Selective C–O Bond Cleavage of Allylic Esters using $[MoH_4(Ph_2PCH_2CH_2PPh_2)_2]$ under Light Irradiation to give Hydridocarboxylatomolybdenum(II) Complexes

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The complex $[MoH_4(dppe)_2]$ (**1**) (dppe = $Ph_2PCH_2CH_2PPh_2$) reacted with allyl carboxylates $RCO_2CH_2CH=CH_2$ (R = H, Me, Et, Pr^n, Bu^t, $CH_2=CMe$, or Ph) in benzene upon irradiation with a high-pressure mercury lamp to give $[MoH(O_2CR)(dppe)_2]$ (**2**), together with propene and H_2. Reaction pathways comprising the oxidative addition of the allyl carboxylates involving allyl–oxygen bond cleavage are proposed on the basis of the results obtained with substituted allylic esters. The complexes (**2**) were characterized spectroscopically as having pentagonal-bipyramidal structures in solution. The similar reaction of complex (**1**) with allyl formate led to selective cleavage of the formic C–H bond to give ultimately the known *cis*-$[Mo(CO)_2(dppe)_2]$ *via* (**2**; R = H).

Organic reactions involving organotransition-metal complexes have been known often to proceed under mild conditions, giving rise to high chemo-, regio-, and/or stereo-selective synthetic routes.[1] The alkylation of allylic compounds utilizing palladium compounds as catalyst which has been developed extensively by Tsuji and Trost is typical.[2,3] These reactions have been studied almost exclusively with the palladium complexes, although some interesting results concerning the complementary selectivities have been reported for molybdenum complexes.[1,4] Much work has been carried out on the mechanism of the C–O bond cleavage of unsaturated esters using Group 8 transition-metal organometallics,[5] however studies utilizing early transition-metal compounds are scarce.[6]

As an extension of our studies on the photochemically or thermally activated molybdenum tetrahydride $[MoH_4(dppe)_2]$ (**1**) (dppe = $Ph_2PCH_2CH_2PPh_2$), with various saturated and unsaturated organic compounds, which include carboxylic acids,[7] methacrylic esters,[8] allylic carbonates,[9] and carbon dioxide,[10] we have investigated its reaction with allylic esters under irradiation with a high-pressure mercury lamp with a view to shedding some light on the mechanistic aspect of catalytic alkyl allylation utilizing molybdenum complexes.[4]

Results and Discussion

(*a*) *Reactions of Complex* (**1**) *with Allyl Carboxylates and Related Compounds.*—The yellow suspension of complex (**1**) in an excess of allyl acetate and benzene as the solvent changed to a deep red solution after irradiation with a 100-W high-pressure mercury lamp at room temperature for 2 h. Orange crystals of $[MoH(O_2CMe)(dppe)_2]$ (**2**) were isolated from the resulting solution in 45% yield, together with H_2 and propene each in corresponding amounts [equation (1) (R = Me) and Table 1]. In addition, small amounts of propane and propyl acetate were

$$\underset{(1)}{[MoH_4(dppe)_2]} + RCO_2CH_2CH=CH_2 \xrightarrow{h\nu} \underset{(2)}{[MoH(O_2CR)(dppe)_2]} + H_2 + MeCH=CH_2 \quad (1)$$

formed as by-products. Furthermore, a yellow powder, hardly characterizable due to its insolubility in common organic solvents, was obtained as a molybdenum-containing by-product, the formation of which resulted in a reduction in the yield of (**2**).

The reactions of complex (**1**) with allyl carboxylates other than acetate under similar conditions resulted in essentially analogous results, yielding the corresponding hydridocarboxylato complexes (**2**) [equation (1); R = H, Et, Pr^n, Bu^t, $CH_2=CMe$, or Ph] shown in Table 1 (runs 1—7). These findings provide a new route for the syntheses of a series of hydrido(carboxylato)molybdenum complexes with a variety of alkyl groups including unsaturated ones (run 6). The hydridoformato complex (**2**; R = H) formed by the reaction of (**1**) with allyl formate has been prepared recently by the photoreaction between (**1**) and carbon dioxide in benzene.[10] That the light irradiation is indispensable in these reactions was confirmed by the fact that no reaction of (**1**) with allyl acetate and formate took place in the dark.

