Inorganic Grignard Reagents. Preparations and Reactions of [Bromobis(tetrahydrofuran)magnesio]bis(η-cyclopentadienyl)hydridomolybdenum

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The compound [Mo(η-C_5H_5)$_2$H{MgBr(thf)$_2$}] is described. It reacts with CO_2, $PhCH_2Br$, C_3H_5Br, MeI, and MeCOCl to give [Mo(η-C_5H_5)$_2$(CO)], [Mo(η-C_5H_5)$_2$(CH_2Ph)$_2$], [Mo(η-C_3H_5)(η-C_5H_5)$_2$][PF_6], [Mo(η-C_5H_5)$_2$HI], Mo(η-C_5H_5)$_2$(COMe)H], and [Mo(η-C_5H_5)$_2$(COMe)$_2$] respectively. Reaction paths for these products are discussed.

INTEREST in preparing electron-rich transition-metal compounds *via* formation of covalent M–M′ bonds (M = transition metal, M′ = very electropositive metal)[1] has been further stimulated by the implication that compounds containing covalent M–Mg bonds are intermediates in the activation of Grignard reagents by transition-metal compounds.[2] However, few compounds containing transition-metal–magnesium bonds have been reported.[1,3,4] Here we describe the preparation and reactions of [Mo(η-C_5H_5)$_2$H{MgBr(thf)$_2$}] which contains a Mo–Mg covalent bond and which unlike the previously described Mo–M′ (M′ = Mg, Li, or

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[1] F. W. Benfield, B. R. Francis, M. L. H. Green, N. T. Luong-Thi, G. Moser, J. S. Poland, and D. M. Roe, *J. Less-Common Metals*, 1974, **36**, 187.

[2] H. Felkin and G. Swierczewski, *Tetrahedron*, 1975, **31**, 2735.

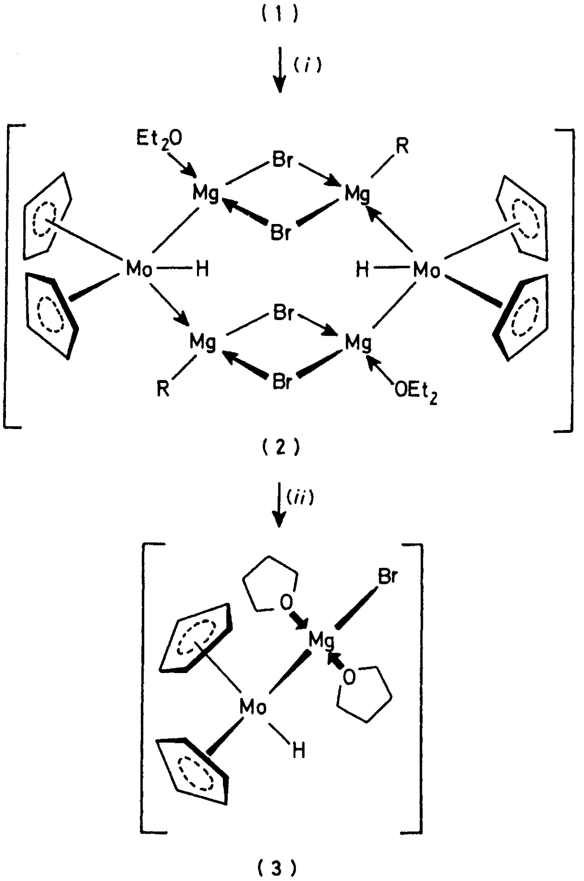
[3] (*a*) H. Felkin and P. J. Knowles, *J. Organometallic Chem.*, 1972, **37**, C14; (*b*) H. Felkin, P. J. Knowles, B. Meunier, A. Mitschler, L. Ricard, and R. Weiss, *J.C.S. Chem. Comm.*, 1974, 44; (*c*) H. Felkin and B. Meunier, *Nouveau J. Chim.*, 1977, **1**, 281.

[4] M. L. H. Green, T. L.-Thi, G. A. Moser, I. Packer, F. Petit, and D. M. Roe, *J.C.S. Dalton*, 1976, 1988.

