Preparation and Characterization of (1—2-η-Ethylene)bis[1,2-bis(diphenylphosphino)ethane]molybdenum(0) and Bis[1,2-bis(diphenylphosphino)ethane]hydrido(pentane-2,4-dionato)molybdenum(II)

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Treatment of [Mo(acac)$_3$] (acac = pentane-2,4-dionato) and 1,2-bis(diphenylphosphino)ethane (dppe) in toluene with AlEt$_3$ under an argon atmosphere yields the η-ethylene complex [Mo(C$_2$H$_4$)(dppe)$_2$], (I), and [MoH(acac)(dppe)$_2$], (II). The relative yields of complexes (I) and (II) depends on the amount of AlEt$_3$ used. Characterization of these complexes has been achieved chemically and spectroscopically. Complex (II) is also produced by the reaction of (I) with pentane-2,4-dione. Reversible interconversion of complex (I) and *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] has been observed. Reaction of complex (I) with tetracyanoethylene (tce) yields an η-tce complex. Complex (II) has been found to initiate polymerization of acrylonitrile.

THE chemistry of molybdenum is currently being studied by several groups of workers with respect to the special roles of molybdenum played in nitrogenase [1] and olefin-metathesis reactions,[2] where co-ordination of dinitrogen and olefin, respectively, to molybdenum is believed to be a key intermediate step. Amongst the molybdenum complexes investigated, carbonyl and cyclopentadienyl complexes have been studied extensively, and several ethylene,[3-7] hydrido-,[8-11] and alkyl [6,8,12] complexes have been reported. However, examples of isolated low-valent molybdenum complexes free from such ligands as carbonyl and cyclopentadienyl are few. *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] [13-16] [dppe = 1,2-bis(diphenylphosphino)ethane] is one of the most extensively studied molybdenum(0) complexes in this category, and some tertiary-phosphine hydrido-complexes have been reported recently: [(Haryl)Mo(H)$_2$(tertiary phosphine)$_2$]; [17] [Mo(H)$_4$(tertiary phosphine)$_4$]; [18] and [Mo(H)$_2$(dppe)$_2$] and [(dppe)(H)$_2$Mo(μ-dppe)Mo(H)$_2$(dppe)].[13] In the course of our systematic study on the preparation of transition-metal alkyl and hydride complexes, η-ethylene and (pentane-2,4-dionato)hydrido-complexes of molybdenum were obtained with dppe.[19] The present paper reports in detail the preparation and characterization of these new complexes.

RESULTS AND DISCUSSION

Preparation.—Hidai *et al.* reported that treatment of molybdenum(III) pentane-2,4-dionate with triethylaluminium, AlEt$_3$, in the presence of dppe under an

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[1] See for example, J. Chatt and G. J. Leigh, *Chem. Soc. Rev.*, 1972, **1**, 121 and refs. therein.

[2] N. Calderon, *Accounts Chem. Res.*, 1972, **5**, 127.

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[17] M. L. H. Green and W. E. Silverthorn, *J.C.S. Chem. Comm.*, 1973, 301.

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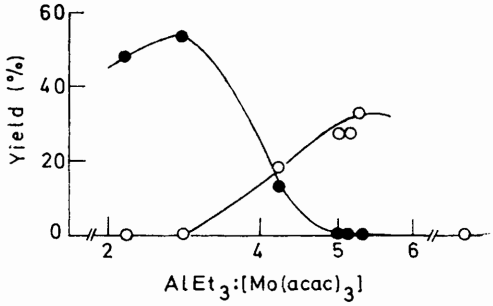
[19] T. Ito, T. Kokubo, T. Yamamoto, A. Yamamoto, and S. Ikeda, *J.C.S. Chem. Comm.*, 1974, 136.

atmosphere of dinitrogen at room temperature afforded the bis(dinitrogen) complex *trans*-[$Mo(N_2)_2(dppe)_2$].[13] When the same reaction was carried out under an argon atmosphere instead of dinitrogen, orange prisms of (1—2-η-ethylene)bis[1,2-bis(diphenylphosphino)ethane]-molybdenum(0), (I), and deep brown fine needles of [1,2-bis(diphenylphosphino)ethane]hydrido(pentane-2,4-dionato)molybdenum(II), (II), were formed [equation (1)]. The ratio of the products (I) and (II) was found to

$$[Mo(acac)_3] + 2dppe + nAlEt_3 \xrightarrow{Ar} \underset{(I)}{[Mo(C_2H_4)(dppe)_2]} + \underset{(II)}{[MoH(acac)(dppe)_2]} \quad (1)$$

depend on the amount of $AlEt_3$ used (Figure); use of over 5 equivalents of $AlEt_3$ yielded complex (I) almost exclusively, whereas 2—3 equivalents gave (II) predominantly. Both complexes were obtained with 3—5 equivalents of $AlEt_3$.