In order to obtain insight into the mechanism of selective cleavage of the allyl–oxygen bond in this reaction, reactions of complex (**1**) with several other acetates were examined. The results are also included in Table 1. When propyl acetate was employed as the substrate no appreciable reaction took place except for evolution of hydrogen (Table 1, run 8), suggesting that the carbon–carbon double bond of the allyl group is playing an important role in the selective bond cleavage. It is known that complex (**1**) releases 2 mol of hydrogen when irradiated in solution in the absence of substrate.[11]

The reactions of complex (**1**) with substituted allylic acetates such as but-3-en-2-yl acetate (α-methylallyl acetate) and *trans*-but-2-enyl acetate (*trans*-crotyl acetate) also proceeded similarly, although the apparent rates were low for both esters compared with unsubstituted allyl acetate. Butenes formed by the reactions consisted solely of but-1-ene and *trans*-but-2-ene and no other C_4 component was detected by g.l.c. As shown in the footnote of Table 1, the main product was but-1-ene in the case of but-3-en-2-yl acetate (but-1-ene/*trans*-but-2-ene 5.3:1), whereas *trans*-but-2-ene is formed in preference to but-1-ene in the case of *trans*-but-2-enyl acetate (ratio 0.5). These facts may imply that there is, if any, very little opportunity for rearrangement of alkenes during the course of the reaction. Furthermore, inspection of the time dependency of this regioselectivity for the reaction of but-3-en-2-yl acetate revealed that the high value of the selectivity (r.e. = 86 ± 1)† is attained at a very early stage

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† r.e. (regioisomeric excess) = 100 × |([but-1-ene] − [*trans*-but-2-ene])/([but-1-ene] + [*trans*-but-2-ene])|.

Table 1. Reactions of $[MoH_4(dppe)_2]$ (**1**) with allylic carboxylates RCO_2R' in benzene at room temperature

Run	R	R′	RCO_2R'/(**1**)	*t*/h	Products [% based on (**1**)] (**2**)	H_2	R′H	Others
1	H	$CH_2CH{=}CH_2$	72	1.5	42	73	42	CO_2 10
2	Me	$CH_2CH{=}CH_2$	83	2	45	56	53	Pr^nO_2CMe 31
3	Et	$CH_2CH{=}CH_2$	66	2	48	62	72	
4	Pr^n	$CH_2CH{=}CH_2$	100	2	50	66	83	
5	Bu^t	$CH_2CH{=}CH_2$	55	2	44	67	101	
6	$CH_2{=}CMe$	$CH_2CH{=}CH_2$	64	2	35	79	86	
7	Ph	$CH_2CH{=}CH_2$	57	2	36	49	77	
8	Me	$CH_2CH_2CH_3$	126	3	0	22	0	
9	Me	$CH(Me)CH{=}CH_2$	69	2	31	76	38[a]	
10	Me	$CH_2CH{=}CHMe$	106	3	10	56	12[b]	Bu^nO_2CMe 19
11	Me	$CH{=}CH_2$	96	1	47	51	66	EtO_2CMe 8
12	Me	CH_2Ph	48	12	16	64	5	$PhCH_2CH_2Ph$ 17

[a] But-1-ene (32%) + *trans*-but-2-ene (6%). [b] But-1-ene (4%) + *trans*-but-2-ene (8%).

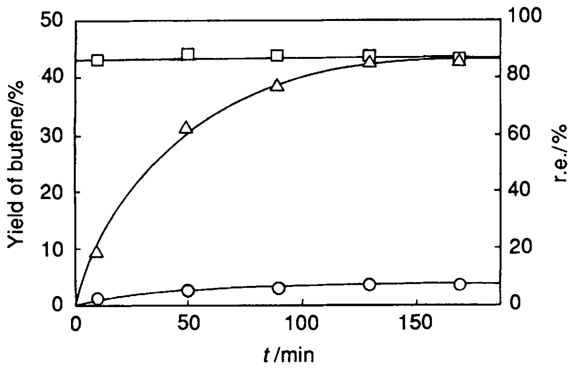


Figure 1. Time course of the yields (%) of butenes (but-1-ene, △; *trans*-but-2-ene, ○) and the regioisomeric excess (r.e.) (%) (□)

