Preparations and Reactions of Bis(η-cyclopentadienyl) Compounds of Molybdenum or Tungsten containing Covalent Bonds to Magnesium

By **Malcolm L. H. Green,* Tuyet Luong-thi, Glenn A. Moser, Ian Packer, Francis Pettit,** and **David M. Roe,** Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

The dihydride $[Mo(\eta\text{-}C_5H_5)_2H_2]$ reacts with bromo(cyclohexyl)magnesium to give the cyclic dimer $[H(\eta\text{-}H_5C_5)_2Mo\{\mu\text{-}(H_{11}C_6)MgBr_2Mg(OEt_2)\}_2Mo(\eta\text{-}C_5H_5)_2H]$, (III). The Grignard reagents MgRX (RX = Pr^iBr, Bu^nBr, MeI, or PhBr) give generally similar products. Derivative (III) reacts with carbon dioxide, carbon monoxide, benzyl bromide, or butadiene to give the compounds $[Mo(\eta\text{-}C_5H_5)_2(CO)]$, $[Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)(CO)_2]$, $[Mo(\eta\text{-}C_5H_5)_2(CH_2Ph)_2]$, and $[Mo(\eta^3\text{-}C_4H_7)(\eta\text{-}C_5H_5)_2][PF_6]$ respectively. The isopropyl analogue of (III) reacts similarly. Also, with iodomethane, the compound $[MoMe(\eta\text{-}C_5H_5)_2I]$ is formed. The methyl and phenyl analogues of (III) react with benzyl bromide to give $[MoMe(\eta\text{-}C_5H_5)_2(CH_2Ph)]$ and $[Mo(\eta\text{-}C_5H_5)_2Ph(CH_2Ph)]$ respectively. The dihydride $[W(\eta\text{-}C_5H_5)_2H_2]$ reacts with the Grignard reagents MgRX (RX = MeI, Pr^iBr, or PhBr) to give tungsten–magnesium compounds which appear to be generally similar to the molybdenum adducts.

THE general objective of this work was to prepare electron-rich transition-metal compounds *via* formation of covalent M–M′ bonds where M is a transition metal and M′ is a very electropositive metal such as Li, Mg, or Al. The general principles have been discussed previously.[1] Here we describe the preparation and reactivity of compounds containing covalent molybdenum- or tungsten-magnesium bonds. Parts of this work have been previously communicated.[2,3]

RESULTS

The reactions between the dihydrides $[Mo(\eta\text{-}C_5H_5)_2H_2]$, (I), and $[W(\eta\text{-}C_5H_5)_2H_2]$, (II), and a selection of Grignard reagents gave yellow adducts which were highly reactive and not recrystallisable. It was possible to obtain crystals of the cyclohexyl adduct which were suitable for study by *X*-ray diffraction. Therefore, we describe first the preparation and reactions of the cyclohexyl adduct and this is followed by a description of the other adducts formed from the dihydrides (I) and (II) and Grignard reagents.

Treatment of the dihydride (I) with bromo(cyclohexyl)-magnesium at 70 °C gave yellow-orange crystals. The analytical (Table 1), i.r., and especially the *X*-ray diffraction data[2] show the product to be the compound $[H(\eta\text{-}H_5C_5)_2Mo\{\mu\text{-}(H_{11}C_6)MgBr_2Mg(OEt_2)\}_2Mo(\eta\text{-}C_5H_5)_2H]$, (III). The structure is represented in Scheme 1. The presence of the Mo–H groups is shown by comparison of the i.r. spectrum of (III) with that of the deuteriated analogue prepared from $[Mo(\eta\text{-}C_5H_5)_2D_2]$. Whereas (III) showed bands at 1 740 and 1 720 cm^{-1} assignable to ν(Mo–H), the spectrum of the deuteriated analogue did not have these bands but showed a new band at 1 260 cm^{-1} assignable to ν(Mo–D); ν(Mo–H)/ν(Mo–D) = 1.3. Compound (III) is very readily oxidised by oxygen, it is insoluble in toluene and diethyl ether, and reacts immediately with protonic solvents such as ethanol or water. Hydrolysis gives the parent dihydride (I) in essentially quantitative yield, together with cyclohexane and diethyl ether in *ca.* 1 : 1 ratio (g.l.c.). Compound (III) dissolves readily in tetrahydrofuran (thf) giving stable orange solutions, and it is probable that the diethyl ether ligand is replaced by thf in these solutions. The solutions gave crystalline thf adducts when concentrated.

