Reactions of Bis[1,2-bis(diphenylphosphino)ethane](η-Ethylene)molybdenum(0) with some Electrophilic Reagents and Carbon Dioxide

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The reactions of [$\mathrm{Mo(C_2H_4)(dppe)_2}$] [dppe = 1,2-bis(diphenylphosphino)ethane] with $\mathrm{CF_3CO_2H}$ and organic halides RX (R = Ph, X = Cl, Br, and I; R = $\mathrm{PhCH_2}$, X = Cl; R = Me, X = I) have been studied. Reaction with $\mathrm{CF_3CO_2H}$ affords two types of complex, [$\mathrm{Mo(O_2CCF_3)_2(dppe)_2}$] and [$\mathrm{Mo(O_2CCF_3)(dppe)_2}$]$^+$ (isolated as [$\mathrm{BPh_4}$]$^-$ salt); that with RX gives [$\mathrm{MoX_2(dppe)_2}$]. The complex [$\mathrm{Mo(C_2H_4)(dppe)_2}$] reacts with $\mathrm{CO_2}$ giving two types of product depending on the reaction conditions: with light irradiation, a $\mathrm{CO_2}$ adduct is obtained, whereas with heat *cis*-[$\mathrm{Mo(CO)_2(dppe)_2}$] is the main product.

ALTHOUGH chemical properties of molybdenum complexes containing cyclopentadienyl and/or carbonyl ligands have been studied extensively,[1] the properties of molybdenum(0) complexes without these ligands have received less attention. Apart from the chemistry of η-arene complexes developed by Green *et al.*,[2-6] oxidative reactions of zerovalent molybdenum complexes hitherto reported are limited to those of iodine [7] and hydrogen [8,9] with the bis(dinitrogen) complex and the oxidative addition of pentane-2,4-dione (Hpd) to the η-ethylene complex, [$\mathrm{Mo(C_2H_4)(dppe)_2}$] [dppe = 1,2-bis(diphenylphosphino)ethane].[10] Chatt *et al.*[11,12] reported the oxidation of the dinitrogen complex by acid chloride or hydrogen bromide involving the reduction of ligating dinitrogen.

As an extension of the work on the chemistry of the complex [$\mathrm{Mo(C_2H_4)(dppe)_2}$],[10] its reactions with several electrophilic reagents have now been investigated. The reaction of the complex with carbon dioxide is also reported, a part of which has been briefly communicated.[13]

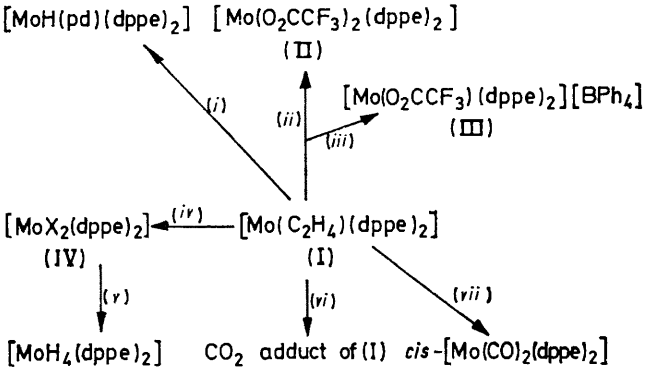
RESULTS AND DISCUSSION

The reactions investigated in the present paper are summarized in the Scheme.

Reaction with Trifluoroacetic Acid.—Our finding [10] that pentane-2,4-dione (Hpd) undergoes oxidative addition with bis[1,2-bis(diphenylphosphino)ethane[(η-ethylene)-molybdenum(0), (I), with elimination of the ethylene ligand, to give bis[1,2-bis(diphenylphosphino)ethane]-hydrido(pentane-2,4-dionato)molybdenum(II) [equation (1)] prompted us to search for other examples of such

$$\underset{\text{(I)}}{[\mathrm{Mo(C_2H_4)(dppe)_2}]} + \mathrm{Hpd} \longrightarrow [\mathrm{MoH(pd)(dppe)_2}] + \mathrm{C_2H_4} \quad (1)$$

reactions of (I) with protonic reagents. Complex (I) did not react with acetic acid at room temperature in toluene and heating the reaction mixture under reflux led to decomposition of the complex. Trifluoroacetic acid, however, reacted with (I) giving two types of product. Reaction with 10 equivalents of $\mathrm{CF_3CO_2H}$ in toluene at ambient temperature gave a deep red solution accompanied by evolution of ethane. Replacement of the solvent of the red solution by ethanol afforded a yellow precipitate and a violet solution.



