Selective Activation of Olefinic C–H Bonds. Reaction of a Hydridomolybdenum Complex with Methacrylic Esters To Form Hydrido–Alkenyl Complexes

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$MoH_4(dppe)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) (1) reacted thermally or photochemically with an excess of alkyl methacrylates to give red complexes which analyzed as $\overline{\mathrm{MoH[CH{=}C(CH_3)C(O}}\mathrm{)OR](dppe)_2}$ (**2**, R = C_2H_5, i-C_3H_7, n-C_4H_9, and c-C_6H_{11}) together with H_2 and alkyl isobutyrates. Seven-coordinate complexes **2** were spectroscopically characterized and were found to be stereochemically nonrigid on the basis of temperature-dependent $^{31}P\{^1H\}$ NMR spectra. The mechanism of the formation of **2** and its intramolecular exchange process are discussed.

Introduction

The selective activation of organic C–H bonds is one of the most intriguing problems in applications of the organo-transition-metal complexes to organic syntheses. The olefinic C–H bond cleavage to afford σ-alkenyl complexes has been reported for ruthenium and iron hydrido complexes, copper alkyls, and several other complexes including cluster compounds.[3-9] Most of such reactions hitherto reported have been restricted to the group 8–10 metals and copper, and no such reaction is known for the group 6 metals. $W(\eta\text{-}C_5H_5)_2H_2$ is known to activate aromatic and even certain aliphatic C–H bonds in the presence of light.[10] Although the reactions of its molybdenum analogue, $Mo(\eta\text{-}C_5H_5)_2H_2$, with substituted olefins have been extensively investigated with special reference to the insertion of substituted olefins into the Mo–H bond,[11] no indication of C–H bond activation of the aromatic or olefinic group even with UV irradiation has been found.[11,12] In the course of a study designed to investigate the reactivity of another type of molybdenum polyhydride, $MoH_4(PR_3)_4$, toward olefins, we found that $MoH_4(dppe)_2$ (**1**) (dppe = $Ph_2PCH_2CH_2PPh_2$) thermally and photochemically reacted with methacrylates to give a series of hydrido–σ-alkenyl complexes, as the result of selective olefinic C–H bond cleavage.

Results and Discussion

The yellow suspension of tetrahydrido complex **1** in an excess of isopropyl methacrylate (i-PrMA) either with or without toluene or cyclohexane as the solvent changed to a deep red solution on heating at 80–100 °C, from which a red solid which analyzed as $\overline{\mathrm{MoH[CH{=}C(CH_3)C(O}}\mathrm{)OCH(CH_3)_2](dppe)_2}$ (**2a**) was isolated in 41% yield. The reaction was accompanied by the formation of H_2 and isopropyl isobutyrate, both in amounts about equimolar to **1**, together with some poly(isopropyl methacrylate). Furthermore, a certain amount of free dppe was isolated in the course of the purification of **2a**, indicating that the reaction was concurrent with decomposition of some portion of the starting complex **1**. Similar results were obtained when the system was irradiated with a 100-W high-pressure mercury lamp at room temperature. Examination of the resulting red complex **2a** by means of IR and NMR spectroscopy and through its chemical reactions showed that it has a hydrido–σ-alkenyl structure (vide infra). Ethyl, n-butyl, and cyclohexyl methacrylates reacted similarly to give corresponding hydrido–σ-alkenyl complexes. When methyl methacrylate was employed, complex **2** was not obtained, but cis-$Mo(CO)_2(dppe)_2$ and methyl isobutyrate, together with an uncharacterized red complex, were produced. Formation of the carbonyl complex in this case suggests occurrence of a reaction involving cleavage of the acyl–O bond in the ester group followed by decarbonylation.

$$\underset{\textbf{1a–d}}{MoH_4(dppe)_2} + CH_2{=}C(CH_3)C(O)OR \xrightarrow{\Delta \text{ or } h\nu}$$

$$\underset{\textbf{2a–d}}{\overline{\mathrm{MoH[CH{=}C(CH_3)C(O}}\mathrm{)OR](dppe)_2}} +$$

$$(CH_3)_2CHC(O)OR + H_2 + \text{poly(alkyl methacrylate)} \quad (1)$$

$$R = i\text{-}C_3H_7\ (\mathbf{a}),\ C_2H_5\ (\mathbf{b}),\ n\text{-}C_4H_9\ (\mathbf{c}),\ \text{and c--}C_6H_{11}\ (\mathbf{d})$$