Al)[1,4,5] compounds is monomeric. Part of this work has been previously communicated.[6]

RESULTS

The dihydride $[Mo(\eta\text{-}C_5H_5)_2H_2]$ (1) reacts with isopropylmagnesium bromide in diethyl ether to give the previously reported yellow crystalline compound $[H(\eta\text{-}H_5C_5)_2Mo\text{-}\{\mu\text{-}PrMg(\mu\text{-}Br)_2Mg(OEt_2)\}_2Mo(\eta\text{-}C_5H_5)_2H]$ (2).[4] Dissolving (2) in hot tetrahydrofuran (thf) gave a red solution which on concentration and cooling yielded an orange crystalline compound $[Mo(\eta\text{-}C_5H_5)_2H\{MgBr(thf)_2\}]$ (3). Compound (3) could be recrystallised from thf. The crystal structure of (3) is shown in Scheme 1.[6] The Mo–Mg bond length (2.732 Å) is the same as that reported previously for a Mo–Mg bond in which the Mo acts as a one-electron donor.[7] The i.r. spectrum of (3) shows a band at 1 850 cm^{-1} which may be assigned to ν(Mo–H).



SCHEME 1 Synthesis of compounds (2) and (3). (*i*) MgBrPr–Et_2O; (*ii*) thf

Compound (3) is insoluble in toluene and diethyl ether and is very readily oxidised by air. Treatment of (3) with proton sources such as water, ethanol, acetone, or ethyl acetate produces the dihydride (1) in essentially quantitative yields. Reaction of (3) with carbon dioxide gave a green solution from which the carbonyl compound $[Mo(\eta\text{-}C_5H_5)_2(CO)]$ (4) was isolated. This reduction of CO_2 appears to be characteristic of transition-metal–alkali-metal bonds.[2] Reaction of (3) with benzyl chloride or benzyl bromide gave the derivative $[Mo(\eta\text{-}C_5H_5)_2(CH_2Ph)_2]$ (5), while reaction with allyl bromide produced the allyl cation $[Mo(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)_2][PF_6]$ (6). Treatment of (3) with methyl iodide gave the compound $[Mo(\eta\text{-}C_5H_5)_2H(I)]$ (7); however, no reaction was observed with MeCl, MeBr, PhBr, or $SiMe_3Cl$.

Reaction of (3) with acetyl chloride followed by evaporation and extraction with water and toluene gave two products. The toluene solution yielded the compound $[Mo(\eta\text{-}C_5H_5)_2(COMe)H]$ (8) while the aqueous solution produced $[Mo(\eta\text{-}C_5H_5)_2(COMe)_2]$ (9). Compound (8) is sensitive to water producing (1) and acetic acid. Reaction of (8) with HCl gave the dichloride $[Mo(\eta\text{-}C_5H_5)_2Cl_2]$ presumably *via* the dihydride (1). Treatment of (8) with CCl_4–$CHCl_3$ gave $[Mo(\eta\text{-}C_5H_5)_2(COMe)Cl]$ (10). Treatment of (8) with Na[OD]–D_2O–thf did not lead to any hydrogen–deuterium exchange and the starting compound was recovered unchanged.

The orange bis(acetyl) compound (9) is readily protonated to give the purple salt (11). Compound (9) could be regenerated from (11) by careful titration (purple $\longrightarrow$ orange) with base; excess of sodium hydroxide led to decomposition of (9). A solution of (9) in DCl–D_2O showed no H–D exchange after 16 h (n.m.r. spectroscopy). Although compound (9) is analogous to pentane-2,4-dione, all attempts to make (9) act as a ligand to Ni, Pd, Pt, or Cu were unsuccessful. However, when (9) was recrystallised from aqueous thf solutions containing sodium chloride, elemental analysis indicated the presence of 1 equivalent of NaCl.

The reactions are summarised in Scheme 2.