SCHEME (*i*), Hpd, 110 °C;[10] (*ii*), $\mathrm{CF_3CO_2H}$, then EtOH, room temperature; (*iii*), Na[$\mathrm{BPh_4}$]; (*iv*), PhX (X = Cl, Br, or I) or $\mathrm{PhCH_2Cl}$ at 110 °C, or MeI at room temperature; (*v*), X = Cl, Li[$\mathrm{AlH_4}$], room temperature; (*vi*), $\mathrm{CO_2}$, room temperature, light; (*vii*), $\mathrm{CO_2}$, 110 °C

Treatment of the violet solution with sodium tetraphenylborate yielded fine violet crystals. The yellow precipitate is stable to air in the solid state and is soluble only in warm tetrahydrofuran (thf) and dichloromethane, from which a fine yellow crystalline complex was obtained. It was characterized as [$\mathrm{Mo(O_2CCF_3)_2}$-$\mathrm{(dppe)_2}$], (II), on the basis of its i.r. spectrum and microanalysis. I.r. bands for $\nu_{\mathrm{asym}}(\mathrm{CO_2})$ [1 705s (sh) and 1 690s cm^{-1}] and $\nu_{\mathrm{sym}}(\mathrm{CO_2})$ (1 400m cm^{-1}) are characteristic of those of the unidentate trifluoroacetato-com-

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plexes observed for palladium[14,15] and platinum.[16] Poor solubility of (II) prevented its n.m.r. study, hence the steric configuration was not clarified. Violet crystals, analysed as $[\mathrm{Mo(O_2CCF_3)(dppe)_2}][\mathrm{BPh_4}]$, (III),

$$(\mathrm{I}) + 10\mathrm{CF_3CO_2H} \overset{(ii)}{—} \begin{cases} \longrightarrow [\mathrm{Mo(O_2CCF_3)_2(dppe)_2}] \\ \qquad\qquad (\mathrm{II}) \\ \xrightarrow{(ii)} [\mathrm{Mo(O_2CCF_3)(dppe)_2}][\mathrm{BPh_4}] \\ \qquad\qquad (\mathrm{III}) \end{cases} \qquad (2)$$

(*i*), Toluene then EtOH; (*ii*), $\mathrm{Na[BPh_4]}$

are air-stable and were recrystallized from acetone–water–methanol. The frequency of $\nu_{\mathrm{asym}}(\mathrm{CO_2})$ (1 580s cm^{-1}) is quite low in comparison with that of (II) and $\nu_{\mathrm{sym}}(\mathrm{CO_2})$ was at 1 425m (sh) cm^{-1}. These i.r. data suggest that the trifluoroacetato-ligand in (III) behaves as a bidentate ligand.[14] Conductivity measurement of (III) in nitrobenzene showed it to be a 1 : 1 electrolyte.

Yields of (II) and (III) depended on the amount of $\mathrm{CF_3CO_2H}$ used. Employment of 2 equivalents of $\mathrm{CF_3CO_2H}$ yielded the violet complex (III) predominantly (yield 57%) with a small amount of the yellow complex (II) (3%), whereas use of a large excess of $\mathrm{CF_3CO_2H}$ produced (II) exclusively (27%). The gas evolved during the reaction was mainly ethane and a trace amount of ethylene as analysed by g.l.c. and ^{1}H n.m.r. spectroscopy. The first step in this reaction may be protonation of (I) by $\mathrm{CF_3CO_2H}$ forming the cationic hydride intermediate $[\mathrm{MoH(C_2H_4)(dppe)_2}][\mathrm{O_2CCF_3}]$, analogous to the process reported by Green *et al.* for $[(\eta\text{-}\mathrm{C_6H_6})\mathrm{Mo(PR_3)_3}]$.[2] The similar cationic species $[\mathrm{WH(N_2)_2(dppe)_2}][\mathrm{HCl_2}]$ has been reported by Chatt *et al.*[12] In the present case, ethylene ligand may be released as ethane through the ethyl intermediate. Kemmit *et al.*[16] reported the isolation of a tetrafluoroethyl complex on reaction of $\mathrm{CF_3CO_2H}$ with $[\mathrm{Pt(C_2F_4)(PR_3)_2}]$.[16]