The red complexes **2** are soluble in common organic solvents including hexane and are somewhat difficult to purify and obtain free from polymers and free dppe ligand. Thus characterization of these complexes has been performed by using samples which were specially purified by means of repeated recrystallization (5–6 times). Complexes **2** are moderately insensitive to air in the solid state but deteriorate in solution. Complex **2a** melted in vacuo at

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Table I. IR Spectral Data (cm^{-1}) of $MoH[CH{=}C(CH_3)C(O)OR](dppe)_2$ (2)[a]

R	ν(MoH)	ν(C=O)	ν(C=C)	others
$(CH_3)_2CH$ (**2a**)	1800 m	1500 m	1455 m	1400 m, 1365 m, 1320 s, 1210 m, 1105 m
CH_3CH_2 (**2b**)	1720 m	1520 m	1450 m	1410 m, 1330 m, 1255 m, 1210 m, 1105 m
$CH_3(CH_2)_2CH_2$ (**2c**)	1725 m	1525 m	1455 w	1420 m, 1355 w, 1340 m, 1260 w, 1215 m, 1110 s
$CH_2(CH_2)_4CH$ (**2d**)	1835 m	1530 m	1450 m	1380 s, 1355 s, 1340 m, 1320 s, 1210 s, 1110 s

[a] KBr disk.

175–177 °C with decomposition. In contrast to the ruthenium σ-alkenyl complex $RuH[CH{=}C(CH_3)C(O)OR](PPh_3)_3$,[3] complex **2a** did not react with CH_3I but reacted with dry HCl in hexane at room temperature to afford an almost quantitative amount of isopropyl isobutyrate, the hydrogenation product of the parent methacrylate, and the dichloromolybdenum complex **3**.

$$\underset{\mathbf{2a},\ R\ =\ (CH_3)_2CH}{MoH[CH{=}C(CH_3)C(O)OR](dppe)_2} + 2HCl \rightarrow (CH_3)_2CHCOOR + \underset{\mathbf{3}}{MoCl_2(dppe)_2} \quad (2)$$

In the IR spectra of **2**, ν(Mo–H) bands are observed at 1720–1835 cm^{-1}, together with some new bands which are absent in the parent tetrahydrido complex as shown in Table I. No distinct band was observed in the region of ν(C=O) for the ester group which gives rise to an intense band at 1710 cm^{-1} in free methacrylates. The medium bands at around 1525 and 1455 cm^{-1} in **2** were tentatively assigned to the stretching vibrations of the coordinated C=O and C=C bonds, respectively.

The hydrido–σ-alkenyl structure for **2** was deduced mainly from the ^1H, ^{13}C, and ^{31}P NMR spectra of the isopropyl methacrylate complex **2a**. As shown in Figure 1, the ^1H NMR spectrum of **2a** in benzene-d_6 at room temperature exhibits a Mo–H signal at δ −4.25 as doublet of quintets, suggesting coupling of the hydridic proton with four equivalent phosphorus nuclei (^2J(PH) = 46 Hz) and a trans sp^2-methine proton (^3J(H–H) = 6.5 Hz). The signal of the latter appeared at δ 9.88 as a sextet, indicating that the coupling constant with four equivalent phosphorus nuclei is accidentally equivalent to that with trans-hydrido hydrogen (^3J(H–H) = ^3J(P–H) = 6.5 Hz). This sextet methine signal turned to a doublet (^3J(H–H) = 6.5 Hz) on irradiation of ^{31}P nuclei at their resonance frequency. The methine proton signal appearing as a septet at δ 3.68 of the isopropyl group showed no sign of change on decoupling with ^{31}P. The other signals due to ligating ester and dppe appeared in the normal region as shown in Figure 1 and Table II. Complexes **2b** (R = Et), **2c** (R = *n*-Bu), and **2d** (R = cyclohexyl), all showed ^1H NMR spectra consistent with the structure analogous to that proposed for **2a**.

