of acetic acid on irradiation in ethanol with high pressure mercury lamp for 5 h to yield the neutral monohydrido acetato complex **4a** (21%).[17)]

$$\mathbf{2a} \xrightarrow{h\nu,\,EtOH} \underset{(\mathbf{4a})}{[MoH(O_2CCH_3)(dppe)_2]} + CH_3COOH \qquad (5)$$

The reaction was accompanied by the side reaction to form H_2 in 70% yield and acetaldehyde (32%) together with the orange complex which was tentatively assigned to $[Mo(O_2CCH_3)_2(dppe)_2]$ (12%) on the basis of its IR spectrum (see Experimental).

$$\mathbf{2a} + CH_3CH_2OH \xrightarrow{h\nu} [Mo(O_2CCH_3)_2(dppe)_2] + CH_3CHO + 2H_2 \qquad (6)$$

The mechanism of the oxidation of ethanol to aldehyde with **2a** is not clear at the present stage.

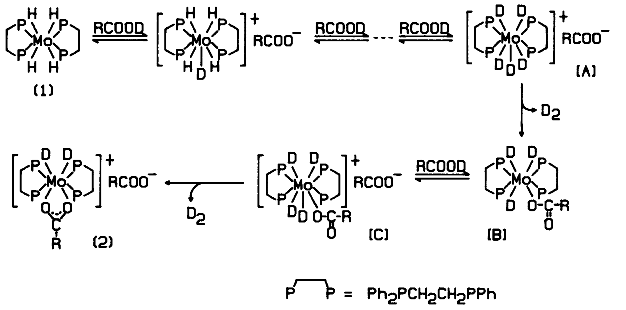
Under the Hg-lamp irradiation, **2a** reacted with 1 atm of CO in EtOH to yield, after 37 h, a small amount of the known dicarbonylmolybdenum complex together with the uncharacterized carbonyl complexes.

$$\mathbf{2a} + CO \xrightarrow{h\nu,\,EtOH} cis\text{-}[Mo(CO)_2(dppe)_2] + \text{Mo-carbonyls} \qquad (7)$$

Finally, the carboxylato ligands of the cationic carboxylatodihydrido complexes **3** were found to be thermally labile in the presence of carboxylic acid to exhibit ligand exchange. Thus, by heating the acetato complex **3a** in acetone in the presence of excess methacrylic acid at 60 °C for 7 h, the methacrylato complex **3d** was obtained in a quantitative yield as is judged from the ^1H NMR spectrum of the isolated compound. The formation of equimolar amount of acetic acid in this reaction was confirmed by the GLC measurement. Conversely, complex **3d** was converted into acetato complex **3a** by stirring **2d** in acetone at 60 °C for 17 h in the presence of acetic acid.

$$\underset{(\mathbf{3a})}{[MoH_2(O_2CCH_3)(dppe)_2]^+} + CH_2{=}C(Me)COOH \rightleftharpoons \underset{(\mathbf{3d})}{[MoH_2(O_2CC(Me){=}CH_2)(dppe)_2]^+} + CH_3COOH \qquad (8)$$

Discussion as to the Formation of the Cation $[MoH_2(O_2CR)(dppe)_2]^+$ (2). The first stage of the reaction between tetrahydrido complex **1** and carboxylic acid RCOOH to form carboxylatodihydrido cation **2** may be the protonation of **1** to give intermediate pentahydrido cation (**A**) (Scheme). Although this intermediate species was not able to be observed in the present system, the corresponding tungsten pentahydride has been prepared by the reaction between $[WH_4(PMePh_2)_4]$ and trifluoroacetic acid.[3)] The selective evolution of D_2 gas when **1** was allowed to react with CH_3COOD [equation (3)] suggests that the equilibrium between **1** and the protonated molybdenum cation (**A**) as shown in the Scheme may be attained rapidly followed by a fairly slow reductive elimination of D_2. This process may be accompanied by the transfer of the acetate anion from the outer sphere to the inner sphere to yield the neutral 18-electron intermediate species (**B**).



Scheme

The trideuterido intermediate possessing the unidentately coordinated acetato ligand (**B**) may be protonated by another mole of acetic acid to give the cationic intermediate (**C**), which releases D_2 with the concomitant transfer of the acetato ligand from the unidentate to the bidentate fashion to attain 18-electrons of the metal center in the final product **2a**. The alternative path from (**B**) to **2a** which involves intermediary formation of monohydride **4a** by reductive elimination of H_2 from (**B**) was ruled out since **4a** was found to be inert to RCOOH.[17] The evolution of a small amount of H_2 in the reaction of **1** with CH_3COOD suggests that there exists, in addition to that shown in the Scheme, a minor process where H_2 is released prior to the deuteriation of **1** leading to (**A**). The dihydridomolybdenum(II) intermediate thus formed may be rapidly converted into (**B**) by reversible protonation with RCOOD as is judged from the absence of an HD component in the evolved gas.