Effect of the molar ratio $AlEt_3$: [$Mo(acac)_3$] on yields of the complexes [$Mo(C_2H_4)(dppe)_2$] (○) and [$MoH(acac)(dppe)_2$] (●)

Complex (II) was also prepared from (I) by oxidative addition of pentane-2,4-dione (Hacac) in toluene at 110 °C [equation (2)]. Conversely, attempts to prepare

$$(I) + Hacac \xrightarrow[110\,°C]{toluene} (II) + C_2H_4 \qquad (2)$$

complex (I) from (II) by further reduction with $AlEt_3$ were unsuccessful and only a red oily material, possibly [$MoH(acac)(dppe)_2$],$AlEt_3$, resulted. Treatment of this oil with ethanol gave the starting complex (II) accompanied by vigorous effervescence.

Characterization and Properties of Complex (I).—Complex (I) is diamagnetic and only slowly decomposed in air. It is soluble to a limited extent in warm tetrahydrofuran (thf), toluene, and benzene, and can be recrystallized from these solvents. Thermolysis of the complex at 210 °C evolved 109% of the theoretical amount of ethylene, and 73% ethylene was detected on iodolysis. Decomposition of complex (I) by conc. H_2SO_4 also released 81% ethylene. The action of hydrochloric acid on the complex caused evolution of C_2H_4 and C_2H_6 (2 : 1), while only ethylene was detected on alcoholysis. The i.r. spectrum of complex (I) showed a weak band at 2 950 cm^{-1}, assignable to ν(C–H) of the co-ordinated ethylene, as well as bands from the dppe ligands.

Table 1 shows ^1H n.m.r. data for complex (I). Some deviation of observed integrated areas from the calculated values may be caused by the low signal to noise ratio of the spectrum due to the poor solubility of the complex. The observation of signals due to thf, the intensity of which corresponded to half that of the co-ordinated ethylene protons, suggests that the solvent used for recrystallization is incorporated in the crystal lattice. In fact, the thf signals disappeared completely when the recrystallized sample was washed with n-hexane; the latter caused the destruction of the crystal form and gave an orange powder. A CD_2Cl_2 solution of the complex was stable enough for n.m.r. measurement but deteriorated after 1 day at room temperature. The ^1H n.m.r. spectrum of the deteriorated sample showed no signal due to co-ordinated ethylene but gave a sharp singlet at 5·37 p.p.m. due to free ethylene. The proton-decoupled ^{31}P n.m.r. spectrum of the complex showed a sharp singlet both at room temperature in CD_2Cl_2 and at −80 °C in thf, indicating complete equivalence of the four phosphorus atoms.

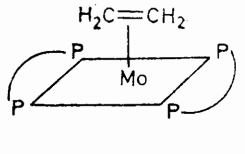
TABLE 1

^1H N.m.r. data for the complex [$Mo(C_2H_4)(dppe)_2$] (I) (220 MHz, in CD_2Cl_2 at room temperature, tetramethylsilane as internal standard)

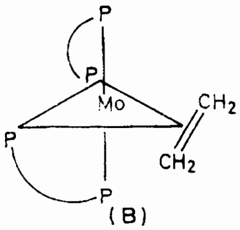
δ/p.p.m.	Multiplicity	Integrated area	Assignment (expected areas in parentheses)
1·50	Broad singlet	1	Not assignable
1·79	Triplet	2	$-CH_2CH_2-$ of thf
2·13	Doublet [a]	4	Co-ordinated ethylene protons(4)
2·82	Broad singlet	5	$-CH_2CH_2-$ of dppe(8)
3·63	Triplet	2	$-CH_2OCH_2-$ of thf
5·25	Singlet		Protons of solvent impurity, CH_2Cl_2
6·59	Complex	9	*ortho*-Protons of Ph rings (8) [b]
7·00	Triplet	42	*meta*-Protons of Ph rings (8) [b]
7·12	Triplet		*para*-Protons of Ph rings (8) [b]
7·25	Complex		*meta*- and *para*-Protons of Ph′ rings (12) [b]
7·35	Complex		*ortho*-Protons of Ph′ rings (8) [b]

[a] The coupling constant was 10 Hz. The same value was obtained in the 100 MHz spectrum. [b] The phenyl ring protons are of two types designated as Ph and Ph′ (see text).