An observation of the ^1H NMR signal of the vinylic hydrogen attached to molybdenum at as low as 9.88 ppm suggests the possibility of the carbenoid structure for **2a**. To shed light on this structural problem, 125-MHz ^{13}C NMR spectra of **2a** were measured (Figure 2). Besides the signals due to the coordinated dppe (signals c and f) and the isopropyl group (b and d), those assignable to the coordinated methacrylate were observed at 19.82 (a, α-CH_3), 115.38 (e, α-carbon), 167.95 (g, carbonyl carbon), and 251.69 ppm (h, β-carbon attached to the molybdenum). Assignment of each signal was confirmed by the off-resonance measurement, the results of which are shown in Figure 2. It is again noteworthy that the alkenyl carbon attached to molybdenum in **2a** resonates at δ 251.69, which is much lower than the chemical shifts of that in the ordinary alkenyl complexes.[13] However, it is difficult to conclude that **2a** has the carbenoid structure rather than the σ-alkenyl-type structure since a fairly wide range of chemical shifts, i.e., 230–430 ppm, have been reported for the molybdenum carbene complexes.[13] It is probable that complex **2a** possesses the conjugated nature of two canonical forms (I and II) shown. Allen et al. have prepared

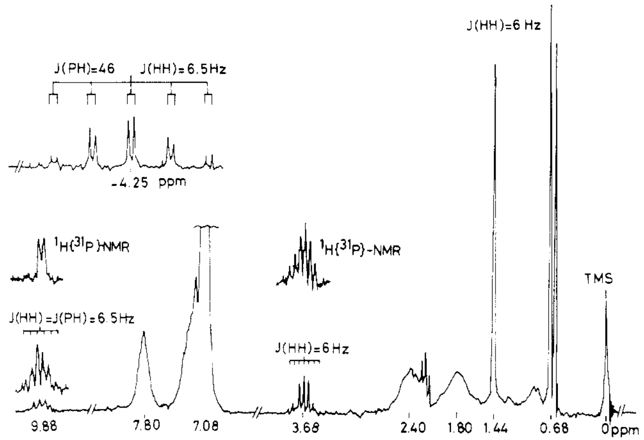
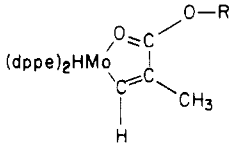
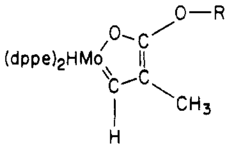


Figure 1. ^1H and $^1H\{^{31}P\}$ NMR spectra of $MoH[CH{=}C(CH_3)C(O)OCH(CH_3)_2](dppe)_2$ (**2a**) (100 MHz in benzene-d_6 at room temperature). Chemical shifts (δ) are in parts per million with reference to tetramethylsilane (Me_4Si) as an internal reference.



I



II

the closely related type of complex $(\eta\text{-}C_5H_5)(CO)_2Mo[C(CH_3){=}C(CH_3)C(O)R]$ via a different route which showed a ^{13}C NMR resonance of molybdenum-attached carbon at 261.0 ppm and proposed the similar canonical forms as above with a slight preference for type II on the basis of the X-ray structural analysis.[14] The similarity of the ^{13}C NMR chemical shifts between **2a** and the Allen's complex suggests the considerable contribution of II in the present system. The absence of an intense ν(C=O) band in IR of **2a** may also be interpreted by considering the canonical form II. Charrier et al. have also discussed the possibility of the type II canonical form for their complex $(\eta\text{-}C_5H_5)(CO)_2Mo[C(CH_3){=}CHC(O)OCH_3]$ on the basis of ^{13}C NMR chemical shift (246.1 ppm).[15]

The $^{31}P\{^1H\}$ NMR spectrum of **2a** in toluene-d_8 at room temperature showed a sharp singlet at 85.6 ppm downfield

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Table II. Selected ^{1}H NMR Data of $MoH[CH{=}C(CH_3)C(O)OR](dppe)_2$ (2)[a]