In order to examine the applicability of this reaction to the other zerovalent molybdenum complexes, the reaction of *trans*-$[\mathrm{Mo(N_2)_2(dppe)_2}]$ with $\mathrm{CF_3CO_2H}$ was carried out in thf at 0 °C. An immediate reaction took place to yield a reddish brown solution accompanied by evolution of nitrogen (34% of the total $\mathrm{N_2}$ in the complex). A pale orange powder was isolated as a crude product whose i.r. spectrum had no bands due to $\nu(\mathrm{N_2})$. Elemental analysis of the product showed it to contain nitrogen (2.2%). Attempted purification of the crude product failed and led to formation of complex (II). The elementary analysis and i.r. data suggest that this nitrogen-containing complex may be $[\mathrm{Mo(N_2H_2)(O_2CCF_3)(dppe)_2}][\mathrm{O_2CCF_3}]$: 1 740m, $\nu_{\mathrm{asym}}(\mathrm{CO_2})$ of $\mathrm{CF_3CO_2}^-$ anion; 1 710s, $\nu_{\mathrm{asym}}(\mathrm{CO_2})$ of unidentate $\mathrm{CF_3CO_2}$ ligand; and 1 415m cm^{-1}, $\nu_{\mathrm{sym}}(\mathrm{CO_2})$ of unidentate $\mathrm{CF_3CO_2}$ ligand.

Reactions with Aryl and Alkyl Halides.—Since oxidative addition of alkyl or aryl halides to low-valent transition-metal complexes is known to provide alkyl or aryl transition-metal complexes, we investigated reactions of (I) with several organic halides. However, all attempts to isolate alkyl or aryl molybdenum complexes by this method using (I) were unsuccessful and resulted in formation of the dihalogeno-complex, $[\mathrm{MoX_2(dppe)_2}]$ (IV).

Apart from the dihalide clusters, dicarboxylates, and carbonyls, only a few bivalent molybdenum complexes are known,[17,18] which were prepared by reduction of Mo$^{\mathrm{III}}$ complexes. More recently Chatt and Wedd[19] briefly communicated the formation of $[\mathrm{MoCl_2(dppe)_2}]$ on reduction of $[\mathrm{MoCl_3(thf)_3}]$ by sodium amalgam in the presence of dppe under argon. Heating the orange suspension of the ethylene complex (I) in excess of chlorobenzene at 120 °C yielded a yellow product, accompanied by evolution of 1 equivalent of ethylene. The yellow complex was characterized as $[\mathrm{MoCl_2(dppe)_2}]$, (IVa). Similarly, bromo- and iodo-benzene reacted with (I) in boiling toluene to yield $[\mathrm{MoBr_2(dppe)_2}]$, (IVb), and $[\mathrm{MoI_2(dppe)_2}]$, (IVc), respectively. Preparation of the analytically pure di-iodo-complex was impossible due to its poor solubility. The i.r. spectra of (IVa)—(IVc) were almost identical and little change was observed between them and that of starting complex (I). Complex (IVa) was also obtained on reaction of (I) with benzyl chloride. The purified complex obtained by this reaction was identified as $[\mathrm{MoCl_2(dppe)_2}]\cdot\mathrm{CH_2Cl_2}$, the solvent for recrystallization being incorporated in the crystalline lattice.

Methyl iodide reacted with complex (I) at room temperature to yield, ultimately, di-iodo-complex (IVc), with evolution of methane, ethylene, and ethane. As the reaction proceeded, the initial reddish orange clear solution gradually became heterogeneous, yielding a reddish orange precipitate. The latter then dissolved and finally the yellow complex (IVc) deposited. This feature of the reaction and the formation of methane and ethane suggest intermediate formation of a methylmolybdenum complex, as a result of oxidative addition of methyl iodide to (I). This intermediate may further disproportionate or be attacked by methyl iodide to yield the di-iodo complex (IVc). Failure to isolate the intermediate suggests that it is very unstable with a very short life-time.

Treatment of (IVa) with $\mathrm{Li[AlH_4]}$ in thf at room temperature yielded the tetrahydrido-complex $[\mathrm{MoH_4(dppe)_2}]$,[20,21] $\nu(\mathrm{Mo{-}H})$ at 1 725 cm^{-1}, whose ^{1}H n.m.r. spectrum in $\mathrm{CH_2Cl_2}$ at room temperature consisted of the hydride proton at 4.02 p.p.m. upfield from tetramethylsilane (1 : 4 : 6 : 4 : 1 quintet).