The n.m.r. evidence suggests that the complex (I) may have the square-pyramidal structure (A). The trigonal-bipyramidal structure, (B), however, cannot be ruled out if rapid rearrangement of the dppe ligands in the complex by a Berry mechanism[20] occurs. The eight phenyl groups of the dppe ligands in (A) and (B) are



(A)



(B)

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[20] R. S. Berry, *J. Chem. Phys.*, 1960, **32**, 933.

divided into two types with regard to their magnetic environments, those nearest to the ethylene ligand and the others farther from it. Both structures are in agreement with the observed separation of the phenyl signals at 6·6—7·4 p.p.m. into two equally integrated types (Ph and Ph′ in Table 1).

Reversible interconversion of (I) and a bis(dinitrogen) complex was observed. Thus, on passing dinitrogen gas into a solution of complex (I) heated under reflux in toluene, *trans*-[Mo(N_2)$_2$(dppe)$_2$] was obtained. Conversely, the bis(dinitrogen) complex was converted into (I) on passing ethylene into a boiling toluene solution of the former [equation (3)]. The fact that this inter-

$$(\mathrm{I}) + 2\mathrm{N_2} \rightleftharpoons \textit{trans}\text{-}[\mathrm{Mo(N_2)_2(dppe)_2}] + \mathrm{C_2H_4} \qquad (3)$$

conversion took place only at elevated temperatures implies that there may be a fairly high energy barrier to release of C_2H_4 or N_2 from the molybdenum complexes. When complex (I) is heated under reflux with Hacac, C_2H_4 is presumably released first and then the enolate of Hacac attacks the unstable intermediate [Mo(dppe)$_2$] giving the oxidative-addition product, (II).

On the other hand, a strongly electron-deficient olefin such as tetracyanoethylene (tce) easily replaced ethylene from (I), forming a stable η-tce zero-valent complex. Thus, addition of tce to a toluene dispersion of complex (I) at room temperature caused an immediate colour change from orange to green and then to purple accompanied by evolution of ethylene. The resulting purple complex, whose i.r. spectrum showed at least four ν(C≡N) bands at 2 180—2 100 cm^{-1} and ν(C=C) at 1 470 cm^{-1}, was tentatively assigned as [Mo(tce)$_2$(dppe)$_2$]. The lowering of ν(C=C) by 200 cm^{-1} compared with the free ligand indicates that tce is co-ordinated to molybdenum through the olefinic double bond.

$$(\mathrm{I}) + \mathrm{tce} \longrightarrow [\mathrm{Mo(tce)_2(dppe)_2}] + \mathrm{C_2H_4} \qquad (4)$$

Characterization and Properties of Complex (II).—Complex (II) is diamagnetic. It is soluble in thf, benzene, and toluene and was recrystallized from toluene–ethanol. Although dihydrogen was not released on thermolysis, iodolysis, or acidolysis, the i.r. spectrum of the complex showed a band of medium intensity at 1 803 cm^{-1} ascribable to ν(Mo–H). I.r. bands originating from the acac ligand are listed in Table 2. The assignment of each band was made by comparison with those of the complex [Mo(acac)$_3$]. Further evidence for the presence of the acac ligand stems from the fact that Hacac was extracted by Et_2O from a mixture of complex (II) and D_2SO_4 in 60% yield (determined spectrophotometrically).