DISCUSSION

The reactions of (3) described above show it to be a base and a weak nucleophile. Felkin and Meunier[3c] have shown that the inorganic Grignard reagent $[Fe(\eta\text{-}C_5H_5)(MgBr)(dppe)]$ [dppe = 1,2-bis(diphenylphosphino)ethane] reacts readily with alkyl bromides and a radical mechanism has been proposed. However, we have found no evidence for radical paths in the reactions of (3). For example, treatment of (3) with hex-5-enyl bromide at 60 °C produced after work-up $[Mo(\eta\text{-}C_5H_5)_2H_2]$ (95%) and only *ca.* 10% of a mixture of hex-1-ene and methylcyclopentane (ratio 8 : 3).

Reactions of dimers of type (A) (Scheme 3) with organic halides produce a surprising variety of products. The precise products depend on the original Grignard reagent (MgRX) used to form (A) and on the organic halide (R′X). Products of the types $[Mo(C_5H_5)_2R'(H)]$ (B), $[Mo(C_5H_5)_2R(R')]$ (C), $[Mo(C_5H_5)_2R'(X)]$ (D), $[Mo(C_5H_5)_2R'_2]$ (E), and $[Mo(C_5H_5)_2X_2]$ (F) have been observed. The reactions of compound (3) can obviously only produce products of types (B), (E), and (F) since there is no MgBrR present. Products of all three types have been observed. A mechanism that accounts for all these products is given in Scheme 3 and some illustrative reactions with the proposed reaction routes are given in the Table.

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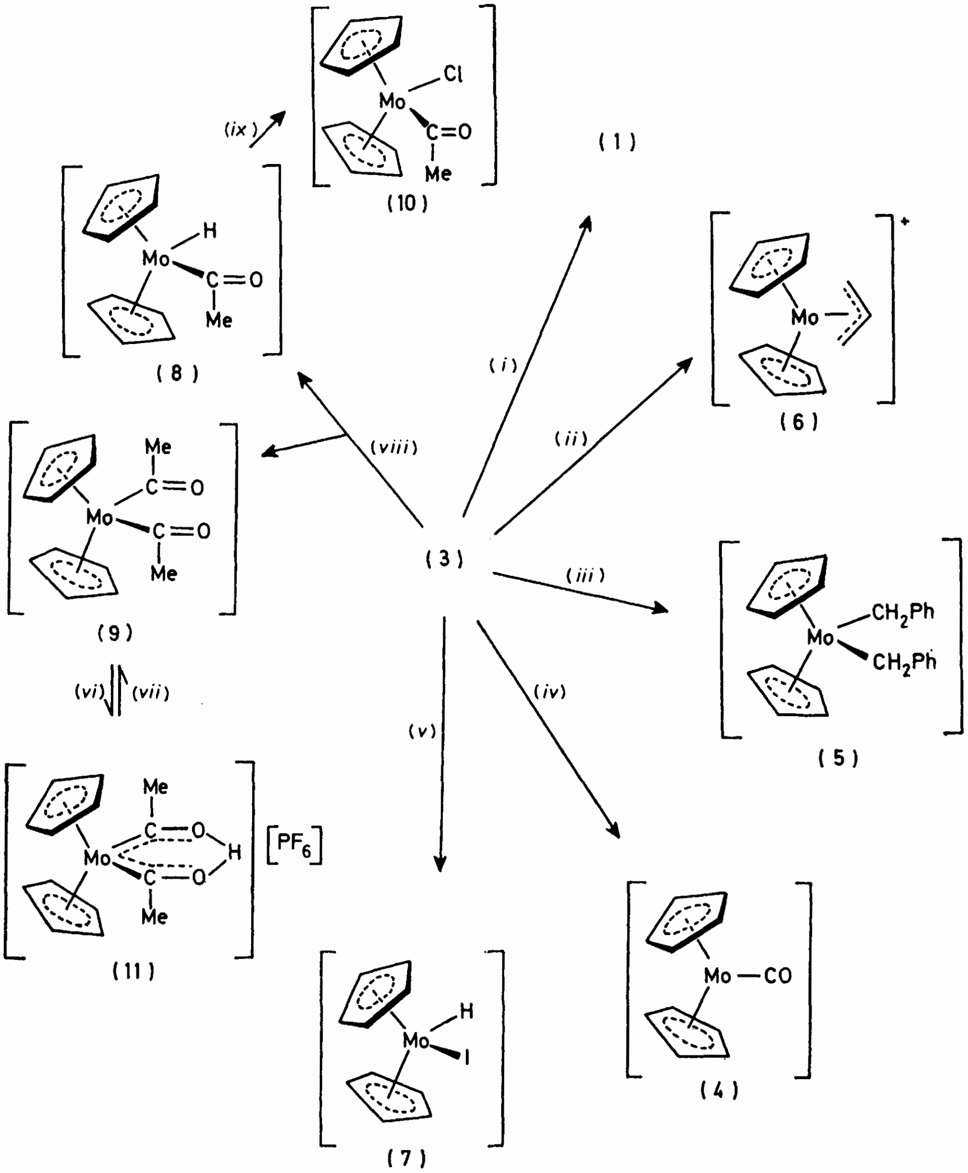
[5] B. R. Francis, M. L. H. Green, T. L-thi, and G. A. Moser, *J.C.S. Dalton*, 1976, 1339; M. L. H. Green, R. E. MacKenzie, and J. S. Poland, *ibid.*, 1976, 1993.