R	δ(MoH)	δ(α-CH$_3$)	δ(MoCH=)	δ(R)
$(CH_3)_2CH$ (**2a**)	-4.25 (1 H, dq), J(PH) = 46 Hz, J(HH) = 6.5 Hz	1.44 (3 H, s)	9.88 (1 H, sx), J(HH) = 6.5 Hz	0.68 (6 H, d), 3.68 (1 H, sp), J(HH) = 6 Hz
CH_3CH_2 (**2b**)	-4.29 (1 H, dq), J(PH) = 45 Hz, J(HH) = 6.6 Hz	1.37 (3 H, s)	9.82 (1 H, sx), J(HH) = 6.6 Hz	0.84 (3 H, t), 3.11 (2 H, q), J(HH) = 7 Hz
$CH_3(CH_2)_2CH_2$ (**2c**)	-4.29 (1 H, dq), J(PH) = 46 Hz, J(HH) = 6.5 Hz	1.34 (3 H, s)	9.81 (1 H, sx), J(HH) = 6.5 Hz	~0.9 (br, m), ~1.2 (br, m), ~3.1 (m)
$CH_2(CH_2)_4CH$[b] (**2d**)	~-5 (br)	1.10 (3 H, s)	9.59 (1 H, Br)	1.0–1.3 (br), 3.50 (1 H, br)

[a] 100 MHz, at room temperature in C_6D_6 unless otherwise noted. Chemical shifts (δ) are in parts per million with tetramethylsilane as an internal standard, downfield positive. Abbreviations for signal multiplicities are dq = doublet of quintets, s = singlet, sx = sextet, d = doublet, sp = septet, t = triplet, q = quartet, m = multiplet, and br = broad. [b] In CD_2Cl_2.

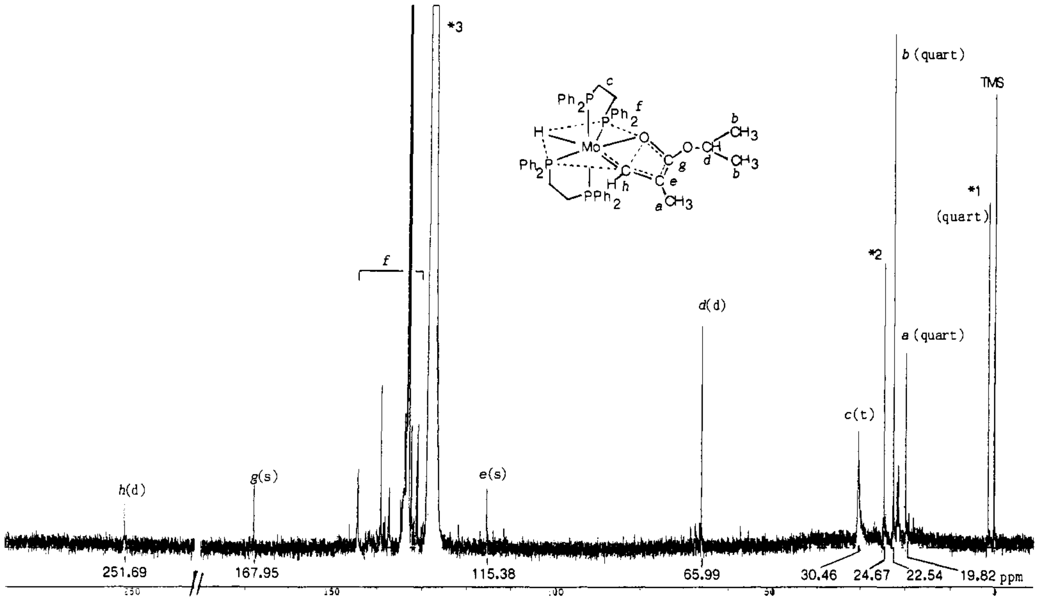

Figure 2. $^{13}C\{^1H\}$ NMR spectrum of $MoH[CH{=}C(CH_3)C(O)OCH(CH_3)_2](dppe)_2$ (**2a**) (125.65 MHz in benzene-d_6 at room temperature). Chemical shifts (δ) are in parts per million with reference to tetramethylsilane (Me_4Si) as an internal standard. Symbols in parentheses indicate the multiplicity of each signal observed in the off-resonance spectrum. Signals *1, *2, and *3 are assignable to the contaminated silicone grease, free dppe (CH_2), and the solvent benzene-d_6, respectively.

