Photoreaction of $[MoH_4(Ph_2PCH_2CH_2PPh_2)_2]$ with Allyl Carbonates to give Hydridocarbonatomolybdenum(II) Complexes; *X*-Ray Crystal Structure of a Seven-co-ordinate Molybdenum(II) Complex $[MoH(O_2COEt)(Ph_2PCH_2CH_2PPh_2)_2]$†

Takashi Ito,* Kazuaki Hamamoto, and Susumu Kurishima
Department of Materials Chemistry, Faculty of Engineering, Yokohama National University, 156 Tokiwadai, Hodogaya-ku, Yokohama 240, Japan
Kohtaro Osakada
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4219 Nagatsuta, Midori-ku, Yokohama 227, Japan

Reaction of $[MoH_4(dppe)_2]$ (**1**) (dppe = $Ph_2PCH_2CH_2PPh_2$) with allyl alkyl carbonates $R'O_2COCH_2CH{=}CH_2$ (R' = Me or Et) in benzene under irradiation with a high-pressure mercury lamp afforded $[MoH(O_2COR')(dppe)_2]$ (**2**) together with propene and H_2. The seven-co-ordinate complexes (**2**) were characterized spectroscopically as having a pentagonal-bipyramidal structure in solution and the *X*-ray crystal structure of (**2**; R = Et) has been determined: triclinic, space group $P\bar{1}$ with $a = 16.400(6)$, $b = 18.828(7)$, $c = 11.821(3)$ Å, $\alpha = 96.22(3)$, $\beta = 99.47(3)$, $\gamma = 128.76(2)°$, $Z = 2$, and $R = 0.057$. It has a very distorted pentagonal-bipyramidal geometry with the two phosphorus atoms, hydride, and two oxygens of the carbonato ligand comprising the pentagonal girdle, in which the last two ligands are mutually *trans*.

The alkylation of allylic compounds utilizing palladium compounds as catalyst has been developed extensively by Tsuji and Trost.[1] Recently, the merit of using allyl carbonates as an allylating agent in these reactions has been exploited,[2] and the elemental reactions between allyl alkyl carbonates and ruthenium hydride have been studied.[3] Although, some complementary regioselectivities have been observed by using molybdenum complexes as catalyst,[1a,e,4] the reactions of allylic esters with them have scarcely been studied.[5] In the present report, the photoreactions of allyl alkyl carbonates $CH_2{=}CHCH_2OCO_2R$ (R = Me or Et) with the molybdenum tetrahydride $[MoH_4(dppe)_2]$ (**1**) (dppe = $Ph_2PCH_2CH_2PPh_2$), which is known to give a reactive dihydride intermediate upon light irradiation,[6] were investigated and found to yield the new hydridocarbonato complexes $[MoH(O_2COR)(dppe)_2]$ (**2**), together with propene and hydrogen as a result of selective cleavage of the allyl–oxygen bond. The complexes (**2**) were characterized spectroscopically and an *X*-ray crystal structure study of (**2a**; R = Et) showed that the carbonato ligand attaches asymmetrically to the central metal *via* two oxygen atoms.

Results and Discussion

(*a*) *Reaction of Complex* (**1**) *with Allyl Alkyl Carbonates.*—A yellow solution of $[MoH_4(dppe)_2]$ (**1**) and excess of $CH_2{=}CHCH_2OCO_2Et$ in benzene was irradiated with a 100-W high-pressure mercury lamp at room temperature for 1 h to give a dark red solution, from which the hydrido(ethyl carbonato) complex of molybdenum(II) (**2a**) (see below) was isolated in 45% yield. The reaction was accompanied by the evolution of H_2 (48%) and propene (74%) [equation (1), R = Et]. The presence of propane (13%), CO_2 (29%), and ethanol (56%) together with small amounts of ethylene and ethane in the reaction products indicates the occurrence of the secondary reaction(s).

$$\underset{(1)}{[MoH_4(dppe)_2]} + CH_2{=}CHCH_2OCO_2R \xrightarrow{h\nu} \underset{(2)}{[MoH(O_2COR)(dppe)_2]} + H_2 + MeCH{=}CH_2 \quad (1)$$

The reaction of complex (**1**) with $CH_2{=}CHCH_2OCO_2Me$ proceeded similarly to give the hydrido(methyl carbonato) complex (**2b**) (Table 1, run 2). A longer reaction time did not necessarily improve the yield of (**2a**) but raised the yield of propene and CO_2 (Table 1, run 3), suggesting that complex (**2a**) formed by the reaction may be slowly decomposed under the reaction conditions to release CO_2. As is shown in Table 1 (run 4), C–O bond cleavage did not take place with the saturated alkyl carbonate.