[6] S. G. Davies, M. L. H. Green, K. Prout, A. Coda, and V. Tazzoli, *J.C.S. Chem. Comm.*, 1977, 135.

[7] K. Prout and R. A. Forder, *Acta Cryst.*, 1975, **B31**, 852.

EXPERIMENTAL

All the reactions and purifications were performed under nitrogen in the absence of oxygen. Tetrahydrofuran was dried over sodium–benzophenone and distilled. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer, n.m.r. spectra on a Perkin-Elmer R32 instrument (90 MHz), and mass spectra on an MS9 spectrometer; molecular ions are quoted for Mo having *m/e* 98. Chromatography was performed on alumina (100—120 mesh); columns were made up in light petroleum (b.p. 30—40 °C) under nitrogen and eluted with the solvents indicated. The compound [Mo(η-C_5H_5)$_2$$H_2$] (1) was prepared as described previously.[7,8] Where no analytical data are given the compounds were identified by comparison with previously reported compounds.



SCHEME 2 Some reactions of compound (3). (*i*) Water, EtOH, Me_2CO, or $MeCO_2Et$, 100%; (*ii*) C_3H_5Br then $[NH_4][PF_6]$(aq) (24%); (*iii*) $PhCH_2Cl$ (40%); (*iv*) CO_2 (45%); (*v*) MeI (20%); (*vi*) HCl(aq) then $[NH_4][PF_6]$(aq) (90%); (*vii*) Na[OH](aq) then CH_2Cl_2 (80%); (*viii*) MeCOCl [(8) 75%, (9) 10%]; (*ix*) $CHCl_3$–CCl_4 (80%)

Compound (2), [H(η-H_5C_5)$_2$Mo{μ-PrMg(μ-Br)$_2$Mg(OEt_2)}$_2$-Mo(η-C_5H_5)$_2$H].—Isopropylmagnesium bromide (20 cm^3, 2 mol dm^{-3}) was added to [Mo(η-C_5H_5)$_2$$H_2$] (1) (2.28 g, 0.01 mol) in anhydrous diethyl ether (450 cm^3) in one portion and filtered. After 16 h at 20 °C the yellow crystals of (2) were isolated, washed with diethyl ether, and dried *in vacuo* (5 g, 91%).

[*Bromobis*(*tetrahydrofuran*)*magnesio*]*bis*(η-*cyclopentadienyl*)*hydridomolybdenum*, [Mo(η-C_5H_5)$_2$H{MgBr(thf)$_2$}] (3).—The dimer (2) was dissolved in anhydrous thf at 50 °C and the solution filtered. After concentration *in vacuo* at 20—30 °C to 15 cm^3, large orange crystals of (3) slowly formed. Recrystallisation from thf gave (3) (3.8 g, 89%), $\nu_{max.}$ in Nujol at 1 850 cm^{-1}.