TABLE 2

I.r. bands (cm^{-1}) originating from the acac ligand

Complex	ν(C=C)	ν(C=O)	δ(CH_3)$_{asym}$	ν(C–C)	π(C–H)
[MoH(acac)(dppe)$_2$], (II)	1 560s	1 510s	1 390s	1 265m	766w
[Mo(acac)$_3$]	1 560 (sh)	1 510vs	1 375s	1 275m	780m

The ^1H n.m.r. spectrum of complex (II) (C_6D_6 100 MHz, room temperature) showed an Mo–H signal at −4·1 p.p.m. (upfield of Me_4Si, multiplet) and CH_3 and CH resonances of the acac ligand at 1·16 (singlet) and 4·14 p.p.m. (singlet), respectively. Methylene and phenyl protons of the dppe ligand gave signals at *ca.* 2·5 (broad singlet) and 7·1—7·8 p.p.m. (complex).

The isolation of analytically pure (II) was not possible due to the difficulty of separating unreacted dppe from the complex. The deuteride analogue was prepared by reaction of complex (I) with 3,3-dideuteriopentane-2,4-dione ([$^2H_2$]Hacac) [equation (5)]. The

$$(\mathrm{I}) + [{}^2\mathrm{H_2}]\mathrm{Hacac} \xrightarrow[110\,^{\circ}\mathrm{C}]{\text{toluene}} [\mathrm{MoD([{}^2H_1]acac)(dppe)_2}] + \mathrm{C_2H_4} \qquad (5)$$

ν(Mo-H) band at 1 803 cm^{-1} shifted to 1295 cm^{-1} on deuteriation [ν(Mo–H)/ν(Mo–D) = 1·39]. Formation of complex (II) by direct reaction of (I) with Hacac [equation (2)] and formation of the deuteride analogue [equation (5)] supports the proposed formulation of (II).

Complex (II) was found to behave as an efficient initiator for polymerization of acrylonitrile. On addition of the complex to acrylonitrile at room temperature, an immediate reaction took place and poly(acrylonitrile) was formed. The conversion was 70% complete in 3 h. This is in contrast to the reaction of acrylonitrile with complex (I), where 4% polymer was obtained in 1 day. The polymerization of vinyl monomers by transition-metal hydride complexes has been reported for ruthenium [21] and cobalt.[22] Less electronegative olefins, such as methacrylonitrile, methyl methacrylate, styrene, butadiene, cyclo-octa-1,5-diene, and cyclo-octene were not polymerized by complex (II). Reaction of the complex (II) with 2 mol hydrogen chloride in toluene yielded yellowish orange crystals of formula [MoH(acac)(dppe)$_2$]Cl_2. The i.r. spectrum of this complex retained the acac bands and ν(Mo–H) at 1 880 cm^{-1}. The ionic molybdenum(IV) complex was reconverted to (II) by treatment with methylmagnesium bromide.

Alkyl complexes containing both acac and tertiary phosphine ligands have been recently reported for iron,[23] nickel,[24,25] and platinum.[26] In the system studied here, an alkyl(pentane-2,4-dionato) complex of the type [MoEt(acac)(dppe)$_2$] may be produced as an intermediate, which is converted to (II) by β-elimination or attacked further by triethylaluminium to give a diethylmolybdenum complex which, on splitting and disproportionation of the ethyl groups, gives (I). The

[21] T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 1970, **92**, 3011.

[22] A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *J. Amer. Chem. Soc.*, 1971, **93**, 371; A. Yamamoto and S. Ikeda, *Progr. Polymer Sci. Japan*, 1972, **3**, 49.

[23] Y. Kubo, A. Yamamoto, and S. Ikeda, *J. Organometallic Chem.*, 1972, **46**, C50.

[24] P. W. Jolly, K. Jonas, C. Krüger, and Y.-H. Tsay, *J. Organometallic Chem.*, 1971, **33**, 109.

[25] A. Yamamoto, T. Yamamoto, T. Saruyama, and Y. Nakamura, *J. Amer. Chem. Soc.*, 1973, **95**, 4073.

[26] J. R. Hall and G. A. Swile, *J. Organometallic Chem.*, 1972, **46**, C50.

isolated products (I) and (II) are both stable towards attack by triethylaluminium.

EXPERIMENTAL

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

I.r. spectra were obtained on a Hitachi EIP-G3 spectrometer; KBr pellets were prepared under an inert atmosphere. ^{1}H N.m.r. spectra were recorded on JEOL PS-100 (100 MHz) and Varian HR-220 (220 MHz) spectrometers with tetramethylsilane as internal standard. Proton-decoupled ^{31}P n.m.r. spectra (40·5 MHz) were recorded on a Varian XL-100 spectrometer operating in the Fourier-transform mode. Mass spectra were run on a Hitachi RMU-5B spectrometer. Visible-u.v. measurements were made using a Shimadzu SV-50A spectrometer. Microanalyses were carried out by Mr. T. Saito of our Research Laboratory. Analysis of gases evolved by thermolysis and during the reaction was carried out by gas chromatography 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.