TABLE 1
Analytical and spectral data

Compound	Colour	Analysis (%)[a]		Mass spectral data[b]	^{1}H N.m.r. data[c]
$[H(\eta\text{-}H_5C_5)_2Mo\{\mu\text{-}(H_{11}C_6)MgBr_2Mg(OEt_2)\}_2Mo(\eta\text{-}C_5H_5)_2H]$	Yellow-orange	38.4 (40.5)	5.0 (5.4)[d]		
$[MoMe(\eta\text{-}C_5H_5)_2I]$	Deep green	36.2 (35.8)	3.6 (3.5)	370	6.05, *10*, **s**, $(\eta\text{-}C_5H_5)_2$; 9.30, *3*, **s**, Me[e]
$[MoMe(\eta\text{-}C_5H_5)_2(CH_2Ph)]$	Red	64.6 (64.7)	6.0 (6.0)	334	2.9, *5*, **s**, Ph; 5.95, *10*, **s**, $(\eta\text{-}C_5H_5)_2$; 7.85, *2*, **s**, CH_2; 10.0, *3*, **s**, Me[e]
$[Mo(\eta\text{-}C_5H_5)_2Ph(CH_2Ph)]$	Red	6.8 (69.7)	6.0 (5.55)	396	2.8, *10*, **c**, 2 Ph; 5.33, *10*, **2**, $(\eta\text{-}C_5H_5)_2$; 7.67, *2*, **s**, CH_2[f]
$[W(\eta^3\text{-}C_3H_5)(\eta\text{-}C_5H_5)_2][PF_6]$	Orange	31.1 (31.2)	3.3 (3.0)		4.57, *5*, **s**, $(\eta\text{-}C_5H_5)$; 4.81, *5*, **s**, $(\eta\text{-}C_5H_5)$; 5.88, *1*, **triplet of triplets**[g] (J_{anti} 15, J_{syn} 9), CH; 6.56, *2*, **d**[g] (*J* 9), $H_{2,syn}$; 7.53, *2*, **d**[g] (*J* 15), $H_{2,anti}$[h]

[a] Calculated values are given in parentheses. [b] Parent-ion peak for ^{98}Mo. [c] Given as: chemical shift (τ), *relative intensity*, **multiplicity** (*J* in Hz), assignment. [d] Mo, 15.9 (16.2); Mg, 8.0 (8.2); Br, 27.1 (26.9). [e] In C_6D_6. [f] In CS_2. [g] Further fine structure also apparent. [h] In $S(CD_3)_2O$. ν(C–C) of $\eta\text{-}C_3H_5$ at 1 498 cm^{-1}.

Treatment of thf solutions of (III) with carbon dioxide gas gave a deep green solution from which the monocarbonyl $[Mo(\eta\text{-}C_5H_5)_2(CO)]$, (IV), was isolated in 85% yield. Tetrahydrofuran solutions of (III) also reacted with carbon monoxide giving small yields of (IV) and, as the major

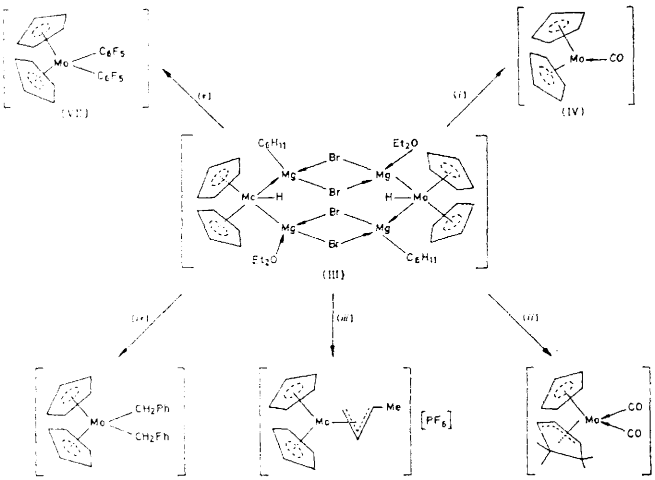
---

[1] B. R. Francis, M. L. H. Green, N-T. Luong-thi, and G. A. Moser, *J.C.S. Dalton*, submitted.

[2] M. L. H. Green, G. A. Moser, I. Packer, F. Pettit, R. A. Forder, and C. K. Prout, *J.C.S. Chem. Comm.*, 1974, 839; C. K. Prout and R. A. Forder, *Acta Cryst.*, 1975, **B31**, 852.