Reactions of Compound (3).—(*a*) *With water*. Compound

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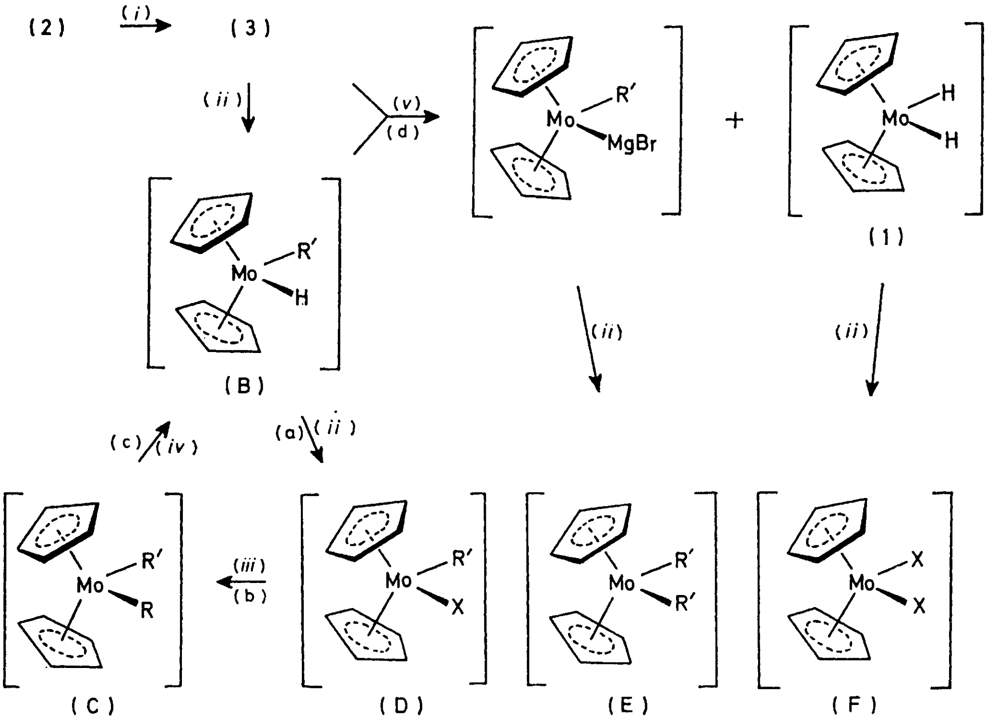
[8] M. L. H. Green and P. J. Knowles, *J.C.S. Perkin I*, 1973, 989.

(3) (0.6 g) in anhydrous thf (25 cm^3) was treated with water (2 cm^3). The orange solution immediately became brown. Evaporation under reduced pressure, extraction with toluene (3 × 20 cm^3), concentration, and chromatography (toluene) gave a yellow solution. Evaporation under reduced pressure yielded yellow crystals of (1) (quantitative). Reactions of thf solutions of (3) with anhydrous acetone, ethanol, or ethyl acetate as above also provided (1) in essentially quantitative yields.



SCHEME 3 (*i*) thf; (*ii*) R′X = $PhCH_2Br$, MeI, C_6F_5Br,[4] C_3H_5Br, or PhI;[4] (*iii*) MgBrR (R = Pr^i, C_6H_{11}, Bu^n, Me, or Ph); (*iv*) β-elimination (R = Pr^i or C_6H_{11}); (*v*) slow reaction becoming major path when step (*iv*) regenerates (B). When R has a β-hydrogen (D), (E), or (F) are formed; when R has no β-hydrogen (C) or (D) are formed. (a)—(d) are reaction routes (Table)

(*b*) *With carbon dioxide.* Compound (3) (1.5 g) in anhydrous thf (50 cm^3) was treated with a stream of carbon dioxide gas at 20 °C for 4 h during which time the solution became dark green. Evaporation under reduced pressure, extraction with toluene (3 × 20 cm^3), and concentration under reduced pressure gave green crystals. Recrystallisation from light petroleum gave [Mo(η-C_5H_5)$_2$(CO)] (4) (0.35 g, 45%).