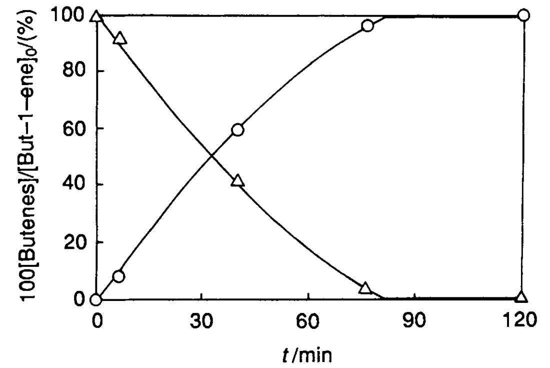


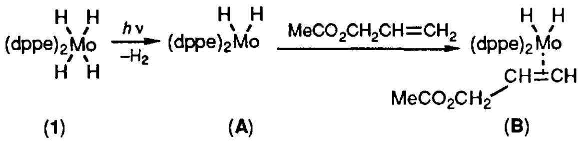
Figure 2. Time course of the photoisomerization of but-1-ene (△) to *trans*-but-2-ene (○) with $[MoH_4(dppe)_2]$

of the reaction (Figure 1). Parallel results were obtained also for *trans*-but-2-enyl acetate although the results were less unambiguous due to the low yield of butenes over a similar reaction period.

Graff *et al.*[12] reported that complex (**1**) catalyses the photochemical isomerization of pent-1-ene to pent-2-enes at a rate that is less than the competitive hydrogenation reaction of the former. In the present system too, there is a possibility that the detected but-2-ene might have been formed by the subsidiary photoisomerization of but-1-ene. In order to investigate this, the time course of the photoisomerization of but-1-ene was examined. As shown in Figure 2, but-1-ene slowly isomerized solely to but-2-ene. The rate of isomerization is slower than the rate of formation of butene in Figure 1, even though the r.e. value is the same after 10 as after 100 min. The results suggest that the isomerization process does not significantly affect the ratio of the two isomers of butene in the present reaction.

Besides the allylic esters, vinyl acetate reacted similarly to allyl acetate to give complex (**2**), ethene, and dihydrogen (Table 1, run 11). The reaction of (**1**) with benzyl acetate proceeded analogously, but much more slowly (Table 1, run 12). In this case 1,2-diphenylethane, the coupling product of R′, was found in the reaction mixture as a by-product, in contrast to the case of unsaturated esters.

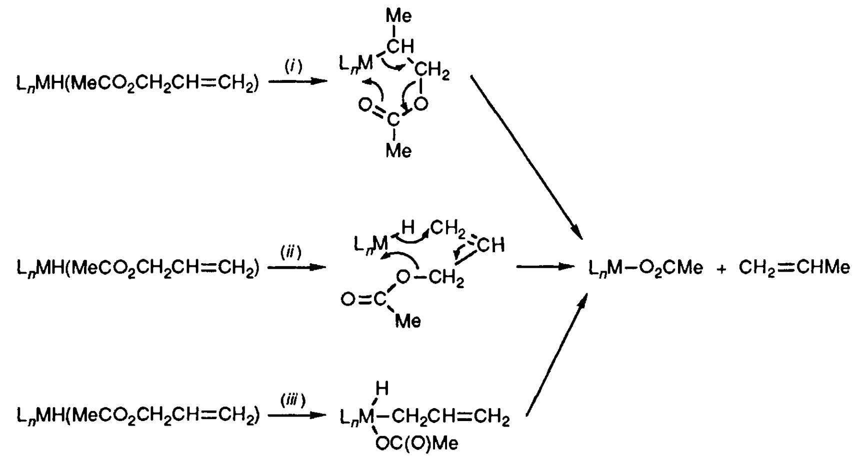
(*b*) *The Possible Reaction Path.*—Tetrahydrido complex (**1**) is known to release 1 mol of dihydrogen and yield the dihydrido intermediate $[MoH_2(dppe)_2]$ (**A**) on irradiation with 355-nm light.[12,13] Consequently, it may be natural to conceive that the initial stage of the present reaction may be the formation of (**A**) and the co-ordination of an allyl group to (**A**) to give the 18-electron molybdenum(II) intermediate (**B**) [equation (2)], which