Molybdenum(III) pentane-2,4-dionate [27] and 1,2-bis(diphenylphosphino)ethane (dppe) [28] were prepared according to the reported methods. Triethylaluminium was used as purchased from Ethyl Corp. Ltd. Pentane-2,4-dione (Hacac) (guaranteed grade) was used as purchased from Tokyo Kasei Ltd. without further purification. 3,3-Dideuteriopentane-2,4-dione ([^{2}H$_2$]Hacac) was prepared by repeated deuteriation of Hacac with deuterium oxide in the presence of sodium deuteroxide; the degree of deuteriation, from ^{1}H n.m.r. spectroscopy, was 80·5%. *trans*-Bis[1,2-bis(diphenylphosphino)ethane]bis(dinitrogen)molybdenum(0) was prepared as described previously.[14] Tetracyanoethylene (tce) (guaranteed grade) was used as purchased from Yoneyama Chemicals Ltd. Acrylonitrile and the other olefinic compounds were dried and distilled under a nitrogen atmosphere and transferred to the reaction flask by means of a trap-to-trap method. Dry hydrogen chloride was generated by the reaction of sodium chloride with concentrated sulphuric acid in a vacuum system and the volume produced was measured with a manometer.

Preparations.—*(1—2-η-Ethylene)bis[1,2-bis(diphenylphosphino)ethane]molybdenum*(0), (I). Into a suspension of molybdenum(III) pentane-2,4-dionate (4·0 g, 10·2 mmol) and 1,2-bis(diphenylphosphino)ethane (8·4 g, 21·1 mmol) in toluene (150 cm^3), triethylaluminium (7 cm^3, 50 mmol) was added dropwise at −50 °C under an argon atmosphere. The mixture was gradually brought to room temperature, with stirring, and the reaction continued for 10 days. The resulting orange precipitate was separated by filtration from the dark brown solution, washed with diethyl ether (3 × 30 cm^3) and hexane (3 × 30 cm^3), and dried *in vacuo*. The orange microcrystalline powder thus obtained was recrystallized from warm tetrahydrofuran (thf) to yield orange *prisms* which were washed well with hexane to remove solvated thf (yield 1·90 g, 22%) (Found: C, 70·7; H, 6·15. Calc. for $C_{54}H_{52}MoP_4$: C, 70·4; H, 5·7%).

Bis[1,2-bis(diphenylphosphino)ethane]hydrido(pentane-2,4-dionato)molybdenum(II), (II).—This complex was prepared as above but with the use of triethylaluminium (4 cm^3, 30 mmol) which afforded a deep brown solution. On reducing the volume of the solution *in vacuo* to a third of the initial volume, a dark brown solid was precipitated, which was filtered off and crystallized from toluene–ethanol as deep brown fine *needles* (5·4 g, 57%) [Found: C, 70·0; H, 5·8. *M*(cryoscopically in benzene), 600 ± 100. Calc. for $C_{57}H_{56}MoO_2P_4$: C, 69·0; H, 5·7%. *M*, 993].

An alternative route for the preparation of this complex is as follows. Pentane-2,4-dione (0·33 g, 3·3 mmol) in toluene (15 cm^3) was added to complex (I) (0·30 g, 0·33 mmol) by means of a trap-to-trap method. The resulting mixture was heated under reflux in toluene under a nitrogen atmosphere for 15 min. The deep brown solution was then concentreated *in vacuo* to half its original volume. On addition of ethanol (15 cm^3) to the solution, deep brown fine needles were precipitated, which were filtered off, washed with diethyl ether (5 cm^3) and hexane (3 × 5 cm^3), and dried *in vacuo*. The complex thus obtained was identified as (II) on the basis of its i.r. spectrum and microanalysis.

The deuteride [MoD([^{2}H$_1$]acac)(dppe)$_2$] was prepared analogously using 3,3-dideuteriopentane-2,4-dione in the place of Hacac. This time, hexane, instead of ethanol, was used to precipitate the product.