TABLE
Reaction routes for some Mo–Mg compounds

Compound	R in MgBrR	R′X	Proposed route	Products [4]
(A)	Me	$PhCH_2Br$	(a) → (b)	[MoMe(η-C_5H_5)$_2$(CH_2Ph)]
(A)	Ph	$PhCH_2Br$	(a) → (b)	[MoPh(η-C_5H_5)$_2$(CH_2Ph)]
(A)	Pr^i	Me	(a)	[MoMe(η-C_5H_5)$_2$I]
(A)	Pr^i	C_3H_5Br	(a) → (b) → (c) → (d)	[Mo(η-C_3H_5)(η-C_5H_5)$_2$]$^+$
(A)	C_6H_{11}	$PhCH_2Br$	(a) → (b) → (c) → (d)	[Mo(η-C_5H_5)$_2$(CH_2Ph)$_2$] + [MoBr$_2$(η-C_5H_5)$_2$]
(3)		$PhCH_2Br$	(d)	[Mo(η-C_5H_5)$_2$(CH_2Ph)$_2$] + [MoBr$_2$(η-C_5H_5)$_2$]
(3)		MeI	(d)	[Mo(η-C_5H_5)$_2$H(I)] + [Mo(η-C_5H_5)$_2$I$_2$]
(3)		C_3H_5Br	(d)	[Mo(η-C_3H_5)(η-C_5H_5)$_2$]$^+$

(*c*) *With benzyl bromide.* Compound (3) (1.3 g) in anhydrous thf (50 cm^3) was treated with freshly distilled benzyl bromide (480 mg, 1 equivalent) in thf (10 cm^3) in one portion at 20 °C. After 1 h the dark red solution was evaporated under reduced pressure at 20 °C. The brown residue was extracted with toluene (3 × 50 cm^3). After concentration of the toluene extracts under reduced pressure, chromatography [light petroleum–toluene (1 : 4)] gave a fast-moving orange band. Concentration to 15 cm^3, followed by addition of light petroleum (15 cm^3) and cooling to 0 °C, yielded bright orange crystals of [Mo(η-C_5H_5)$_2$(CH_2Ph)$_2$] (5) (485 mg, 43%), *m/e* 410. Reaction of (3) with benzyl chloride as above also produced (5) (40%).

(*d*) *With allyl bromide.* Compound (3) (1.2 g) in anhydrous thf (50 cm^3) was treated with allyl bromide (1 equivalent) in one portion at 20 °C. After 3 h the dark red solution was evaporated under reduced pressure. The brown residue was extracted with water (2 × 20 cm^3) and toluene (50 cm^3). Aqueous ammonium hexafluorophosphate was added to the dark red aqueous extracts to produce a pink precipitate. The precipitate was isolated, washed with water (2 × 5 cm^3), and dissolved in acetone (10 cm^3). Chromatography (acetone) gave a dark red band which on concentration yielded red crystals of [Mo(η-C_3H_5)-(η-C_5H_5)$_2$][PF_6] (6) (245 mg, 24%).

(*e*) *With methyl iodide.* Compound (3) (1.5 g) in anhydrous thf (50 cm^3) was treated with methyl iodide (1 equivalent) in one portion at 20 °C. After 2 h the green-red dichroic solution was filtered to give black crystals of [Mo(C_5H_5)$_2$$I_2$] (50 mg) and then evaporated. The residue was extracted with toluene (2 × 50 cm^3) to give a red solution. Concentration under reduced pressure and chromatography (toluene) gave a green band, which on concentration gave green crystals of [Mo(η-C_5H_5)$_2$H(I)] (7) (225 mg, 20%).

(*f*) *With hex-*5-*enyl bromide.* Compound (3) (1.5 g) in thf was treated with hex-5-enyl bromide (1 equivalent) and warmed to 60 °C for 8 h. After another 16 h at 20 °C water (10 cm^3) was added. G.l.c. showed the presence of hex-1-ene (8%) and methylcyclopentane (3%). Evaporation, extraction with toluene, and chromatography gave (1) (95%).