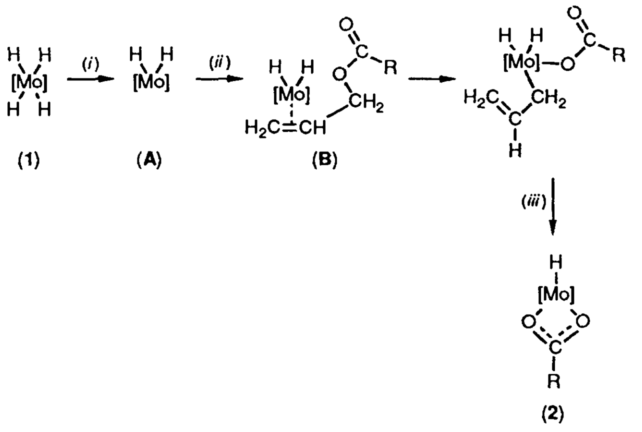
(2)

may be rationalized by the fact that no reaction was observed with the saturated ester. The reduced reaction rate for *trans*-but-2-enyl acetate also supports the intermediacy of (**B**) because the introduction of the bulky methyl substituent at the olefinic part of the allylic ester may hinder formation of (**B**).

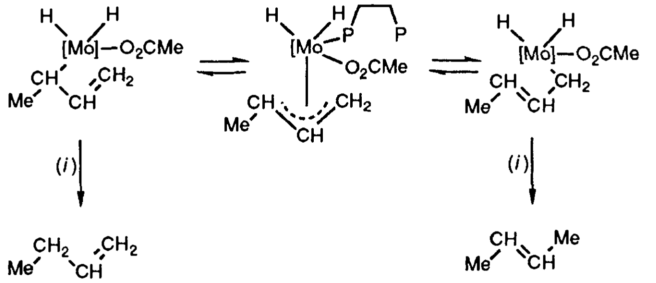
As for the mechanism of the subsequent allyl–oxygen bond cleavage, three pathways (Scheme 1) may generally be conceived. Mechanism (*i*) involving insertion of a C=C group into a M–H bond has been proposed for the evolution of ethene upon reaction of vinyl acetate with $[RuH_2(PPh_3)_4]$,[5a] whereas the S_N2' type mechanism (*ii*) has been observed for the reaction of $[RhH(PPh_3)_4]$ with $CH_2{=}CHCH_2OCO_2Ph$ to yield propene, CO_2, and $[Rh(OPh)(PPh_3)_4]$.[5d] For the present system, these two mechanisms may not be applicable since both should accompany migration of the C=C double bond from the original position. Thus *trans*-but-2-ene and but-1-ene should be major products when but-3-en-2-yl acetate and *trans*-but-2-enyl acetate, respectively, react according to these mechanisms. The alternative path to that shown in (*i*) (Scheme 1) which involves insertion of the allylic group into the Mo–H bond in the opposite direction, *i.e.* in an anti-Markovnikov mode, seems to be less important, since it cannot involve the resonance form



Scheme 1. Three possible pathways for the allyl–oxygen bond cleavage promoted by the transition-metal hydride: (*i*) insertion of allylic group into M–H bond, (*ii*) concerted S_N2' mechanism, and (*iii*) direct oxidative addition



Scheme 2. [Mo] = $Mo(dppe)_2$. (*i*) *hv*, $-H_2$; (*ii*) $RCO_2CH_2CH{=}CH_2$; (*iii*) $-CHMe{=}CH_2$



Scheme 3. (*i*) Reductive elimination

shown in (*i*) which may be important in the succeeding C–O cleavage reaction. The formation of a small amount of saturated ester in the reaction of allyl acetate suggests that the reaction *via* path (*i*) is also taking place as a minor process.

Most results obtained in the present study can be rationalized by considering mechanism (*iii*), the oxidative-addition mechanism, as the main reaction path. Thus the reaction path shown in Scheme 2 is proposed. That the reductive elimination [step (*iii*) Scheme 2] directly from the hydrido(η^1-allyl) intermediate (**B**) is a primary route was implied by the experimental evidence that the value of the regioselective excess differs between the reactions of but-3-en-2-yl acetate and *trans*-but-2-enyl acetate: the same value for the two acetates would be obtained if an η^3-allyl structure had been involved (Scheme 3).