Reactions of *trans*-$MeCH{=}CHCH_2OCO_2Et$ and $CH_2{=}CHCH_2CH_2OCO_2Et$ with complex (**1**) under similar conditions also gave complex (**2a**), H_2, and butenes (runs 5 and 6). Butenes formed from the former consist mainly of *trans*-but-2-ene whereas those from the latter solely of but-1-ene, indicating that isomerization during the course of C–O cleavage is a minor process. The situation is similar to that found in the reaction of (**1**) with allylic esters under similar conditions.[7]

No reaction took place without light irradiation at room temperature (run 7), however the dark reaction at 80 °C afforded complex (**2a**) in low yield with concomitant formation of propene and CO_2 each in high yield (run 8). These results and the existence of the dicarbonyl complex *cis*-$[Mo(CO)_2(dppe)_2]$[8] (**3**) as a by-product in the latter reaction (see Experimental section) indicate that the primary product complex (**2a**) may be decomposed at elevated temperature to give (**3**) and CO_2. This was confirmed by an additional experiment in which complex (**2a**) was heated in toluene at 80 °C to give (**3**) together with H_2 and CO_2 [equation (2)]. The dicarbonyl complex $[Mo(CO)_2(dppe)_2]$

$$\underset{(2a)}{[MoH(O_2COEt)(dppe)_2]} \xrightarrow[\text{toluene}]{80\,°C} \underset{(3)}{[Mo(CO)_2(dppe)_2]} + H_2 + CO_2 \quad (2)$$

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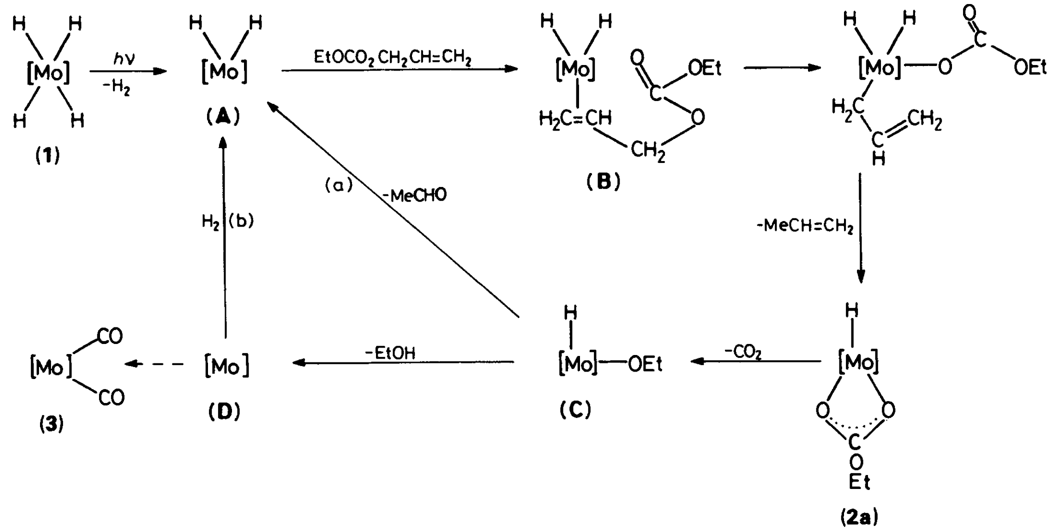
† Bis[1,2-bis(diphenylphosphino)ethane](ethyl carbonato-*O,O'*)-hydridomolybdenum(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Reactions of $[MoH_4(dppe)_2]$ (**1**) with allyl alkyl carbonates in benzene at room temperature

	$R'OCO_2R$				Products [% for (**1**)]				
Run	R′	R	mol/(**1**)	t^a/h	(**2**)	H_2	RH	C_3H_8	CO_2
1	Et	$CH_2CH{=}CH_2$	70	1	45	48	74	13	29
2	Me	$CH_2CH{=}CH_2$	28	1	46	61	93	18	29
3	Et	$CH_2CH{=}CH_2$	37	22	49	66	93	16	64
4	Et	Pr	56	2	0	19	trace	—	0
5	Et	*trans*-$CH_2CH{=}CHMe$	43	2	35	40	31^b	—	4
6	Et	$CH_2CH_2CH{=}CH_2$	40	2	*c*	15	21^d	—	43
7	Et	$CH_2CH{=}CH_2$	127	20^e			no reaction		
8	Et	$CH_2CH{=}CH_2$	32	$2^{e,f}$	24	79	214	3	171
9	Et	$CH_2CH{=}CH_2{}^g$	35	1	74	—	300	59	49

[a] With light irradiation except where indicated otherwise. [b] But-1-ene (10%) + *trans*-but-2-ene (21%). [c] Qualitatively detected by i.r. spectroscopy. [d] But-1-ene only. [e] In the dark. [f] Reaction at 80 °C. [g] Hydrogen bubbled through the solution during the reaction.