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

product, the dicarbonyl $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})(\eta^3\text{-}\mathrm{C_5H_7})(\mathrm{CO})_2]$, (V). Treatment of (III) with benzyl bromide gave the bisbenzyl derivative $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{CH_2Ph})_2]$, (VI). Bromopentafluorobenzene reacted rapidly with (III), and a small yield of the bis(pentafluorophenyl) derivative $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{C_6F_5})_2]$, (VII), could be isolated from the products. Finally, treatment of (III) with butadiene gave small quantities of the η^3-but-2-enyl derivative $[\mathrm{Mo}(\eta\text{-}\mathrm{C_4H_7})(\eta\text{-}\mathrm{C_5H_5})_2][\mathrm{PF_6}]$, (VIII). Compounds (IV),[4,5] (V),[1] (VI),[1] (VII),[1] and (VIII) [1] have been previously described.



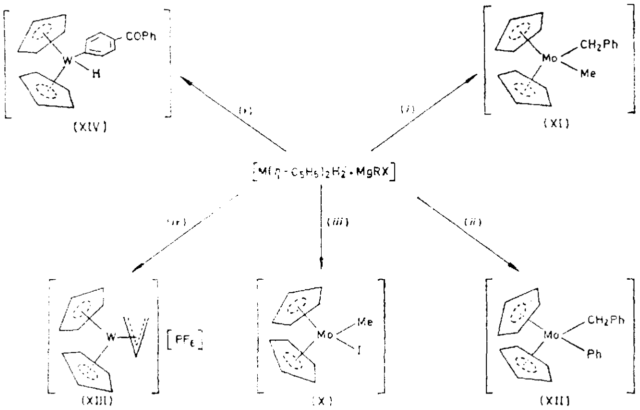
SCHEME 1 Some reactions of compound (III): (*i*) $\mathrm{CO_2}$, 1 atm; (*ii*) CO, 1 atm; (*iii*) butadiene, 1 atm; (*iv*) $\mathrm{PhCH_2Br}$; (*v*) $\mathrm{C_6F_5Br}$

The dihydride (I) reacted readily with bromo(isopropyl)-magnesium giving yellow crystals which analytical and partial *X*-ray diffraction data strongly suggest to be the analogue of (III), namely $[\mathrm{H}(\eta\text{-}\mathrm{H_5C_5})_2\mathrm{Mo}\{\mu\text{-}\mathrm{Pr^iMgBr_2Mg}(\mathrm{OEt_2})\}_2\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{H}]$, (IX). The crystal-structure data [2] clearly show that (IX) has the same cyclic $\mathrm{MoMgBr_2MgMoMgBr_2Mg}$ system as (III). However, local disordering prohibited unambiguous identification of the isopropyl or diethyl ether groups. Thermal decomposition of (IX) gives propane and a trace amount of propene (97 : 3, g.l.c.) and diethyl ether. The parent dihydride (I) is formed both by pyrolysis and hydrolysis of (IX). The proposal that (III) and (IX) are analogues is also supported by the observations that they gave closely similar reactions. For example reaction with benzyl bromide and bromopentafluorobenzene gives (VI) and (VII) respectively. Also, (IX) reacted with carbon dioxide giving (IV), and with carbon monoxide (IV) and (V) were formed. Treatment of (IX) with iodobenzene gave only the known di-iodo-compound $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{I_2}]$. However, with methyl iodide (IX) reacted to give the iodo(methyl) derivative $[\mathrm{MoMe}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{I}]$, (X), which is characterised by the data in Table 1. Apart from compounds (III) and (IX), we also made preliminary studies of reactions of the dihydrides (I) and (II) with various other Grignard reagents MgRX in diethyl ether where RX = $\mathrm{Bu^nBr}$, $\mathrm{PhCH_2Br}$, MeBr, MeI, or PhBr for (I) and RX = MeBr, $\mathrm{Pr^iBr}$, PhBr, and $\mathrm{Bu^nBr}$ for (II). Each reaction between (I) or (II) and the above Grignard reagents gave yellow crystals or powders which were sensitive to oxidation and hydrolysis. In all cases the products were either insoluble or could not be recovered from solutions unchanged. Analysis of the first-formed products gave, in all cases, ratios for Mo (or W) : Mg of *ca.* 1 : 1 or *ca* 1 : 2. We studied various reactions of these products which we will refer to as the adducts $[\mathrm{M}(\eta\text{-}\mathrm{C_5H_5})\mathrm{H_2}\cdot\mathrm{MgRX}]$ in order to signify their origin.