Apart from the unsaturated esters, the photoreaction of benzyl acetate with complex (**1**) may be considered to proceed *via* a different pathway on the basis of the following: first the coordination of the ester in the form of intermediate (**B**) seems to be less likely in this case, and secondly the yield of toluene is very low compared with that for the corresponding alkene in the reaction of unsaturated esters. Taking into account that a considerable amount of 1,2-diphenylethane was formed as a by-product (Table 1), we are inclined to consider that the reaction proceeds primarily *via* a radical pathway which includes the direct oxidative addition of benzyl acetate associated with homolytic cleavage of the benzyl–oxygen bond induced by light irradiation.

(*c*) *Spectral Characterization of the Hydrido(carboxylato)-molybdenum*(II) *Complexes* (**2**).—The reddish orange crystals of hydrido(carboxylato)molybdenum(II) complexes (**2**) were moderately stable to the air in the solid state and were readily soluble in aromatic hydrocarbons such as benzene and toluene to give brown air-sensitive solutions. They were partially soluble in acetone and diethyl ether, slightly soluble in ethanol and hexane, and insoluble in pentane. Melting points and analytical results are listed in Table 2.

The i.r. data for complexes (**2**) are also included in Table 2. The acetato complex (**2**; R = Me) shows ν(Mo–H) bands at 1 870 cm^{-1} and two ν(OCO) bands of the bidentate carboxylato ligands at 1 540 and 1 450 cm^{-1}.[14] Analogous spectra were obtained for the rest of the complexes except for formate (R = H), in which a symmetric OCO stretching band appeared at 1 360 cm^{-1}, lower than for the other complexes by about 100 cm^{-1}.[10]

The ^1H n.m.r. spectrum of acetato complex (**2**; R = Me) in C_6D_6 showed a singlet at δ 1.10 and a triplet of triplets of an A_2M_2X system at δ −6.23 (Table 3). In the ^{13}C n.m.r. spectrum two singlets at δ 24.3 and 179.5 p.p.m. assignable to the methyl and carboxyl carbons, respectively, of the acetato ligand were observed in addition to the characteristic signals due to dppe ligands. In the ^{31}P-{^1H} n.m.r. spectrum a pair of triplets due to an A_2X_2 spin system was observed at δ 101.0 and 75.4 p.p.m. downfield from the external reference PPh_3. These spectral features are very similar to those observed for the hydridoformato complexes (**2**; R = H)[10] and $[MoH(O_2CH)(PMe_3)_4]$,[15] and suggest that the complex has a pentagonal-bipyramidal structure in solution at room temperature as shown below, with the hydride, two phosphorus atoms, and two oxygens of the acetato ligand constituting a pentagonal girdle.

Table 2. Analytical and i.r. spectral data for $[\mathrm{MoH(O_2CR)(dppe)_2}]$

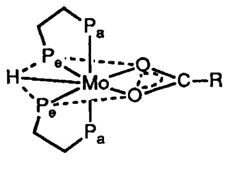
R	M.p.[a] θ/°C	Analyses[b] (%)		I.r.[c]/cm^{-1}		
		C	H	ν(Mo–H)	ν_{asym}(OCO)	ν_{sym}(OCO)
H	213	67.6 (67.8)	5.5 (5.4)	1 810	1 550	1 360
Me	217	68.1 (68.0)	5.7 (5.4)	1 870	1 540	1 450
Et	224	67.6 (68.3)	5.8 (5.7)	1 875	1 530	1 470
Pr^n	204	68.6 (68.6)	6.3 (5.8)	1 890	1 530	1 440
Bu^t	240	68.3 (68.8)	6.0 (5.9)	1 810	1 520	1 460
CH$_2$=CMe	214			1 830	1 510	1 455

[a] With decomposition. [b] Calculated values in parentheses. [c] As KBr disk.