Scheme. [Mo] = $Mo(dppe)_2$

obtained here consisted of both *cis* and *trans* isomers. On heating the mixture in solution the latter isomerized gradually to the more stable *cis* isomer.[8,9]

Noteworthy is that more than 2 equivalents of propene were evolved in the thermal reaction of complex (**1**) with $CH_2{=}CHCH_2OCO_2Et$ (Table 1, run 8), which means that more than 2 mol of the latter react with 1 mol of (**1**). The possibility of catalytic cleavage of the allyl–oxygen bond of the carbonate was substantiated by carrying the photoreaction under a stream of hydrogen, where the yield of propene reached three times that of the stoicheiometric amount (Table 1, run 9). The detailed catalytic aspects of the present system will be described elsewhere.

On the basis of these experimental results, a reaction path for the present reaction was proposed as shown in the Scheme. Considering that complex (**1**) is known photochemically to generate the co-ordinatively unsaturated intermediate $[MoH_2(dppe)_2]$, (**A**) in the Scheme,[6] we assume that an allyl alkyl carbonate may co-ordinate to the dihydride intermediate through its C=C bond to give (**B**). Subsequent cleavage of the allyl–oxygen bond associated with the oxidative addition to Mo^{II} as in the case of allylic carboxylate[7] gives the hydridocarbonato complex (**2**) and propene. Complex (**2**) may then either photochemically or thermally decarboxylate to give hydridoalkoxo intermediate (**C**), which decomposes either *via* β elimination from the ethoxo ligand to regenerate (**A**) [path (a) in the Scheme] or *via* reductive elimination of alcohol to give the molybdenum(0) species (**D**) to which dihydrogen oxidatively adds to regenerate (**A**) [path (b)]. Intervention of the zerovalent intermediate (**D**) was supported by the formation of *trans*-$[Mo(N_2)_2(dppe)_2]$ when (**2a**) in toluene was thermally decomposed at 80 °C under a dinitrogen atmosphere. The formation of the dicarbonyl complex under thermal conditions may be the result of the reaction of (**D**) with acetaldehyde formed in path (a). The interaction of low-valent metal complexes with a formyl group to give carbonyl complexes has been amply precedented.[10]

Spectroscopic and X-Ray Crystallographic Analyses of the Hydrido(alkyl carbonato) Complexes (**2**).—The hydrido(alkyl carbonato) complexes of molybdenum(II) $[MoH(O_2COR)(dppe)_2]$ [R = Et, (**2a**); or Me, (**2b**)] prepared in the present study were fairly stable to the air for at least a few days in the solid state, but easily deteriorate in solution. They were readily soluble in benzene or toluene and soluble in acetone, tetrahydrofuran, or Et_2O. In a halogenated solvent such as chloroform or dichloromethane, they were soluble but deteriorated slowly even under anaerobic conditions.

In the i.r. spectra of complexes (**2**) the Mo–H stretching vibrations were observed at around 1 850 cm^{-1}, which are higher than for the parent complex (**1**) (1 810w and 1 740m cm^{-1}). They showed three bands between 1 300 and 1 600 cm^{-1} characteristic of the bidentate alkyl carbonate ligand[11] (Table 2).

In the ^1H n.m.r. spectrum of complexes (**2**) hydride signals

Table 2. Spectroscopic data for $[MoH(O_2COR)(dppe)_2]$ (**2**)

	I.r.[a]/cm^{-1}		^1H N.m.r.[b]			$^{31}P-\{^1H\}$ N.m.r.[b]		
R	ν(Mo–H)	ν(OCO_2)	δ(MoH)	$J(P_eH)$	$J(P_aH)$	δ(P_e)	δ(P_a)	$J(P_eP_a)$
Me	1 810	1 585, 1 482, 1 365	−6.04 (1 H, tt)	65.2	29.3	97.7	68.5	14.7
Et	1 880	1,565, 1 482, 1 365	−6.01 (1 H, tt)	65.6	29.0	98.1	68.7	14.7, 17.1

[a] KBr disk. [b] In C_6D_6. δ Values downfield positive from internal $SiMe_4$ (for ^1H n.m.r.) and external PPh_3 (for ^{31}P n.m.r.) references; J values in Hz.