Treatment of the adduct $[(\mathrm{I})\cdot\mathrm{MgBrMe}]$ with benzyl bromide gave a smooth reaction and following chromatographic separation the benzyl(methyl) derivative $[\mathrm{MoMe}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{CH_2Ph})]$, (XI), was isolated. The adduct $[(\mathrm{I})\cdot\mathrm{MgBrPh}]$ also reacted with benzyl bromide and in this case the benzyl(phenyl) derivative $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Ph}(\mathrm{CH_2Ph})]$, (XII), was formed. Compounds (XI) and (XII) are characterised by the data given in Table 1. The adduct $[(\mathrm{I})\cdot\mathrm{MgBrBu^n}]$ is soluble in thf and treatment of the solution with benzyl bromide gave the bisbenzyl derivative (VI).

The adduct $[(\mathrm{II})\cdot\mathrm{MgMeI}]$ is rapidly decomposed by methanol giving the parent compound (II) and methane (g.l.c.). It is soluble in thf and these solutions reacted with carbon monoxide to give the monocarbonyl $[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{CO})]$ and the dihydride (II). Unlike the molybdenum adducts, the product $[(\mathrm{II})\cdot\mathrm{MgMeI}]$ gave no reaction with carbon dioxide, and with benzyl bromide only the dibromo-compound $[\mathrm{WBr_2}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{W}]$ was isolated and there was no evidence for the tungsten analogue of (XI). When a suspension of $[(\mathrm{II})\cdot\mathrm{MgMeI}]$ in toluene was heated under reflux for 1 h methane was evolved and a yellow powder remained which is similar in appearance to the original adduct. However, this powder is not soluble in thf and did not yield methane on treatment with methanol. With methyl iodide, the adduct $[(\mathrm{II})\cdot\mathrm{MgMeI}]$ gave the di-iodide $[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{I_2}]$.

The adduct $[(\mathrm{II})\cdot\mathrm{MgBrPr^i}]$ gave propane on treatment with methanol and reacted with methyl iodide to give the di-iodo-compound $[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{I_2}]$. Thermal decomposition occurred at *ca.* 100 °C to give propane. The adduct $[(\mathrm{II})\cdot\mathrm{MgBrPr^i}]$ reacted with allyl bromide to give the η^3-allyl compound $[\mathrm{W}(\eta\text{-}\mathrm{C_3H_5})(\eta\text{-}\mathrm{C_5H_5})_2][\mathrm{PF_6}]$, (XIII), and with benzophenone the aromatic ring was substituted giving $[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{C_6H_4COPh}\text{-}p)\mathrm{H}]$, (XIV). Compound (XIV) has previously been described.[1] Some of these reactions are illustrated in Scheme 2.



SCHEME 2 Some reactions of the adducts $[\mathrm{M}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{H_2}\cdot\mathrm{MgRX}]$: (*i*) M = Mo, RX = MeBr, $\mathrm{PhCH_2Br}$; (*ii*) M = Mo, RX = PhBr, $\mathrm{PhCH_2Br}$; (*iii*) M = Mo, RX = $\mathrm{Pr^iBr}$,MeI; (*iv*) M = W, RX = $\mathrm{Pr^iBr}$, $\mathrm{C_3H_5Br}$; (*v*) M = W, RX = $\mathrm{Pr^iBr}$, PhCOPh

---

[4] H. H. Brintzinger and J. L. Thomas, *J. Amer. Chem. Soc.*, 1972, **94**, 1386.

[5] F. W. S. Benfield, B. R. Francis, and M. L. H. Green, *J. Organometallic Chem.*, 1972, **44**, C13; F. W. S. Benfield and M. L. H. Green, *J.C.S. Dalton*, 1974, 1244.

DISCUSSION

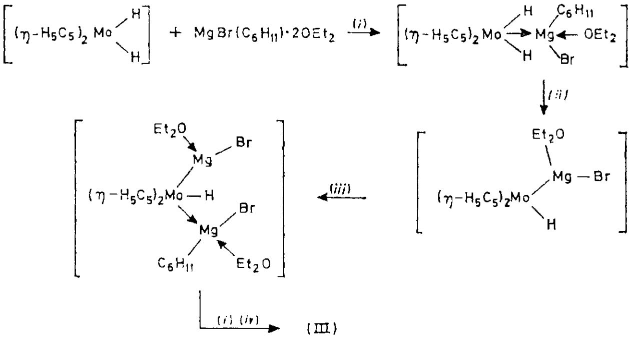
Discrete molecules containing a covalent bond between magnesium and a transition metal are rare. Some magnesium–metal carbonylate species were thought to have such bonds,[6] but the best evidence to date suggests the magnesium may be co-ordinated to the metal carbonylate system *via* the carbonyl oxygen as in $[Mg(py)_4\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$.[7] Felkin and Knowles[8] reasonably postulated the presence of a Ni–Mg bond in the compound $[Ni(\eta\text{-}C_5H_5)(MgBr)(PPh_3)]$ based on its nucleophilic reactions; for example, with carbon dioxide it gives nickel carbonyl compounds. The first unambiguous evidence for a covalent transition-metal–magnesium bond arose from the crystal structure of $[(dppe)(\eta\text{-}H_5C_5)FeMgBr{\cdot}3thf]$ [dppe = 1,2-bis(diphenylphosphino)ethane].[9] The Fe–Mg distance of 2.593(7) Å is strongly indicative of covalent character.