Table 3. N.m.r. data for $[\mathrm{MoH(O_2CR)(dppe)_2}]$[a]

R	^{1}H[b]			^{31}P-{^{1}H}[c]		
	δ(Mo–H)	$J(\mathrm{P_{eq}H})$	$J(\mathrm{P_{ax}H})$	$\delta(\mathrm{P_{eq}})$	$\delta(\mathrm{P_{ax}})$	$J(\mathrm{P_eP_a})$
H	−6.47 (tt)	66.9	27.1	101 (br)	76 (br)	—
Me	−6.23 (tt)	64.8	30.7	101 (t)	75.4 (t)	17.7
Et	−6.04 (tt)	66.7	28.2	96.5	70.8	14.7
Pr^n	−6.13 (tt)	67.6	27.0	95.8	70.3	14.6
Bu^t	−7.04 (m)	—	—	87.0	64.8	—
CH$_2$=CMe	−5.56 (m)	—	—			

[a] Chemical shifts δ are in p.p.m., downfield positive from internal SiMe$_4$ (for ^{1}H) and external PPh$_3$ (for ^{31}P) references; J values in Hz. [b] 90 MHz in C$_6$D$_6$, room temperature (r.t.). [c] 36.2 MHz in toluene–C$_6$D$_6$, r.t.



As shown in Table 3, the other carboxylato complexes prepared in the present study all showed similar spectra indicating that they have an analogous configuration in solution. In the table, the assignment of the two sets of phosphorus atoms, those in the equatorial plane (P$_e$) and in the apical position (P$_a$), was accomplished by referring to those reported for $[\mathrm{MoH(O_2CH)(PMe_3)_4}]$.[15] In the case of the complexes with bulky carboxylato ligands such as pivalate and methacrylate, the hydride signal distorted significantly from the characteristic triplet of triplets, resulting in a complex multiplet, which suggests a considerable deviation from the symmetrical pentagonal-bipyramidal configuration due to the steric bulk of the ligand. Similarly to the related seven-co-ordinate hydridocarboxylato complex $[\mathrm{MoH(O_2CCF_3)\{P(OMe)_3\}_4}]$, which has been reported to show fluxional behaviour on the basis of the hydride signal,[16] the present acetato complex (**2**) exhibited a dynamic signal in its ^{31}P-{^{1}H} n.m.r. spectrum between 25 and 130 °C in toluene. The results indicate that this complex is also fluxional in solution, which is common for seven-co-ordinate complexes.[8,17]

(*d*) *Reaction of Complex* (**1**) *with Formic Esters*.—As is shown in Table 1, allyl formate reacted with complex (**1**) under light irradiation to give hydridoformato complex (**2**; R = H) in 42% yield after 1.5 h [equation (3)]. The by-products in this

$$\underset{(\mathbf{1})}{[\mathrm{MoH_4(dppe)_2}]} + \mathrm{HCO_2CH_2CH{=}CH_2} \xrightarrow{h\nu} \underset{(\mathbf{2})}{[\mathrm{MoH(O_2CH)(dppe)_2}]} + \mathrm{H_2} + \mathrm{MeCH{=}CH_2} + \mathrm{CO_2} \qquad (3)$$

reaction included CO$_2$ in addition to H$_2$ and propene which are common to the analogous reactions with other allylic esters.

When the reaction was carried out for 20 h the yield of hydridoformato complex was reduced to only trace amounts, instead formation of a mixture of *cis*- and *trans*-$[\mathrm{Mo(CO)_2(dppe)_2}]$[18,19] was confirmed by the i.r. spectrum, in addition to the gaseous by-products (see Experimental section). Noticeably, 114% of propene was evolved in this reaction. Since irradiation of hydridoformato complex (**2**; R = H) in benzene did not afford dicarbonyl complexes, it is conceivable that the former, which was formed *via* an analogous route to that of the other allylic esters (see above), reacted with a further mole of allyl formate to give ultimately the carbonyl complexes [equation (4)]. The fate of the oxygen atoms may be ascribable to the

$$\underset{(\mathbf{2})}{[\mathrm{MoH(O_2CH)(dppe)_2}]} + \mathrm{HCO_2CH_2CH{=}CH_2} \xrightarrow{h\nu} [\mathrm{Mo(CO)_2(dppe)_2}] + \{\mathrm{Mo{=}O}\} + \mathrm{H_2} + \mathrm{MeCH{=}CH_2} + \mathrm{CO_2} \qquad (4)$$

formation of a oxomolybdenum complex, as suggested by the observation of a strong absorption at 950 cm^{-1} in the i.r. spectrum of the crude product.[20]