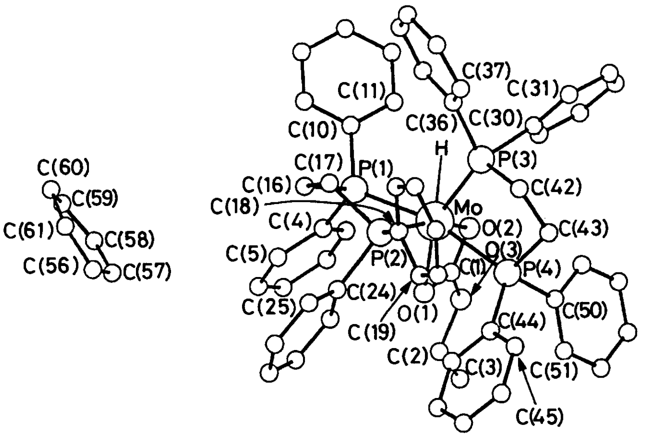


Figure 1. Molecular structure of $[MoH(O_2COEt)(dppe)_2]\cdot C_6H_6$ (**2a**) with the atom-labelling scheme

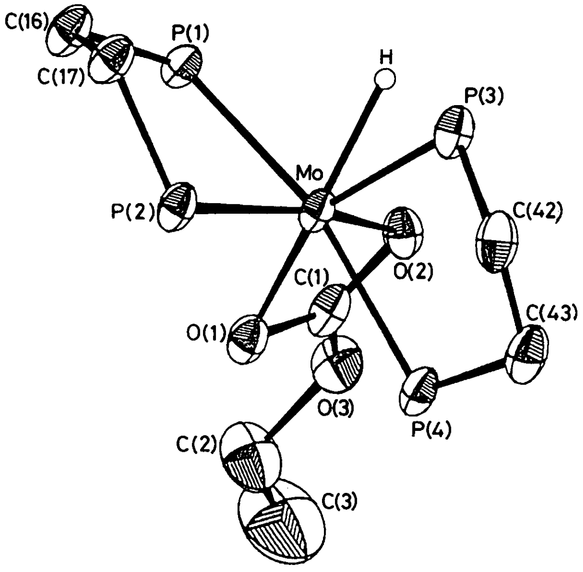
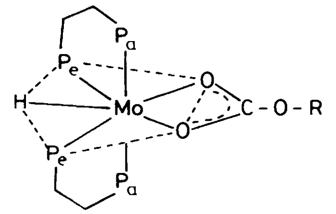


Figure 2. ORTEP drawing of $[MoH(O_2COEt)(dppe)_2]\cdot C_6H_6$ (**2a**) showing thermal ellipsoids at 30% probability. Phenyl rings are omitted for clarity

were observed at around δ − 6 as a triplet of triplets, which is similar to those observed for the related formato complex $[MoH(O_2CH)(dppe)_2]$,[12] suggesting the existence of two pairs of phosphorus nuclei each comprising equivalent atoms. The ^{31}P n.m.r. spectral results are consistent with the ^1H n.m.r. spectra (Table 2) and suggest that (**2**) adopts the pentagonal-bipyramidal structure shown below in solution at room temperature. The ^{31}P n.m.r. signals of (**2a**) in benzene broadened reversibly on raising the temperature to 100 °C, suggesting a fluxional character which is common for seven-co-ordinate complexes of this type.[13] The unstable nature of the complex at elevated temperature in solution prevented detailed study of these dynamic properties. A tentative assignment of the two sets of phosphorus atoms shown in Table 2 was made by referring to those reported by Lyons *et al.*[14] for the related seven-co-ordinated complex $[MoH(O_2CH)(PMe_3)_4]$.



In order to obtain more detailed information on the mode of co-ordination of the alkyl carbonato ligand the molecular structure of the complex $[MoH(O_2COEt)(dppe)_2]\cdot C_6H_6$ (**2a**) was investigated. Diagrams of the molecule are shown in Figures 1 and 2 and selected bond lengths and angles in Table 3.

As shown in Figure 2, (**2a**) has a very distorted pentagonal-bipyramidal geometry with the hydride and bidentate alkyl carbonato ligands in a mutually *trans* arrangement in accordance with the structure in solution determined by n.m.r. spectroscopy. Among P(2), P(3), the hydride, and two oxygens of the carbonato ligand, which comprise the pentagonal girdle, P(3) deviates from the plane considerably towards apical P(4). The hydride ligand, whose location was determined from the Fourier difference map, was found to shift greatly from the centre of P(2) and P(3) towards P(3). The small H–Mo–P(3) angle (45.0°) has been precedented in the related complex *cis*-$[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)(dppe)_2]$ [H–Mo–P 50.5(34)°].[15]