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Reaction with Carbon Dioxide.—No interaction was observed when carbon dioxide was bubbled through a suspension of complex (I) in toluene at room temperature in the dark. However, when the system was irradiated, CO_2 apparently reacted with the complex to yield an adduct. The adduct showed a broad strong i.r. absorption centred at 1 680 cm^{-1}. On thermolysis and decomposition by conc. H_2SO_4, the adduct evolved ethylene and CO_2. Some examples of the interactions of CO_2 with zerovalent transition-metal complexes to give CO_2 complexes have been reported for platinum,[22] nickel,[23] and rhodium.[24] Poor solubility of the adduct in common solvents and its unstable nature prevented an unambiguous assignment.

On the other hand, passing CO_2 through a boiling toluene solution of (I) yielded a yellow complex identified as *cis*-[Mo(CO)$_2$(dppe)$_2$] [8,25] on the basis of the i.r. spectrum and elemental analysis. Carbon monoxide in this reaction system may be produced by reduction of CO_2 on molybdenum metal with concomitant formation of diphosphine oxide, as indicated by the i.r. spectrum of the crude product. The reaction of CO_2 with the reaction product of $[(\eta\text{-}C_5H_5)_2MoH_2]$ and $AlMe_3$ to yield, after hydrolysis, $[(\eta\text{-}C_5H_5)_2Mo(CO)Br]^+$ has been reported recently,[26] and is, to our knowledge, the sole example of direct formation of a carbonyl complex from CO_2.

EXPERIMENTAL

All manipulations were carried out under an atmosphere of oxygen-free dry nitrogen or argon where appropriate or *in vacuo*. Solvents were dried in the usual manner, distilled, and stored under nitrogen or argon.

I.r. spectra were recorded on a Hitachi EPI-G3 spectrometer using KBr pellets prepared under an inert atmosphere. Measurement of ^{1}H n.m.r. spectra on a JEOL PS-100 spectrometer was carried out by Mr. Y. Nakamura and microanalyses by Mr. T. Saito of our research laboratory. Gases evolved during the reaction and on thermal decomposition were analysed by g.l.c. and/or mass spectrometry after collecting the gas with the aid of a Toepler pump, by which means the volume of the gas was also measured.

Bis[1,2-bis(diphenylphosphino)ethane](η-ethylene)molybdenum(0), (I),[10] and *trans*-bis[1,2-bis(diphenylphosphino)-ethane]bis(dinitrogen)molybdenum(0) were prepared according to the literature.[19] Trifluoroacetic acid (guaranteed grade), sodium tetraphenylborate, lithium tetrahydridoaluminate, and organic halides were used as purchased without further purification. Carbon dioxide was dried by passing the gas through a trap cooled at −78 °C before introducing it into the reaction flask.

Reactions of $[Mo(C_2H_4)(dppe)_2]$, (I), *with Trifluoroacetic Acid*.—To complex (I) (0.37 g, 0.40 mmol) suspended in toluene (15 cm^3) was added trifluoroacetic acid (0.32 cm^3, 4.1 mmol) by means of a syringe. The system, which turned red immediately, was stirred for 1 h at room temperature. Solvent was then evaporated off *in vacuo* to leave a deep violet oily material to which ethanol (20 cm^3) was added to yield a yellow precipitate and a violet solution.

The precipitate was separated by filtration from the violet solution. (As the precipitate was too fine to be collected effectively by filtration, its partial loss was unavoidable.) The fine yellow powder thus obtained was washed with ethanol and diethyl ether and dried *in vacuo* (0.10 g, 22%). This was recrystallized from warm tetrahydrofuran to yield fine yellow *crystals* of $[Mo(O_2CCF_3)_2(dppe)_2]$, m.p. 224—226 °C (decomp.) (Found: C, 59.0; H, 4.2; F, 10.3. Calc. for $C_{56}H_{48}F_6MoO_4P_4$: C, 60.1; H, 4.3; F, 10.2%).