from external PPh_3, indicating that the four phosphorus atoms in **2a** are all magnetically equivalent, in agreement with the ^{1}H NMR observation described above. On lowering the temperature, however, the $^{31}P\{^1H\}$ NMR signal of **2a** gradually broadened and shifted slightly upfield and almost flattened at -20 °C. On further cooling, two broad unsymmetrical signals appeared at -40 °C and finally a complicated spectrum pattern was obtained at -80 °C (Figure 3). The spectrum at -80 °C basically consistes of one set of an AB quartet ($\delta(P_A)$ 89.72 and $\delta(P_B)$ 80.30, $^2J(P_AP_B)$ = 126.0 Hz), each split into doublets ($^2J(P_BP_M)$ = 17.6 Hz and $^2J(P_AP_X)$ = 22.0 Hz), and a pair of apparent triplets, each centered at 110.09 ppm ($\delta(P_M)$, $^2J(P_AP_M)$ = 0 Hz, $^2J(P_MP_X)$ = 17.6 Hz) and 83.67 ppm ($\delta(P_X)$, $^2J(P_BP_X)$ = 0 Hz). This assignment as an ABMX spin system was confirmed by a computer simulation using an NMR simulation program developed by Satake et al.[16] (Figure 4). The hydride signal in the ^{1}H NMR spectrum also showed a similar temperature dependence as observed in the $^{31}P\{^1H\}$ NMR, but the analysis of the limiting spectrum taken at -80 °C was not feasible owing to its poor resolution.

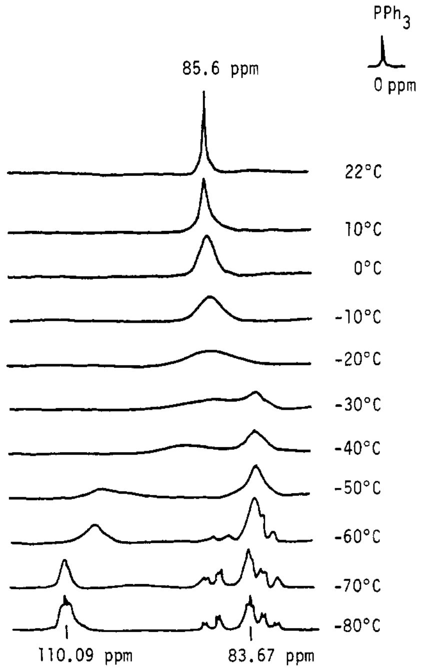

Figure 3. Temperature-dependent $^{31}P\{^1H\}$ NMR spectra of $MoH[CH{=}C(CH_3)C(O)OCHC(CH_3)_2](dppe)_2$ (**2a**) (36.27 MHz in toluene-d_8). Chemical shifts are in δ values (ppm) with respect to triphenylphosphine as external standard.

The spectrum analyses described above suggest the unsymmetrical structure of the complex in the ground state with the coordination of the ester carbonyl group to the molybdenum atom forming a seven-coordinate complex. Although capped octahedral (C_{3v}), monocapped trigonal prismatic (C_{2v}), and pentagonal-bipyramidal (D_{5h}) structures are conceivable for the seven-coordinate complex,[17] a distorted pentagonal-bipyramidal structure with

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[16] Satake, K.; Hara, Y.; Murata, H.; Yamamoto, K. *Kagaku* **1984**, *No. 3*, Supplement 1–8.