There are two sets of Mo–P distances which are in accord with those of related complexes such as *trans*-$[Mo(N_2)_2(dppe)_2]$ [2.454(1) Å],[16] $[Mo(CO)(dppe)_2]$ [2.452(2) Å],[17] *trans*-$[Mo(CO)(N_2)(dppe)_2]$ [2.448(4) Å],[17] and *cis*-$[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)(dppe)_2]$ [Mo–P_{ax} 2.465(2) and 2.454(2); Mo–P_{eq} 2.411(2) and 2.380(2) Å]:[15] Mo–P bond distances of the mutually *trans* phosphorus atoms in complex (**2a**) [Mo–P(1) 2.446(2) and Mo–P(4) 2.507(2) Å] are longer than those *trans* to the oxygen atoms of the carbonato ligand [Mo–P(2) 2.357(2) and Mo–P(3) 2.365(1) Å], reflecting the greater *trans* influence of the phosphine ligand than of the carbonato-*O*,*O*′ ligand. Relatively long Mo–P distances have been reported for octahedral *trans*-bis(dppe) complexes of Mo^{II}, *e.g.* 2.535—2.553 Å for *trans*-$[MoF(\eta^2\text{-}PhC_2H)(dppe)_2]BF_4$[18] and 2.501—2.514 Å for *trans*-$[Mo(CCPh)_2(dppe)_2]$.[19]

The large deviations from the symmetrical structure resulted in an asymmetric mode of ligation of the bidentate carbonato ligand [Mo–O(1) 2.271(2) *vs.* Mo–O(2) 2.333(4); C(1)–O(1) 1.265(3) *vs.* C(1)–O(2) 1.234(6) Å], although these values are within the normal range of values reported for the carboxylato ligand of molybdenum(II) complexes such as $[MoH(O_2CCF_3)\{P(OMe)_3\}_4]$[20] and $[MoH(O_2CH)(PMe_3)_4]$.[14] Since the carbonato ligand is flanked by four phenyl groups on P(2) and P(4) (Figure 1), and since the reported carbonato or formato ligands usually have almost symmetrical co-ordination,[14,21] it is reasonable to consider that this distortion is caused by the steric congestion around the carbonato ligand.

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 and 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} n.m.r.) spectrometers, respectively. Gases evolved during the reaction were quantitatively analysed by g.l.c. by means of an internal reference method using molecular sieve 5A (for H_2, N_2, and O_2) and Gaskuropack-54 (for hydrocarbons) columns. Analyses of the organic compounds were performed by g.l.c. using PEG-20M and silicon DC 410 columns. G.l.c. was performed on a Shimadzu GC-3BT or GC-7APTF gas chromatograph using helium as carrier gas. Alkyl carbonates were synthesized by alcoholysis of the corresponding chloroformic esters in accord with the related reported method [equation (3)] (R′ = Me or Et; R = allyl, Pr^n, but-2-enyl, or but-3-enyl).[22] The complex [$MoH_4(dppe)_2$] (**1**) was prepared as previously reported.[23]

$$\mathrm{ClCO_2R' + ROH \xrightarrow[Et_2O]{pyridine} ROCO_2R'} \qquad (3)$$

Reaction of Complex (**1**) *with Allyl Ethyl Carbonates.*—(*a*) *The photoreaction.* A Pyrex Schlenk flask containing a yellow solution of complex (**1**) (0.324 g, 0.361 mmol) and $CH_2=CHCH_2OCO_2Et$ (3.28 g, 25.2 mmol) dissolved in benzene (15 cm^3) was irradiated by light under vacuum at room temperature for 1 h to give a dark red solution. The release of H_2 [0.48 mol per mol of (**1**)], propene (0.74 mol), propane (0.13 mol), CO_2 (0.29 mol), and small amounts of ethylene and ethane was observed. In the resulting solution ethanol (0.56 mol) was detected. Removal of the solvent from the solution by a trap-to-trap method left a reddish brown solid, to which was added toluene (11 cm^3). After removing a toluene-insoluble yellow solid by filtration, hexane (15 cm^3) was added to the filtrate. On cooling the mixture at −35 °C a yellow precipitate of unreacted (**1**) was obtained (0.089 g, 23%). To the supernatant solution was added pentane (15 cm^3) and cooling the solution at −78 °C gave purple prisms, which were filtered off, washed with pentane, and dried *in vacuo*. The bis[1,2-bis(diphenylphosphino)ethane](ethyl carbonato-*O,O′*)hydridomolybdenum(II) (**2a**) thus obtained (0.160 g, 0.162 mmol, 45%) contained 1 mol of toluene of crystallization. Carbon-13 n.m.r. spectrum in C_6D_6: δ 203.7 (br s, carbonate), 163—162 (m, Ph), 61.35 (s, CH_2 of Et), 35—21 (br m, CH_2 of dppe), and 14.46 p.p.m. (s, CH_3 of Et). The rest of the analytical data are listed in Table 4. Complex (**2a**) was also obtained as a benzene solvate when recrystallized from benzene–hexane (see Table 4).