To the violet filtrate, sodium tetraphenylborate (0.41 mmol) was added to yield a violet precipitate. On addition of water (*ca.* 10 cm^3) the solution became colourless. The violet precipitate was filtered off and washed with water. The crude product thus obtained was dissolved in acetone (10 cm^3) and on addition of methanol (10 cm^3) and water violet *crystals* of $[Mo(O_2CCF_3)(dppe)_2][BPh_4]$ were formed, filtered off, and dried *in vacuo* (0.26 g, 49%), m.p. 122—123 °C (decomp.), molar conductivity in nitrobenzene (7.562×10^{-4}M) at 20 °C, 14.3 S cm^2 mol^{-1} (Found: C, 69.2; H, 5.4; F, 4.2. Calc. for $C_{78}H_{68}BF_3MoO_2P_4$: C, 70.7; H, 5.2; F, 4.3%).

The reaction with a large excess of CF_3CO_2H was conducted without solvent as follows. On addition of CF_3CO_2H (3.0 cm^3, 39 mmol) to the solid complex (I) at room temperature, immediate reaction took place to afford a dark red solution with effervescence and loss of heat. The evolved gas was examined by g.l.c. and found to consist mainly of ethane with a trace of ethylene. After 30 min stirring, ethanol (10 cm^3) was added to yield a fine yellow precipitate, which was filtered off, washed with ethanol, diethyl ether, and n-hexane, and dried *in vacuo*. The product analysed as $[Mo(O_2CCF_3)_2(dppe)_2]$.

Reaction of trans-$[Mo(N_2)_2(dppe)_2]$ *with Trifluoroacetic Acid*.—On addition of CF_3CO_2H (0.15 cm^3, 2.0 mmol) to an orange suspension of *trans*-$[Mo(N_2)_2(dppe)_2]$ (0.15 g, 0.16 mmol) in thf (5 cm^3) at −15 °C, an immediate reaction took place yielding a reddish brown solution. The mixture was stirred for 3 h at −15 to 0 °C. Ethanol (10 cm^3) was added to the solution to give a reddish brown solution. Solvent was evaporated off *in vacuo* to give a pale orange solid which was washed with n-hexane and dried *in vacuo*. The pale orange powder (0.20 g) thus obtained was tentatively assigned to $[Mo(O_2CCF_3)(N_2H_2)(dppe)_2][O_2CCF_3]$. Attempted purification of the crude product by recrystallization from tetrahydrofuran–diethyl ether–ethanol only led to formation of $[Mo(O_2CCF_3)_2(dppe)_2]$.

Reactions of Complex (I) *with Organic Halides*.—*Reaction with chlorobenzene*. Chlorobenzene (5.0 cm^3, 49 mmol) was distilled over calcium hydride into a flask containing complex (I) (0.1798 g, 0.1953 mmol) under a high vacuum. The mixture was heated at 120 °C with stirring for 7 h. The initial orange suspension became a dark orange solution, from which, on cooling to room temperature, a yellow precipitate was obtained. The gas evolved on reaction was mainly ethylene with a trace amount of ethane [0.209 mmol, 107% on the basis of the complex (I)]. The yellow precipitate was filtered off, washed with diethyl ether, and dried *in vacuo*. The yellow *powder* thus obtained was characterized as $[MoCl_2(dppe)_2]$, (IVa) (0.1395 g, 74%). Recrystallization of (IVa) from hot thf

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yielded yellow crystals which contained 1 mol of solvated thf, [MoCl$_2$(dppe)$_2$]·C$_4$H$_8$O (Found: C, 65.0; H, 5.8; Cl, 6.9. Calc. for C$_{56}$H$_{56}$Cl$_2$MoOP$_4$: C, 64.9; H, 5.5; Cl, 6.8%).

Reaction with bromobenzene. Into an orange suspension of (I) (0.21 g, 0.23 mmol) in toluene (7.5 cm^3), bromobenzene (0.50 cm^3, 4.5 mmol) was added by means of a syringe. The mixture was heated under reflux for 2 h. On cooling the pale orange clear solution to the room temperature a yellow precipitate was obtained, which was filtered off, washed with diethyl ether and n-hexane, and dried *in vacuo*. The crude product was reprecipitated by hot thf to yield a yellow *powder*, which was analysed as [MoBr$_2$(dppe)$_2$], (IVb) (0.17 g, 71%) (Found: C, 59.0; H, 5.0; Br, 14.4. Calc. for C$_{52}$Br$_2$H$_{48}$MoP$_4$: C, 59.3; H, 4.6; Br, 15.2%).

Reaction with iodobenzene. Reaction as above, using (I) (0.17 g, 0.19 mmol) and iodobenzene (0.50 cm^3, 4.4 mmol), yielded a yellowish brown *powder* {0.10 g, 47% as [MoI$_2$(dppe)$_2$], (IVc)}. This complex, being insoluble in common solvents, could not be purified.