Reactions of Complex (I).—*With dinitrogen*. (a) Complex (I) (1·00 g, 1·09 mmol) was dissolved in toluene (60 cm^3) at 110 °C and dinitrogen gas bubbled into the solution for 2 h at 110 °C. The resulting solution was cooled to room temperature under bubbling dinitrogen, condensed to 10 cm^3, and stored at −78 °C for 2 days. The orange crystals obtained from the solution were recrystallized from hot toluene under bubbling dinitrogen. The product was characterized as *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] from its microanalysis and i.r. spectrum (0·18 g, 18%).

(b) Ethylene was bubbled through a boiling toluene solution (30 cm^3) of *trans*-bis[1,2-bis(diphenylphosphino)ethane]bis(dinitrogen)molybdenum(0) (0·30 g, 0·325 mmol) for 1 h. On addition of hexane (15 cm^3) to the resulting deep red solution, an orange precipitate was formed, which was filtered off and recrystallized from warm thf to yield an orange crystalline solid (0·15 g, 50%). This was identified as complex (I) from its i.r. spectrum and microanalysis.

With tetracyanoethylene. On addition of tce (0·054 g, 0·392 mmol) to a toluene (5 cm^3) dispersion of complex (I) (0·186 g, 0·196 mmol) at room temperature, the colour of the system changed from orange through green to purple accompanied by evolution of ethylene. A purple complex was isolated from the system and was reprecipitated from toluene–diethyl ether. The product was tentatively assigned as bis[1,2-bis(diphenylphosphino)ethane]bis(1—2-η-tetracyanoethylene)molybdenum(0) on the basis of its i.r. spectrum and microanalysis (Found: C, 65·0; H, 4·4; N, 10·2. Calc. for $C_{64}H_{48}MoN_8P_4$: C, 66·8; H, 4·2; N, 9·8%).

With acrylonitrile. Acrylonitrile (2·5 g, 0·047 mol) was distilled into a flask containing complex (I) (0·0422 g, 0·0459 mmol) *in vacuo*. The system was stirred at room temperature for 1 day to yield a greenish brown emulsion, from which a brown complex and poly(acrylonitrile) (0·106 g, 4%) were isolated. The brown complex was not characterized fully.

Reactions of Complex (II).—*With acrylonitrile*. Acrylonitrile (1·61 g, 0·034 mol) was distilled into a flask containing complex (II) (*ca.* 20 mg) in a vacuum system. On raising the temperature of the system from liquid-nitrogen to room temperature, immediate polymerization took place and poly(acrylonitrile) (1·16 g, 70·7%) was obtained.

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[27] M. L. Larson and F. W. Moore, *Inorg. Chem.*, 1962, **1**, 856.

[28] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1960, 1378.

With hydrogen chloride. Complex (II) (0·628 g, 0·703 mmol) in toluene (15 cm^3) was allowed to react with hydrogen chloride (1·69 mmol) at −10 °C to yield, immediately, a yellowish orange precipitate, which was filtered off and recrystallized from methanol giving yellowish orange crystals. The product was identified as bis[1,2-bis(diphenylphosphino)ethane]hydrido(pentane-2,4-dionato)molybdenum(IV) dichloride on the basis of its i.r. spectrum and microanalysis (Found: C, 64·8; H, 5·2; Cl, 7·4. Calc. for $C_{52}H_{50}Cl_2MoP_4$: C, 64·4; H, 5·3; Cl, 6·7%).

Reaction of Bis[1,2-*bis(diphenylphosphino)ethane*]*hydrido*(*pentane*-2,4-*dionato*)*molybdenum*(IV) *Dichloride with Methylmagnesium Bromide.*—To the complex [MoH(acac)(dppe)$_2$]-Cl$_2$ (0·661 g, 0·621 mmol) was added 5 cm^3 of a diethyl ether solution of methylmagnesium bromide (0·014 mol) *in vacuo* at room temperature. A brown precipitate immediately formed accompanied by evolution of a gas (1·23 mmol) consisting of methane, ethane, and hydrogen (2 : 1 : trace). After being treated with water, the solution was evaporated to dryness. From the residual solid, a brown complex was extracted with toluene and was identified as (II) on the basis of its i.r. spectrum (0·13 g, 21%).

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