Table 3. Selected bond lengths (Å) and angles (°) for [$MoH(O_2COEt)(dppe)_2$]·C_6H_6. Estimated standard deviations are in parentheses

Mo–H	1.69	Mo–O(1)	2.271(2)
Mo–P(1)	2.446(2)	Mo–O(2)	2.333(4)
Mo–P(2)	2.357(2)	C(1)–O(1)	1.265(3)
Mo–P(3)	2.365(1)	C(1)–O(2)	1.234(6)
Mo–P(4)	2.507(2)	C(1)–O(3)	1.345(6)
P(1)–Mo–P(2)	78.31(6)	P(4)–Mo–O(1)	81.45(13)
P(1)–Mo–P(3)	114.01(6)	P(4)–Mo–O(2)	88.52(13)
P(1)–Mo–P(4)	167.24(5)	P(4)–Mo–H	117.9
P(1)–Mo–O(1)	88.17(14)	O(1)–Mo–O(2)	56.95(13)
P(1)–Mo–O(2)	92.04(13)	O(1)–Mo–H	143.4
P(1)–Mo–H	74.8	O(2)–Mo–H	91.0
P(2)–Mo–P(4)	97.45(6)		
P(2)–Mo–O(1)	106.39(12)	Mo–O(1)–C(1)	91.1(2)
P(2)–Mo–H	101.59(13)	Mo–O(2)–C(1)	89.0(4)
P(3)–Mo–P(4)	77.60(6)	O(1)–C(1)–O(2)	123.0(4)
P(3)–Mo–O(2)	110.12(11)	O(1)–C(1)–O(3)	119.8(4)
P(3)–Mo–H	45.0	O(2)–C(1)–O(3)	117.3(6)

The photoreaction of complex (**1**) (0.368 g, 0.411 mmol) with $CH_2=CHCH_2OCO_2Me$ (1.97 g, 17.0 mmol) was carried out similarly in benzene (15 cm^3) to give bis[1,2-bis(diphenylphosphino)ethane]hydrido(methyl carbonato-*O,O′*)molybdenum(II) (0.183 g, 0.188 mmol, 46%). Characterization data are listed in Tables 1 and 4. The reactions of (**1**) with *trans*-$MeCH=CHCH_2OCO_2Et$ and with $CH_2=CHCH_2CH_2OCO_2Et$ were undertaken under similar conditions and the results are also shown in Table 1.

(*b*) *The photoreaction under a stream of hydrogen.* Into a solution of complex (**1**) (0.200 g, 0.223 mmol) and $CH_2=CHCH_2OCO_2Et$ (1.02 g, 7.80 mmol) in benzene (20 cm^3) was passed dihydrogen while the system was irradiated with light at room temperature. The exhaust was connected to a trap cooled at −198 °C where volatile products were condensed. After reaction for 2 h the condensate at the trap was subjected to g.l.c. analyses to show the presence of propene (300%), propane (59%), and CO_2 (49%). Work-up of the resulting reddish brown solution as described above and recrystallization from benzene–hexane (1:1) yielded complex (**2a**) (0.176 g, 0.179 mmol, 74%).

(*c*) *The thermal reaction.* A yellow solution of complex (**1**) (0.205 g, 0.229 mmol) and $CH_2=CHCH_2OCO_2Et$ (0.95 g, 7.3 mmol) in toluene (15 cm^3) was heated under argon at 80 °C for 2 h to give a reddish brown solution. Hydrogen (79%), propene (214%), propane (3%), CO_2 (171%), and trace amounts of methane, ethene, and ethane were released together with $PrOCO_2Et$ (27%) and ethanol (67%). After removing the solvent from the resulting solution, the residual solid was worked up as above and recrystallized from benzene–hexane to give purple prisms of complex (**2a**) (0.058 g, 24%). From the mother-liquor, yellow crystals was obtained which were assigned to *cis*-[$Mo(CO)_2(dppe)_2$] (0.042 g, 0.045 mmol) on the basis of their i.r. spectrum.[8]

When a prolonged reaction time (10 h) was employed, the amounts of propene and CO_2 yielded were increased to 395 and 368%, respectively, while the isolation of (**2a**) was impossible due to its extensive decomposition. Formation of acetaldehyde

Table 4. Physical and analytical data for [$MoH(O_2COR)(dppe)_2$] (**2**)

			Analysis (%)[a]	
R	Appearance	M.p. (°C)	C	H
Me	Reddish brown prisms	157 (decomp.)	66.05 (66.95)	5.55 (5.40)
Et	Purple prisms	156 (decomp.)[b]	68.80 (69.25)	5.95 (5.80)[b]
			69.00 (69.05)	5.90 (5.70)[c]

[a] Calculated values in parentheses. [b] Data for toluene solvate, [$MoH(O_2COR)(dppe)_2$]·C_6H_5Me. [c] Data for benzene solvate, [$MoH(O_2COR)(dppe)_2$]·C_6H_6.