Reaction with benzyl chloride. Similar reaction of (I) (0.27 g, 0.29 mmol) with benzyl chloride (0.50 cm^3, 4.4 mmol) gave [MoCl$_2$(dppe)$_2$], (IVa). The product was crystallized from dichloromethane and n-hexane to yield pale orange *crystals* of [MoCl$_2$(dppe)$_2$]·CH$_2$Cl$_2$ (0.25 g, 82%) (Found: C, 61.6; H, 5.3; Cl, 13.0. Calc. for C$_{53}$H$_{50}$Cl$_4$MoP$_4$: C, 60.7; H, 4.8; Cl, 13.5%).

Reaction with methyl iodide. Methyl iodide (7.0 cm^3, 110 mmol) was distilled over calcium hydride *in vacuo* to a flask containing (I) (0.36 g, 0.39 mmol). On raising the temperature from -190 °C to room temperature a reddish orange clear solution resulted. On stirring the solution at room temperature the system gradually turned through a red suspension to a dark red solution with a yellow precipitate in 30 h. The gases evolved were CH$_4$ (0.198 mmol, 51% based on Mo atom), C$_2$H$_4$, and a small amount of C$_2$H$_6$ (0.336 mmol, 86% based on Mo atom). On addition of diethyl ether (20 cm^3) to the reaction mixture, a dull yellow powder was precipitated, which was filtered off, washed with n-hexane, and dried *in vacuo*. The yellow *powder* (0.34 g, 87%) thus obtained was identified as [MoI$_2$(dppe)$_2$] on the basis of the i.r. spectrum.

Reaction of Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*dichloromolybdenum*(II) *with Lithium Tetrahydridoaluminate.*—The complex [MoCl$_2$(dppe)$_2$] (0.07 g, 0.07 mmol) was allowed to react with a large excess of Li[AlH$_4$] in thf (10 cm^3). An immediate reaction took place with violent effervescence to afford a brown-grey suspension. The solvent was evaporated off to give a brown oily material which was extracted with toluene (30 cm^3). The extract was concentrated to 5 cm^3 *in vacuo*. On addition of ethanol (15 cm^3) to the concentrated solution a yellow precipitate was obtained which was filtered off, washed with methanol, diethyl ether, and n-hexane, and dried *in vacuo*. The pale yellow crystalline powder thus obtained (0.02 g) was assigned to [MoH$_4$(dppe)$_2$] on the basis of its i.r. and ^{1}H n.m.r. spectrum.

Reaction of Complex (I) *with Carbon Dioxide.*—*With irradiation of light.* Carbon dioxide was bubbled into a toluene suspension (50 cm^3) of complex (I) (0.15 g, 0.16 mmol) at room temperature for 7 h, while the system was irradiated with light (high-pressure mercury lamp, 100 W) through the Pyrex reaction flask. The system was concentrated *in vacuo* and n-hexane (20 cm^3) was added to the mixture. The resulting pale orange precipitate was filtered off, washed with n-hexane, and dried *in vacuo*. The pale orange powder (0.10 g) thus obtained was submitted to i.r. spectral measurement, thermolysis, and decomposition by conc. H$_2$SO$_4$ (see text).

With heat. Carbon dioxide was bubbled through a heated toluene suspension (20 cm^3) of complex (I) (0.43 g, 0.47 mmol) under reflux for 4 h. Evolution of C$_2$H$_4$ and a trace of C$_2$H$_6$ was detected by g.l.c. After being cooled to room temperature in an atmosphere of CO$_2$, the reaction mixture was filtered to remove a small amount of precipitate. The brown filtrate was concentrated to 1 cm^3. On addition of n-hexane to the concentrated solution a pale brown precipitate was obtained, which was filtered off and dried *in vacuo*. This crude product (0.30 g) showed i.r. bands at 1 858s, 1 812m, and 1 780s cm^{-1} [ν(C=O)] and 1 180m and 1 120m cm^{-1} [ν(P=O)]. The crude product was crystallized from tetrahydrofuran–ethanol to yield yellow *needles* which were identified as *cis*-[Mo(CO)$_2$(dppe)$_2$] on the basis of the i.r. spectrum and elemental analysis (Found: C, 68.2; H, 5.3. Calc. for C$_{54}$H$_{48}$MoO$_2$P$_4$: C, 68.4; H, 5.1%).

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