The Mo–Mg distances in (III) and (IX) are 2.74 and 2.85 and 2.76 and 2.81 Å respectively and these are clearly compatible with covalent bonding. A simple valence-bond canonical representation of (III) (Scheme 1) shows that the molybdenum atoms attain an 18-electron configuration whilst the magnesium atoms achieve an octet of valency electrons. The nucleophilic character of the molybdenum atoms in (III), (IX), and the other adducts $[M(\eta\text{-}C_5H_5)H_2{\cdot}MgRX]$ is shown by their reactions. The overall similarity of the reactions of the different adducts, where comparable, strongly suggests that they are essentially similar in nature and therefore that they all contain covalent Mo– or W–Mg bonds.

The formation of (XI) from $[Mo(\eta\text{-}C_5H_5)H_2{\cdot}MgBrMe]$ and benzyl bromide and of (XII) from $[Mo(\eta\text{-}C_5H_5)_2H_2{\cdot}MgBrPh]$ with benzyl bromide shows that these adducts retain the R group of the parent Grignard reagent MgRX. However, the thermal decomposition of $[W(\eta\text{-}C_5H_5)_2H_2{\cdot}MgMe_2]$ to a yellow powder and methane suggests that there may also exist species related to the adducts $[W(\eta\text{-}C_5H_5)_2{\cdot}MgRX]$ where the R group is lost. The ease of formation of (III) and its congeners suggest that the alkane-elimination reaction (1) may provide a

$$M\text{-}H + MgRX \longrightarrow M\text{-}MgX + RH \qquad (1)$$

general route to covalent M–Mg systems when M is a complex transition-metal system which has a ligand environment which precludes stabilisation of discrete stable anions $[M]^-$. We speculate that the formation of (III) proceeds as in Scheme 3.



SCHEME 3 (*i*) $-OEt_2$; (*ii*) $-C_6H_{12}$; (*iii*) $+MgBr(C_6H_{11}){\cdot}2OEt_2$; (*iv*) dimerisation

Finally, it has been proposed that reduction of CO_2 by the Ni–Mg bond proceeds *via* an intermediate Ni-COMg system.[8] The related insertion of carbon dioxide into transition-metal carbon bonds has been observed for rhodium,[10] titanium,[11] zirconium,[11] cobalt,[12] copper,[13] and zinc.[14] Also, reduction of carbon dioxide to carbon monoxide has been observed with some ruthenium[15] and rhodium hydrides.[16] Thus, whilst the reaction of carbon dioxide to give metal carbonyls is probably typical of compounds containing covalent bonds between transition metals and electropositive metals such as magnesium or lithium, this reaction is not exclusive to these systems.

EXPERIMENTAL

All preparations and purifications were in the absence of oxygen. Solvents were dried by refluxing over and distillation from calcium hydride. I.r. spectra were recorded for mulls on a Perkin-Elmer 457 instrument calibrated with polystyrene. Low-resolution mass spectra were obtained on an MS9 spectrometer. Chromatography was on an alumina column (100—120 mesh, Grade III) made up under nitrogen in light petroleum (b.p. 30—40 °C). In each case elution was first with light petroleum followed by the solvents given in the particular preparations. Compounds (I) and (II) were prepared as previously described.[17] Hydrogen-1 n.m.r. spectra were recorded on either a Varian Associates instrument at 100 MHz or on a Perkin-Elmer (60 MHz) instrument.