Table 5. Experimental data for the crystallographic analysis of complex (**2a**)

Formula	$C_{61}H_{60}MoO_3P_4$
M	1 060.98
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	16.400(6)
b/Å	18.828(7)
c/Å	11.821(3)
α/°	96.22(3)
β/°	99.47(3)
γ/°	128.76(2)
U/Å^3	2 699.4(1.4)
Z	2
F(000)	1 104
μ/cm^{-1}	3.95
D_m/g cm^{-3}	1.31
D_c*/g cm^{-3}	1.352
Crystal size (mm)	0.3 × 0.3 × 0.4
2θ Range (°)	3—50
Scan rate	6° min^{-1}
h, k, l Range	$-23 < h < 23$, $-27 < k < 27$, $0 < l < 17$
Unique reflections	9 406
Used reflections [$F_o > 3\sigma(F_o)$]	7 952
R	0.057
R'	0.066
Weighting scheme parameter q in $w = [\sigma^2(F_o) + q^2F_o^2]^{-1}$	0.031

* By flotation in a CCl_4–hexane mixture.

(5%) was observed together with $PrOCO_2Et$ (49%) and ethanol (53%).

Thermolysis of Complex (**2a**) *in Toluene*.—A toluene (5 cm^3) solution of complex (**2a**) (0.043 g, 0.044 mmol) in a Schlenk flask was heated under an argon atmosphere at 80 °C for 10 h to change the colour of the solution from reddish brown to brown. After the reaction, H_2 (56%), CO_2 (106%), methane (7%), and traces of ethene and ethane were detected. In the resulting solution, ethanol (9%) was present and [Mo(CO)$_2$(dppe)$_2$] (**3**) (0.046 g) was isolated from the solution.

X-*Ray Crystallography*.—Crystals of complex (**2a**) suitable for *X*-ray crystallography were grown in benzene–hexane at 6 °C and mounted in glass capillary tubes under argon. The unit-cell parameters were obtained by least-squares refinement of 2θ values of 25 reflections with 19° ⩽ 2θ ⩽ 22°. Intensities were collected on a Rigaku AFC-5 four-circle diffractometer by using Mo-K_α radiation (λ = 0.710 68 Å). Details of the data collection are summarized in Table 5. The standard reflections, monitored after every 200 reflections in data collection, showed no observed decrease in intensity during the measurement.

Calculations were carried out with the program systems SAPI85[24] on a FACOM A-70 computer. No absorption correction was applied. The structure was solved by common Fourier methods. A full-matrix least-squares refinement procedure was used with anisotropic thermal parameters assigned to the non-hydrogen atoms of the complex and isotropic thermal parameters to the carbon atoms of solvated benzene and to all the hydrogen atoms. The hydride was located from the Fourier difference map. Other hydrogen atoms were