Although complex (**1**) did not react with the saturated acetate, it reacted photochemically with propyl formate to give a dicarbonyl complex together with H$_2$ and propanol (see Experimental section). When the work-up was conducted under a dinitrogen atmosphere, *trans*-$[\mathrm{Mo(N_2)(CO)(dppe)_2}]$[21] was detected spectroscopically in the reaction mixture. Furthermore, the ratio of the *trans* to the *cis* isomer of the dicarbonyl complex increased significantly with increasing reaction time.[19] These findings may be accounted for by postulating the reaction paths shown in equations (5)—(7).

$$\underset{(\mathbf{1})}{[\mathrm{MoH_4(dppe)_2}]} + \mathrm{HCO_2Pr^n} \xrightarrow{h\nu} [\mathrm{Mo(CO)(dpe)_2}] + 2\mathrm{H_2} + \mathrm{Pr^nOH} \qquad (5)$$

$$[\mathrm{Mo(CO)(dppe)_2}] + \mathrm{N_2} \longrightarrow trans\text{-}[\mathrm{Mo(N_2)(CO)(dppe)_2}] \qquad (6)$$

$$[Mo(CO)(dppe)_2] + HCO_2Pr^n \xrightarrow{h\nu} cis\text{-}[Mo(CO)_2(dppe)_2] \longrightarrow trans\text{-}[Mo(CO)_2(dppe)_2] \quad (7)$$

No hydridoformato complex was formed by the reaction after 1.5 or 20 h. The results suggest that the oxidative addition involving formic C–H bond cleavage is predominant in this case.[21,22] It is interesting that the cleavage of the formic ester occurs selectively either at the C–O bond or at the formic C–H bond depending on the nature of the ester, whether it contains an unsaturated group or not.

Experimental

Most manipulations were carried out under nitrogen or argon or under vacuum using Schlenk-type flasks. Solvents were dried, purified in the usual manner, and stored under an atmosphere of argon. U.v.–visible light irradiation was performed by using a Riko 100-W high-pressure mercury lamp through a Pyrex glass filter. Infrared (KBr disk) and n.m.r. spectra were recorded on JASCO A 202 and JEOL JNM-PMX-60 (60 MHz, for ^{1}H n.m.r.) or JNM-FX-90Q (90 MHz for ^{1}H and 36.2 MHz for ^{31}P-{^{1}H}) spectrometers, respectively. The amount of dihydrogen gas in the reaction flask was measured by using a Toepler pump. The gaseous hydrocarbons evolved during the reaction were quantitatively analysed by g.l.c. by means of an internal-reference method using Gaskuropack-54 columns. Analyses of the other organic compounds were performed by g.l.c. using PEG-20M and Silicone DC 410 columns. A Shimadzu GC-3BT or GC-7APTF gas chromatograph with helium as carrier gas was used. Decomposition points were measured on a hot plate with the sample in a capillary tube sealed under vacuum and are uncorrected. *trans*-But-2-enyl acetate and allyl propionate were synthesized by alcoholysis of the corresponding acid chlorides using molecular sieve 3A as a dehydrochlorination reagent. The other esters were used as purchased. The complex $[MoH_4(dppe)_2]$ (**1**) was prepared as previously reported.[23]

Photoreactions of Complex (**1**).—*With allyl acetate.* A Pyrex Schlenk flask containing a yellow solution of complex (**1**) (0.268 g, 0.317 mmol) and allyl acetate (3.0 cm^3, 32 mmol) dissolved in benzene (20 cm^3) was irradiated by light under vacuum at room temperature for 2 h to give a reddish brown solution. The release of H_2 [0.56 mol per mol of (**1**)], propene (0.53 mol), propane (0.06 mol), and small amounts of ethene and ethane was observed. Propyl acetate (0.31 mol) was detected in the resulting solution. Removal of the solvent by a trap-to-trap method left a reddish brown solid, to which was added toluene. After removing a toluene-insoluble yellow solid by filtration, hexane was added to the filtrate. The yellow precipitate which formed was filtered off and pentane was added to the filtrate to give, on allowing the solution to stand at −78 °C, reddish orange crystals which were filtered off, washed with pentane, and dried *in vacuo*. Acetatobis[1,2-bis(diphenylphosphino)ethane]hydridomolybdenum(II) (**2**; R = Me) was thus obtained (0.129 g, 0.135 mmol, 45%). Analytical and spectral data are listed in Tables 2 and 3.