Experimental

Most manipulations were carried out either under dry, oxygen-free nitrogen or argon or in vacuo with Schlenk-type flasks. Solvents were dried, purified in the usual manner, and stored under an atmosphere of argon. Commercial carboxylic acids were degassed and introduced into the reaction flask by a trap to trap method in order to avoid contamination with oxygen and moisture.

Infrared spectra were recorded on a JASCO A-202 spectrometer using KBr disks prepared under an inert atmosphere. Nuclear magnetic resonance spectra were measured on JEOL JNM-PMX-60 (^1H, 60 MHz) and JNM-FX-90Q (^1H, 90 MHz; ^{13}C, 22.5 MHz; ^{31}P, 36.2 MHz) spectrometers. $^1H\{^{31}P\}$ NMR spectra were recorded on a JEOL JNM-FX-100 (100 MHz) spectrometer. The molecular weight was measured in acetone at 25 °C using Mechrolab Vapor Pressure Osmometer Model 302. The electric conductivity of the complex solution was measured in acetone at 18 °C with TOA CM-5B conductivity meter. The organic products formed in the reactions were quantitatively analyzed by GLC using internal standard. GLC was recorded on a Shimadzu GC-7APTF or GC-3BT gas chromatography using PEG-20M, SDC-410, and/or SDC-550 columns and helium as carrier gas. Noncondensable gas evolved through the reaction was measured by a Toepler pump and analyzed by a mass spectrometer (Hitachi Model M-80) and GLC using Molecular Sieve 5A column. $[MoH_4(dppe)_2]$ (**1**) was prepared as previously reported.[18] Acetic acid-*d* was prepared from acetic anhydride and D_2O.

Preparation of Acetatodihydridobis[1,2-bis(diphenylphosphino)ethane]molybdenum(IV) Tetraphenylborate (3a). To $[MoH_4(dppe)_2]$ (**1**) (1.45 g, 1.62 mmol) was added 20 ml of acetic acid by means of a trap-to-trap method. The mixture was stirred in vacuo at room temperature for 3 h to give a purple solution. Evolution of H_2 (3.06 mmol) by the reaction was observed in the flask. Unreacted acetic acid was evaporated off from the solution in vacuo to leave a deep purple sticky solid which was dissolved in 75 ml of EtOH, and the solution was filtered. To the red filtrate was added 1.24 g (3.63 mmol) of $NaBPh_4$ to give purple precipitate, which was filtered and washed with EtOH. Recrystallization of the purple product from acetone afforded vermilion needles of $[MoH_2(O_2CCH_3)(dppe)_2]BPh_4\cdot\frac{1}{2}(CH_3)_2CO$ (**3a**) (1.41 g, 72%). Analytical results for **3a** are listed in Table 2. Inclusion of half mole of acetone as crystallization solvent in **3a** was also confirmed by the intensity measurement of its ^1H NMR spectrum.

In a separate experiment which aimed at the isolation of acetatodihydridobis[1,2-bis(diphenylphosphino)ethane]molybdenum(IV) acetate (**2a**), 1.13 g (1.26 mmol) of $[MoH_4(dppe)_2]$ (**1**) was allowed to react with 16 ml of acetic acid at room temperature under argon for 1 h to give a purple solution. After excess acetic acid being evaporated off from the solution, the resulting sticky solid was triturated in hexane at −50 °C or in Et_2O at room temperature to give red precipitate, which was filtered off, washed well with Et_2O and dried in vacuo to give red powder of $[MoH_2(O_2CCH_3)(dppe)_2]CH_3CO_2$ (**2a**) [$\nu(MoH)=1890$ w, br; $\nu(OCO)$ of $CH_3CO_2^-=1710$ s; $\nu(OCO)_{asym}=1465$ m; $\nu(OCO)_{sym}=1407$ w cm^{-1}] (1.09 g, 85%).

The other carboxylato complexes **2** and **3** were obtained similarly. Reaction conditions of each synthesis are listed in Table 1. Complexes **3** were found to contain half (**3c** and **3d**) or one equivalent (**3b**) of acetone as crystallization solvent as is judged from their elemental analyses and ^1H NMR spectra (see Table 2).

Photodegradation of 2a. $[MoH_2(O_2CCH_3)(dppe)_2]CH_3CO_2$ (**2a**) (0.500 g, 0.494 mmol) in 120 ml of EtOH was irradiated with 100 W high pressure mercury lamp at room temperature under N_2 for 5 h to cause the color change of the solution from purple to brown. Evolution of 0.3 mmol (70%) of H_2 in the vapor phase was detected by the GLC analysis. A volatile component, in which acetic acid (0.31 mmol, 63%) and acetaldehyde (0.16 mmol, 32%) were observed to present by its GLC analysis, was removed in vacuo to leave brown powder, which was fractionally crystallized from Et_2O to give orange crystals of $[MoH(O_2CCH_3)(dppe)_2]$[17] (**4a**) (0.101 g, yield 21.4%) and yellow powder. The latter was tentatively assigned to $[Mo(O_2CCH_3)_2(dppe)_2]$ [$\nu(CO_2)=1618$ s, 1580 w, 1360 m, and 1297 vs cm^{-1}] (0.061 g, 12%).

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