(*g*) *With acetyl chloride.* Compound (3) (2.12 g) in anhydrous thf (70 cm^3) was treated with freshly distilled acetyl chloride (0.32 cm^3; 1 equivalent) in one portion. An immediate exothermic reaction resulted in a red solution which was *immediately* evaporated to dryness. Water (15 cm^3) and toluene (50 cm^3) were added and immediately separated. The orange toluene solution was concentrated. Chromatography gave [light petroleum–toluene (1 : 1)] a yellow band and (diethyl ether) an orange band. The yellow solution was evaporated to give yellow crystals of the dihydride [Mo(η-C_5H_5)$_2$$H_2$] (0.05 g). Concentration of the diethyl ether solution gave orange crystals. Recrystallisation from diethyl ether gave [Mo(η-C_5H_5)$_2$-(COMe)H] (8) (900 mg, 75%) (Found: C, 53.6; H, 5.5. $C_{12}H_{14}MoO$ requires C, 53.5; H, 5.2%), τ in C_6D_6 5.60 (10 H, s), 7.45 (3 H, s), and 17.5 (1 H, s, Mo–H), *m/e* 272, $\nu_{max.}$ in Nujol at 1 830 (Mo–H) and 1 615 cm^{-1} (C=O).

After 5 d red crystals separated from the water extract. Recrystallisation [$CHCl_3$–light petroleum (1 : 1)] gave orange crystals of [Mo(η-C_5H_5)$_2$(COMe)$_2$] (9) (140 mg, 10%), *m/e* 312, $\nu_{max.}$ in Nujol at 1 550 cm^{-1} (C=O), τ in S(CD_3)$_2$O 5.0 (10 H, s) and 7.8 (6 H, s).

Compound (10), [Mo(η-C_5H_5)$_2$(COMe)Cl] (10). The compound [Mo(η-C_5H_5)$_2$(COMe)H] (100 mg) was dissolved in $CHCl_3$–CCl_4 (1 : 1, 25 cm^3) to give an orange solution. After 90 min the resulting red solution was evaporated to give a purple powder. Recrystallisation from CH_2Cl_2–light petroleum (1 : 1) gave purple crystals of (10) (105 mg, 93%) (Found: C, 47.0; H, 4.4. $C_{12}H_{13}ClMoO$ requires C, 47.3; H, 4.3%), τ in $CDCl_3$ 5.05 (10 H, s) and 7.30 (3 H, s), $\nu_{max.}$ in Nujol at 1 640 cm^{-1} (C=O).

Compound (11), $[\overline{\mathrm{Mo}(\eta\text{-}C_5H_5)_2\{C(Me)O{\cdot}H{\cdot}OC}(Me)\}][PF_6]$.—A solution of compound (9) (100 mg) in thf (20 cm^3) was treated with aqueous HCl (1 cm^3, 10%) followed by aqueous [NH_4][PF_6]. Evaporation and recrystallisation from acetone–water (1 : 1) gave the purple salt (11) (150 mg, 94%) (Found: C, 37.05; H, 3.75. $C_{14}H_{17}F_6MoO_2P$ requires C, 36.7; H, 3.7%), τ in (CD_3)$_2$CO, 4.50 (10 H, 2) and 7.25 (6 H, s), $\nu_{max.}$ in Nujol at 1 640 and 1 545 cm^{-1} (C=O).

Titration of a thf solution of the salt (11) with aqueous Na[OH] (10%) (purple ⟶ orange) gave an orange solution which on concentration gave red crystals of [Mo(η-C_5H_5)$_2$-(COMe)$_2$]·NaCl·H_2O (Found: C, 41.8; H, 4.6. $C_{14}H_{18}ClMoNaO_3$ requires C, 43.3; H, 4.6%). Recrystallisation from $CHCl_3$–light petroleum (1 : 1) yielded (9).

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