The Compound $[H(\eta\text{-}H_5C_5)_2Mo\{\mu\text{-}(H_{11}C_6)MgBr_2Mg(OEt_2)\}_2\text{-}Mo(\eta\text{-}C_5H_5)_2H]$, (III).—Typically, the dihydride $[Mo(\eta\text{-}C_5H_5)_2H_2]$ (I) (0.50 g, 2.2 mmol) in dry toluene (100 cm^3) at 60 °C was treated with an excess of bromo(cyclohexyl)magnesium in diethyl ether (0.75 g, 4.6 mmol) and the mixture was stirred and allowed to cool slowly to room temperature. After 6 h large bright yellow crystals separated and the mother liquor was decanted. The crystals were washed

---

[6] J. M. Burlitch and S. W. Ulmer, *J. Organometallic Chem.*, 1961, **19**, P21; G. B. McVicker and R. S. Matyas, *J.C.S. Chem. Comm.*, 1972, 972.

[7] S. W. Ulmer, P. M. Skarstad, J. M. Burlitch, and R. E. Hughes, *J. Amer. Chem. Soc.*, 1973, **95**, 4469.

[8] H. Felkin and P. J. Knowles, *J. Organometallic Chem.*, 1972, **37**, C14.

[9] H. Felkin, P. J. Knowles, B. Meunier, A. Mitschler, L. Ricard, and R. Weiss, *J.C.S. Chem. Comm.*, 1974, 44.

[10] I. S. Kolomnikov, A. O. Gusev, T. S. Belopotopova, M. Kh. Grigoryan, T. V. Lysyak, Yu. T. Struchkov, and M. E. Volpin, *J. Organometallic Chem.*, 1974, **69**, 210.

[11] I. S. Kolomnikov, T. S. Lobeeva, and M. E. Volpin, *Zhur. obshchei Khim.*, 1972, **41**, 2231; I. S Kolomnikov, T. S. Lobeeva, M. E. Gurbachevskaja, G. G. Alaksandrov, Yu. T. Struchkov, and M. E. Volpin, *J.C.S. Chem. Comm.*, 1972, 972.

[12] G. N. Schrauzer and J. V. Sibert, *J. Amer. Chem. Soc.*, 1970, **92**, 3510; I. S. Kolomnikov, H. Stepovska, S. Tyrlik, and M. E. Volpin, *Zhur. obshchei Khim.*, 1972, **42**, 1652.

[13] A. Miyashita and A. Yamamoto, *J. Organometallic Chem.*, 1973, **49**, C57.

[14] S. Inoue and Y. Yokoo, *J. Organometallic Chem.*, 1972, **39**, 11.

[15] S. Suoboon, T. S. Belpatapova, and J. Hettlejs, *J. Organometallic Chem.*, 1974, **65**, C37.

[16] I. S. Kolomnikov, T. S. Belopotapova, T. U. Lysyak, and M. E. Volpin, *J. Organometallic Chem.*, 1974, **67**, C25.

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

with dry toluene (2 × 50 cm^3), then with light petroleum (b.p. 30—40 °C, 2 × 50 cm^3), and finally dried under reduced pressure for 2 h, yield *ca.* 95%.

The same procedure was followed in the preparation of the other related yellow compounds (see text). Relevant details which differ from those above are given in Table 2.

Reactions of Compound (III).—(a) *With benzyl bromide.* The adduct (2.6 g, 2.2 mmol) was suspended in toluene (50 cm^3) at −80 °C and treated with benzyl bromide (0.8 g, 4.6 mmol). The mixture was allowed to warm to room temperature and after 4 h methanol (10 cm^3) was added. The mixture was concentrated under reduced pressure to 1 cm^3 and was then chromatographed. Elution with toluene–light petroleum (b.p. 30—40 °C) (3 : 1) gave an orange band which was collected and the solvent was removed under reduced pressure. The residue was recrystallised from benzene–light petroleum (b.p. 80—100 °C) as orange crystals of $[Mo(\eta\text{-}C_5H_5)_2(CH_2Ph)_2]$, (VI) (0.23 g, 0.56 mmol), *ca.* 25%.

TABLE 2

Condition of preparation of the adducts $[M(\eta\text{-}C_5H_5)_2H_2{\cdot}MgRX]$

$[M(\eta\text{-}C_5H_5)_2H_2]$						
M	Amount (g, mmol)	MgRX in OEt_2 [a] (Amount/mmol)	Duration (t/h)	θ_c/°C	Form [b]	Yield (%)
Mo	0.5, 2.2	$MgBr(CH_2Ph)$ (4.60)	6	60	c	95
Mo	2.26, 9.9	$MgBrPr^i$ (40)	2	20	c	90 [c]
Mo	2.0, 8.8	$MgBrBu^n$ (40)	2	20	c	85
Mo	2.0, 8.8	MgBrMe (40) [d]	6	20	p	80
Mo	2.3, 10.1	MgMeI (40)	6	20	p	85
Mo	1.9, 8.3	MgBrPh (40)	6	20	p	80 [e]
W	2.0, 6.3	MgBrPh (30) [f]	48	18	p	80
W	0.5, 1.6	MgMeI (10)	6	18	p	80 [g]