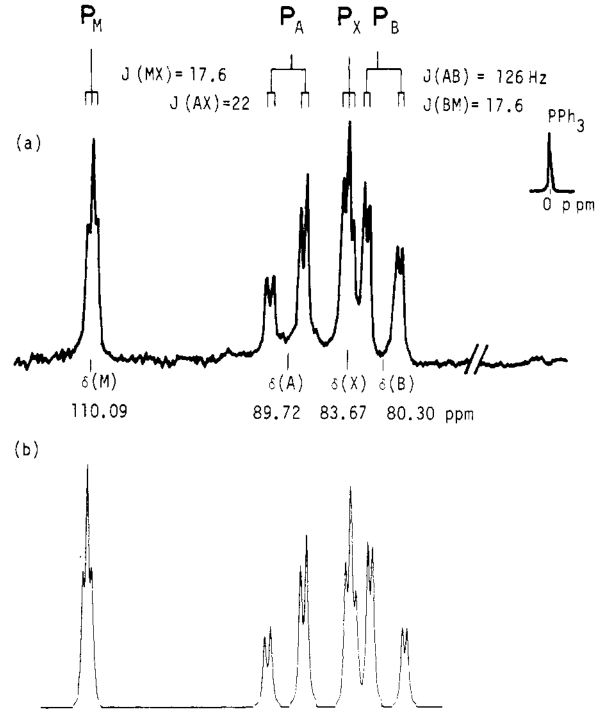


Figure 4. $^{31}P\{^1H\}$ NMR spectra of $MoH[CH{=}C(CH_3)C(O)OCH(CH_3)_2](dppe)_2$ (**2a**) at −80 °C. (a) Observed spectrum (36.27 MHz in toluene-d_8). Chemical shifts are in δ values (ppm) with respect to triphenylphosphine as external standard. (b) Computer-simulated spectrum: $\nu(A) = 3254.22$ Hz, $\nu(B) = 2912.62$ Hz, $\nu(M) = 3993.02$ Hz, $\nu(X) = 3034.70$ Hz; $J(AB) = 126.0$ Hz, $J(AM) = J(BX) = 0$ Hz, $J(AX) = 22.0$ Hz, $J(BM) = J(MX) = 17.6$ Hz.

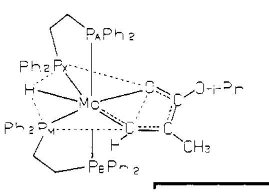
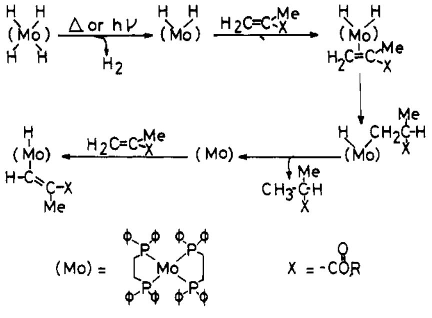


Figure 5. Proposed structure for $MoH[CH{=}C(CH_3)C(O)OCH(CH_3)_2](dppe)_2$ (**2a**).

a plane containing the molybdenum atom, two phosphorus atoms, one hydride, and the vinylic (carbenoid) carbon and the carbonyl oxygen of the coordinated methacrylate, as shown in Figure 5, seems to be most probable on the basis of the spectral evidence. The seven-coordinate complex which is rigid at −80 °C may become stereochemically nonrigid on raising the temperature by the intramolecular pseudorotation mechanism similar to that reported for other seven-coordinate systems.[18] At room temperature, the four phosphorus atoms may exchange rapidly enough on the NMR time scale to give only one sharp signal. The alternative mechanisms for the internal ligand exchange, i.e., those involving the dissociation of either the ester carbonyl group or the phosphine ligand cannot be ruled out, although the latter seems to be less probable as judged from the fact that no exchange was observed between **2a** and the added free dppe ligand in the ^{31}P NMR study even at room temperature.

Taking into account that tetrahydrido complex **1** is converted into *trans*-$Mo(N_2)_2(dppe)_2$ by heating or irradiating the benzene solution of **1** in the presence of dinitrogen, possibly via a thermally or photochemically generated, coordinatively unsaturated intermediate species, $MoH_2(dppe)_2$,[19] we assume that complex **2** is formed via oxidative addition of methacrylate to a coordinatively unsaturated Mo(0) species, $Mo(dppe)_2$, that is produced from $MoH_2(dppe)_2$ via hydrogenation of the methacrylate, by insertion and reductive elimination processes (Scheme I).

Scheme I



Experimental Section

Most manipulations were carried out either under dry, oxygen-free argon or in vacuo with Schlenk-type flasks. Solvents were dried, purified in the usual manner, and stored under an atmosphere of argon. Commercial alkyl methacrylates were dried over CaH_2 and introduced directly into the reaction flask by a trap-to-trap method in order to avoid contamination with oxygen and moisture.

Infrared spectra were recorded on Hitachi Model 295 and JASCO A-202 spectrometers using KBr disks prepared under inert atmosphere. ^1H and ^{31}P NMR spectra were measured on JEOL PS-100, FX-100, and FX-90Q spectrometers. ^{13}C NMR spectra (125.65 MHz) were measured on a JEOL GX-500 spectrometer. The organic products formed in the reactions were quantitatively analyzed by GLC using internal standard. GLC was recorded on a Shimadzu GC-3BT, GC-6A, or GC-7APTF gas chromatography using SDC-550, SDC-410, and/or PEG-20M columns and helium as carrier gas. Noncondensable gas evolved through the reaction was measured by Toepler pump and analyzed by GLC using activated charcoal, silica gel, Unibeads-1S, and/or molecular sieve 5A columns.