The photoreactions of complex (**1**) with other allylic carboxylates as well as vinyl and benzyl acetates were carried out similarly and the results and the analytical and spectral data of the hydridocarboxylates are listed in Tables 1—3. The hydridobenzoato complex (**2**; R = Ph) obtained by the reaction between (**1**) and allyl benzoate could not be purified enough due to its poor solubility and was characterized only by i.r. [ν(Mo–H) 1 840, ν_{asym}(OCO) 1 520, and ν_{sym}(OCO) 1 420 cm^{-1}]. Good analytical results were not obtained for the hydridomethacrylato complex (**2**; R = CH_2=CMe) because of the difficulty of freeing it from contamination by dppe ligand.

With allyl formate. To a Pyrex Schlenk flask containing complex (**1**) (0.278 g, 0.307 mmol) was added allyl formate (2.0 cm^3, 22 mmol) and benzene (20 cm^3) by means of a trap-to-trap method. The resulting solution was irradiated by the light under vacuum at room temperature for 1.5 h to give a reddish brown solution. The release of H_2 [0.73 mol per mol of (**1**)], propene (0.42 mol), propane (0.07 mol), CO_2 (0.10 mol), and small amounts of ethene and ethane was observed. No product was observed in the resulting solution. Removal of the solvent from the solution by a trap-to-trap method left a reddish brown solid, to which was added toluene. After removing a toluene-insoluble yellow solid {i.r. spectrum showed ν(CO) of *cis*-$[Mo(CO)_2(dppe)_2]$ at 1 815 and 1 770 cm^{-1}} by filtration, hexane was added to the filtrate. The yellow precipitate which formed was filtered off and pentane was added to the filtrate to give, on allowing the solution to stand at −78 °C, dark brown crystals which were filtered off, washed with pentane, and dried *in vacuo*. Bis[1,2-bis(diphenylphosphino)ethane]formatohydridomolybdenum(II) (**2**; R = H) was thus obtained (0.122 g, 0.130 mmol, 42%). Analytical and spectral data are listed in Tables 2 and 3.

When the reaction was carried out for 20 h starting from complex (**1**) (0.345 g, 0.384 mmol), allyl formate (3.0 cm^3, 33 mmol), and benzene (15 cm^3) a reddish brown solution resulted. Formation of H_2 [0.86 mol per mol of (**1**)], propene (1.14 mol), propane (0.15 mol), CO_2 (0.25 mol), and trace amounts of ethene and ethane was observed by g.l.c. On removing the solvent from the solution, a pale yellow solid obtained from which an off-white powder was separated as an insoluble portion. This is assigned to a molybdenum oxo species on the basis of its i.r. spectrum (1 600br and 960s cm^{-1}). The toluene-soluble portion was found to consist of a mixture of *cis*-[ν(CO) 1 860 and 1 780 cm^{-1}][18] and *trans*-$[Mo(CO)_2(dppe)_2]$ [ν(CO) 1 810 cm^{-1}] on the basis of its i.r. spectrum.[19]

With propyl formate. A yellow solution of complex (**1**) (0.311 g, 0.347 mmol) and propyl formate (3.0 cm^3, 31 mmol) in benzene (15 cm^3) was irradiated for 90 min, upon which the colour changed to reddish brown. In the gas phase in the reaction vessel, H_2 [1.01 mol per mol of (**1**)] together with small amounts of ethene, ethane, propene, and propane were detected. In the solution the formation of propanol (0.36 mol) was observed by g.l.c. as well as *cis*- and *trans*-$[Mo(CO)_2(dppe)_2]$ identified by i.r. spectroscopy. When the work-up was conducted under nitrogen instead of argon, *trans*-$[Mo(CO)(N_2)(dppe)_2]$ was observed in the product spectroscopically [ν(CO) 1 790, 1 815; $\nu(N_2)$ 2 070, 2 100 cm^{-1}].[21]

Increase of the reaction time to 20 h resulted in increased yields of H_2 (1.32 mol) and propanol (0.89 mol) and of the isomer ratio of *trans*- to *cis*-$[Mo(CO)_2(dppe)_2]$.

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