Table 6. Fractional atomic co-ordinates for complex (**2a**) with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo	0.960 88(2)	0.226 45(2)	0.807 01(2)
P(1)	0.922 52(10)	0.321 37(9)	0.730 40(10)
P(2)	0.906 18(10)	0.262 19(9)	0.960 06(10)
P(3)	1.137 30(10)	0.317 03(10)	0.944 39(10)
P(4)	0.954 76(11)	0.102 02(10)	0.874 69(11)
O(1)	0.804 7(3)	0.096 9(2)	0.667 2(3)
O(2)	0.957 9(3)	0.168 7(2)	0.620 1(3)
O(3)	0.805 6(3)	0.038 8(3)	0.490 4(3)
C(1)	0.858 1(5)	0.104 0(4)	0.596 5(4)
C(2)	0.687 5(6)	−0.038 7(5)	0.464 1(7)
C(3)	0.646 9(11)	−0.109 7(8)	0.362 6(12)
C(4)	0.802 6(4)	0.259 6(4)	0.596 5(4)
C(5)	0.705 5(5)	0.240 4(5)	0.596 0(6)
C(6)	0.618 8(6)	0.190 1(6)	0.489 9(8)
C(7)	0.628 1(6)	0.159 9(5)	0.386 4(7)
C(8)	0.722 9(6)	0.178 8(5)	0.388 2(5)
C(9)	0.807 5(5)	0.227 2(4)	0.490 6(5)
C(10)	1.024 9(4)	0.424 5(4)	0.681 5(4)
C(11)	1.107 4(5)	0.432 1(4)	0.652 0(5)
C(12)	1 188 7(6)	0.513 1(5)	0.620 0(6)
C(13)	1 182 0(7)	0.582 0(5)	0.614 5(7)
C(14)	1 099 0(7)	0.574 1(5)	0.641 3(7)
C(15)	1 018 7(6)	0.493 8(4)	0.671 8(6)
C(16)	0.893 0(5)	0.373 0(4)	0.843 4(5)
C(17)	0.941 4(4)	0.377 8(4)	0.967 6(4)
C(18)	0.949 2(5)	0.272 3(4)	1.119 4(4)
C(19)	0.898 7(6)	0.190 4(5)	1.158 2(5)
C(20)	0.935 4(6)	0.194 3(5)	1.274 2(6)
C(21)	1.023 5(9)	0.280 5(8)	1.353 1(6)
C(22)	1 072 9(7)	0.361 8(6)	1.318 2(5)
C(23)	1 037 1(5)	0.358 9(5)	1.201 2(5)
C(24)	0.757 6(4)	0.191 2(4)	0.939 9(5)
C(25)	0.717 5(5)	0.198 7(5)	1.031 3(6)
C(26)	0.605 8(7)	0.148 3(6)	1.010 0(8)
C(27)	0.533 9(6)	0.089 9(6)	0.898 5(9)
C(28)	0.572 0(5)	0.083 2(5)	0.806 4(7)
C(29)	0.682 1(5)	0.131 8(4)	0.826 4(5)
C(30)	1.242 0(5)	0.331 0(4)	0.880 1(5)
C(31)	1.344 4(5)	0.370 0(5)	0.951 8(6)
C(32)	1.416 8(6)	0.372 9(6)	0.903 2(7)
C(33)	1.388 1(6)	0.337 1(6)	0.780 7(7)
C(34)	1.288 5(6)	0.301 2(5)	0.708 4(6)
C(35)	1.214 9(5)	0.297 9(4)	0.757 9(5)
C(36)	1.221 5(4)	0.441 7(4)	1.030 0(5)
C(37)	1.270 2(6)	0.475 0(6)	1.152 1(6)
C(38)	1.331 1(7)	0.571 0(7)	1.210 0(7)
C(39)	1.345 7(7)	0.632 8(6)	1.147 7(10)
C(40)	1.299 3(7)	0.601 4(5)	1.029 9(9)
C(41)	1.237 2(6)	0.506 3(5)	0.970 2(7)
C(42)	1.140 7(4)	0.257 5(4)	1.057 1(5)
C(43)	1.084 3(5)	0.156 8(4)	0.991 0(5)
C(44)	0.842 6(5)	0.022 6(4)	0.935 6(5)
C(45)	0.854 8(5)	−0.006 3(4)	1.036 2(5)
C(46)	0.763 8(7)	−0.070 7(5)	1.072 5(7)
C(47)	0.663 5(6)	−0.103 8(6)	1.013 2(7)
C(48)	0.650 4(6)	−0.073 6(6)	0.914 7(7)
C(49)	0.740 3(5)	−0.011 2(5)	0.875 3(5)
C(50)	0.942 5(5)	0.013 7(4)	0.768 0(4)
C(51)	0.856 6(5)	−0.082 8(4)	0.739 8(5)
C(52)	0.853 5(7)	−0.145 4(5)	0.659 7(7)
C(53)	0.936 5(7)	−0.109 8(6)	0.606 0(6)
C(54)	1.020 9(6)	−0.014 7(6)	0.633 4(6)
C(55)	1.023 6(5)	0.047 3(4)	0.711 6(5)
C(56)	0.467 2(16)	0.317 2(16)	0.417 0(19)
C(57)	0.467 4(14)	0.285 9(12)	0.315 9(18)
C(58)	0.493 1(14)	0.341 2(14)	0.234 6(15)
C(59)	0.528 6(14)	0.427 2(13)	0.261 2(16)
C(60)	0.558 4(18)	0.473 3(15)	0.377 8(22)
C(61)	0.520 9(19)	0.413 5(19)	0.465 1(21)
H	1.085	0.333	0.826

located at a distance of 1.00 Å from the carbon atoms by assuming an ideal geometry. These hydrogen atoms were included in least-squares calculations without refinement of their parameters. Atomic co-ordinates are listed in Table 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

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