$MoH_4(dppe)_2$ (**1**) was prepared as previously reported.[20] UV irradiation was performed by using a Riko 100-W high-pressure mercury lamp through Pyrex glass filter.

Reaction of $MoH_4(dppe)_2$ (1) with Isopropyl Methacrylate. a. Thermal Reaction. On heating a mixture of $MoH_4(dppe)_2$ (0.247 g, 0.275 mmol), 7.5 mL (52 mmol) of isopropyl methacrylate, and a small amount of *p*-methoxyphenol as an inhibitor for the polymerization under argon at 100 °C, the initial yellow suspension turned to a red solution in 2 h and finally a deep red viscous liquid was obtained after 10 h of heating. From the system, unreacted isopropyl methacrylate was removed by a trap-to-trap method in which isopropyl isobutyrate (0.264 mmol, 0.96 mol/mol of **1**) was detected by GLC analysis. The residual solid, consisting mainly of the product complex and poly(isopropyl methacrylate), was thoroughly dried in vacuo to give a pink mass, from which, on rigorous extraction with hexane followed by recrystallization from hexane at −90 °C, powdery, deep red crystals of $MoH[CH{=}C(CH_3)C(O)OCH(CH_3)_2](dppe)_2$ (**2a**) were obtained (0.116 g, 41%); mp 175–7 °C dec. Anal. Calcd for $C_{55}H_{60}O_2P_4Mo$: C, 69.41; H, 5.92. Found: C, 69.55; H, 6.35. The evolution of H_2 in the reaction was confirmed in a separate experiment in which 0.279 g (0.310 mmol) of **1** was treated with isopropyl methacrylate in vacuo to release 0.267 mmol (0.861 mol/mol of **1**) of H_2. The

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similar results were obtained when toluene or cyclohexane was employed as a reaction solvent in these reactions either under argon or in vacuo.

b. Photochemical Reaction. Isopropyl methacrylate (8.0 mL, 55 mmol) was added to $MoH_4(dppe)_2$ (0.0932 g, 0.103 mmol) in a Pyrex Schlenk flask in vacuo, and the mixture was irradiated with stirring at 20 °C for 7.5 h to give a deep red solution. Polymerization of methacrylate was observed only in the vapor phase to give polymer films on the flask wall, and considerable reduction of contamination by the polymer in the solution was achieved by employing the photochemical reaction. The workup procedure was much easier than that in the thermal reaction. The resulting red solution was worked up as above to give product **2a** (0.0610 g, 57.5%). Similar results, but with lower yield, were obtained when the reaction was carried out under an argon atmosphere or in vacuo in benzene solution.

Reaction of $MoH_4(dppe)_2$ (1) with Ethyl Methacrylate. Complex 1 (0.475 g, 0.419 mmol) and ethyl methacrylate (3.0 mL, 24.7 mmol) in toluene (20 mL) were heated in vacuo at 80 °C for 30 h to give a deep red solution. Formation of H_2 and ethyl isobutyrate (each ca. 1 mol/mol of 1) was observed by GLC analyses of the resulting system. The mixture was dried in vacuo to leave a deep red solid, which was dissolved in 15 mL of toluene. A brown precipitate that was formed on addition of 55 mL of hexane to the solution was filtered, and a red powder (0.25 g) was obtained by evaporating the solvent from the filtrate. The powder was recrystallized from toluene–hexane to give deep red, powdery crystals which were spectroscopically analyzed as $\overline{\mathrm{MoH[CH{=}C(CH_3)C(O)}}\mathrm{OC_2H_5](dppe)_2}$ (**2b**) (0.157 g, 15.6%).