[a] *ca.* 2 mol dm^{-3} solutions. [b] c = Crystalline, p = powder. [c] Mo : Mg = 1.201 : 1; Mg, 9.1 (8.8); Mo, 17.8 (17.3)% (calc. for $C_{34}H_{56}Br_4Mg_4Mo_2O_2$). This adduct crystallises from cold concentrated thf solutions as orange crystals: Mo : Mg = 1 : 1.91; Mg, 7.9 (8.8); Mo, 16.3 (17.4)%. Calc. values for $C_{34}H_{52}Br_4Mg_4Mo_2O_2$. [d] ν(Mo–H) at 1 865 cm^{-1} (KBr). [e] Mo : Mg = 1 : 1.97. [f] W : Mg = 1 : 1; C, 35.3 (38.8); H, 3.7 (3.0); Mg, 5.1 (4.95); W, 39.1 (37.1)%. Calc. values for $[W(\eta\text{-}C_5H_5)_2H_2{\cdot}MgBrPh]$; ν(W–H) at 1 890 cm^{-1}. [g] W : Mg = 1 : 1; C, 28.9 (30.3); H, 3.25 (3.45); Br, 19.7 (18.4); Mg, 5.9 (5.5); W, 42.3 (42.3)%. Calc. values for $[W(\eta\text{-}C_5H_5)_2H_2{\cdot}MgBrMe]$.

(b) *With bromopentafluorobenzene.* The adduct (III) (2.6 g, 2.2 mmol) in dry thf (50 cm^3) at −80 °C was treated with bromopentafluorobenzene (1.1 g, 0.9 cm^3, 4.6 mmol) and then allowed to warm to room temperature. After 4 h methanol (10 cm^3) was added, the mixture was concentrated under reduced pressure, and the concentrate was chromatographed. Elution with light petroleum (b.p. 30—40 °C)–toluene (3 : 1) gave an orange band. This was collected, the solvent was removed under reduced pressure, and the residue was recrystallised from light petroleum (b.p. 60—80 °C) as orange crystals of $[Mo(\eta\text{-}C_5H_5)_2(C_6F_5)_2]$, (VIII) (0.36 g, 0.64 mmol), *ca.* 30%.

(c) *With butadiene.* The adduct (III) (2.6 g, 2.2 mmol) in dry thf was treated in a sealed tube with buta-1,3-diene (1.3 g, 2.4 mmol) at 50 °C for 24 h. The mixture became dark red and some polymeric substance separated. The mother liquor was separated, concentrated under reduced pressure (2 cm^3), and chromatographed. Elution with methanol gave a red band which was collected, concentrated, and treated with aqueous ammonium hexafluorophosphate. A red precipitate separated which was collected and washed with water (3 × 50 cm^3) and dried under reduced pressure. Recrystallisation from ethanol gave coral-pink microcrystals of $[Mo(\eta\text{-}C_4H_7)(\eta\text{-}C_5H_5)_2][PF_6]$, (VIII) (0.12 g, 0.28 mmol), *ca.* 13%.

(d) *With carbon dioxide.* Compound (III) (2.6 g, 2.2 mmol) in dry tetrahydrofuran–toluene (1 : 1, 80 cm^3) was treated with a stream of carbon dioxide gas at room temperature. After 2 h a deep green colour had developed. The solvent was removed under reduced pressure and the residue was treated with water (15 cm^3) and toluene (3 × 50 cm^3). The deep green toluene layer was separated and dried with $Mg[SO_4]$ and then concentrated to 10 cm^3 and chromatographed. Elution with light petroleum (b.p. 30—40 °C) gave a green band which was collected and the solvent was removed under reduced pressure. The residue was further purified either by sublimation (90 °C, 10^{-2} mmHg) * or by crystallisation from light petroleum (b.p. 30—40 °C) giving pure $[Mo(\eta\text{-}C_5H_5)_2(CO)]$, (IV), *ca.* 85%. Further elution of the column with toluene gave the parent dihydride (I).