Reaction of $MoH_4(dppe)_2$ (1) with *n*-Butyl Methacrylate. Complex 1 (0.313 g, 0.349 mmol) and 5.0 mL (31.3 mmol) of *n*-butyl methacrylate in toluene (20 mL) were heated at 80 °C in vacuo for 45 h to give a deep red solution. The formation of about 1 mol/mol of 1 of *n*-butyl isobutyrate was confirmed by GLC analysis. The system was worked up as above to yield 0.174 g of a red solid, which was recrystallized from pentane to give deep red, powdery microcrystals of $\overline{\mathrm{MoH[CH{=}C(CH_3)C(O)}}\mathrm{O}\text{-}n\text{-}\mathrm{C_4H_9](dppe)_2}$ (yield 30.1%). Anal. Calcd for $C_{60}H_{62}O_2P_4Mo$: C, 69.63; H, 6.04. Found: C, 67.35; H, 6.04.

Reaction of $MoH_4(dppe)_2$ (1) with Cyclohexyl Methacrylate. To the flask containing 1 (0.273 g, 0.303 mmol) was added 5 mL (28.7 mmol) of cyclohexyl methacrylate by a trap-to-trap method. The mixture was heated at 100 °C in vacuo for 8 h to yield a red solution. The reaction was found to be accompanied by the formation of H_2 and cyclohexyl isobutyrate (0.43 and 1.28 mol/mol of 1, respectively). From a red solid which was obtained by drying up the reaction mixture, a brick red solid (0.26 g, 81%) was extracted by hexane and was recrystallized from diethyl ether to give red powder of $\overline{\mathrm{MoH[CH{=}C(CH_3)C(O)}}\mathrm{O\text{-}c\text{-}C_6H_{11}](dppe)_2}$ (**2d**) (0.15 g, 14%). Anal. Calcd for $C_{62}H_{64}O_2P_4Mo$: C, 70.19; H, 6.08. Found: 70.42; H, 6.09.

Reaction of $\overline{\mathrm{MoH[CH{=}C(CH_3)C(O)}}\mathrm{OCH(CH_3)_2](dppe)_2}$ (2a) with Dry HCl. Red complex **2a** (0.0826 g, 0.089 mmol) dissolved in 4 mL of hexane was allowed to react in vacuo at room temperature for a day with 1.43 mmol of HCl gas, which was generated from NaCl and concentrated H_2SO_4, to give a pink precipitate. The precipitate was filtered off, washed with toluene, and dried to afford 0.0340 g of pink powder which was analyzed as $MoCl_2(dppe)_2$ (43.6%). From the filtrate, isopropyl isobutyrate (76.4% on the basis of **2a**) was detected by GLC analysis.

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Registry No. 1, 32109-09-4; **2a**, 100351-38-0; **2b**, 100351-39-1; **2c**, 100351-40-4; **2d**, 100351-41-5; isopropyl methacrylate, 4655-34-9; ethyl methacrylate, 97-63-2; *n*-butyl methacrylate, 97-88-1; cyclohexyl methacrylate, 101-43-9.

Asymmetric Catalysis. 29.[1] Optically Active Primary Amines by Enantioselective Catalytic Hydrosilylation of Ketoximes

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Alkyl aryl ketoximes $R^1R^2C{=}NOH$ were shown to undergo a novel catalytic hydrosilylation with diphenylsilane in homogeneous solution. Three moles of H_2SiPh_2 were consumed, giving the products $Ph_2HSiOSiHPh_2$ and the silylamines $R^1R^2HCNHSiHPh_2$ which on hydrolysis yielded the primary amines $R^1R^2HCNH_2$. In situ catalysts consisting of $[Rh(cod)Cl]_2$ and optically active phosphines of the type (−)-diop and (−)-Norphos were used to control the enantioselectivity. Fourteen prochiral ketoximes were studied; optical inductions up to 36% ee (ee = enantiomeric excess) were obtained. Five ketimines, $R^1R^2C{=}NH$, were included in the study to demonstrate that ketimines are intermediates in the oxime hydrosilylation.

Introduction

Enantioselective catalysis with optically active transition-metal compounds is a method of increasing importance for the preparation of optically active compounds.[2] The types of reactions which can be catalyzed enantioselectively have been continuously expanded through the last years. Besides the classical enantioselective hydrogenation, reactions such as hydroformylation, isomerization, hydrovinylation, cross-coupling, allylation, cyclopropanation, hydrocyanation, epoxidation, and hydrosilylation were studied intensively.[3]

Enantioselective hydrosilylation with optically active transition-metal catalysts was used hitherto for the re-

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