(e) *With carbon monoxide.* Compound (III) (2.6 g, 2.2 mmol) in tetrahydrofuran–toluene (1 : 1, 80 cm^3) was treated with a stream of carbon monoxide gas at room temperature for 48 h and a dark red colour developed. The solvent was removed under reduced pressure and the residue was extracted with toluene (2 × 50 cm^3) and water (15 cm^3). The toluene layer was separated, dried ($Mg[SO_4]$), filtered, concentrated, and chromatographed. Elution with light petroleum (b.p. 30—40 °C) gave three bands. The first was collected, the solvent was removed, and the residue was recrystallised from cyclohexane giving pure $[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_7)(CO)_2]$, (V) (0.26 g, 0.92 mmol), *ca.* 40%. The second band was eluted with light petroleum–toluene (1 : 1) and shown to be the dihydride (I) (0.07 g, 0.3 mmol), 14% by the i.r. spectrum. The third band was similarly eluted and characterised as the monocarbonyl (IV) (0.04 g, 0.15 mmol), 7%.

Reactions of the Compound $[H(\eta\text{-}H_5C_5)_2Mo\{\mu\text{-}Pr^iMgBr_2Mg(OEt_2)\}_2Mo(\eta\text{-}C_5H_5)_2H]$, (IX).—(1) *With iodomethane.* Compound (IX) (1.0 g, 0.9 mmol) in dry thf (50 cm^3) at −80 °C was treated with excess of iodomethane (5 cm^3). A smooth reaction occurred and both methane and propane were found in the supernatant vapour (g.l.c.). After 2 h the solvent was removed under reduced pressure and the residue was hydrolysed (water, 5 cm^3) and then extracted with toluene (2 × 50 cm^3). The green extract was concentrated under reduced pressure and chromatographed. Elution with diethyl ether gave a green band which was collected, the solvent was removed under reduced pressure, and the residue was recrystallised from diethyl ether–toluene as green crystals. These were collected, washed with light

---

* 1 mmHg ≈ 13.6 × 9.8 Pa; 1 atm = 101 325 Pa.

petroleum (b.p. 30—40 °C), and dried under reduced pressure to give $[MoMe(\eta\text{-}C_5H_5)_2I]$.

(b) *With iodobenzene.* The reaction was carried out as described in (a) using iodobenzene instead of iodomethane. After 12 h a deep red mixture was formed. Addition of water and benzene to the mixture precipitated a green-black material which was identified (i.r.) as the di-iodide $[Mo(\eta\text{-}C_5H_5)_2I_2]$ (0.22 g, 0.46 mmol), 25%.

(c) *With benzyl bromide.* The reaction and isolation was carried out as described for the reaction of (III) with benzyl bromide. The products were (VI) (0.15 g, 0.37 mmol), *ca.* 20%, and $[MoBr_2(\eta\text{-}C_5H_5)_2]$ (0.6 g), 69%.

(d) *With bromopentafluorobenzene.* The reaction was carried out as described for (c). The products were (VII) (0.4 g), 38%, and (I) (0.12 g).

(e) *With carbon dioxide.* The reaction was carried out as for (III). The product was (IV) (0.38 g), 80%.

(f) *With carbon monoxide.* The reaction was carried out as for (III). The products were (V) 30%, (I) (0.15 mg), 30%, and (IV) (10%).

Benzylbis(η-cyclopentadienyl)methylmolybdenum, (XI).—The adduct [(I)•MgBrMe] [from (I) (0.8 g, 3.5 mmol)] was suspended in toluene (50 cm^3) and the mixture was treated at room temperature with benzyl bromide (1.24 g, 7.25 mmol). A red-orange colour developed and after 3 h water (5 cm^3) was added. The toluene layer was separated and the solvent was removed under reduced pressure. The residue was extracted with toluene and chromatographed. Elution with pentane–benzene (1 : 1) gave an orange band from which was obtained, after recrystallisation from pentane–benzene, pure (XI), 0.32 g (27%). Mass spectrum (for ^{98}Mo): *m/e* 334 $[M]^+$; 319 $[Mo(\eta\text{-}C_5H_5)_2(CH_2Ph)]^+$; 233 $[MoMe(\eta\text{-}C_5H_5)_2]^+$; 228 $[Mo(\eta\text{-}C_5H_5)_2]^+$.

Benzylbis(η-cyclopentadienyl)phenylmolybdenum, (XII).—The adduct [(I)•MgBrPh] [from (I) (0.66 g, 2.9 mmol)] in suspension in toluene was treated with benzyl bromide (0.6 g, 3.5 mmol) at room temperature. A dark red colour developed and after 1 h water was added (5 cm^3). Following chromatography as described for (XI), pure compound (XII) was obtained (0.36 g), 32%. Mass spectrum (for ^{98}Mo): 396 $[M]^+$; 319 $[Mo(\eta\text{-}C_5H_5)_2(CH_2Ph)]^+$; 228 $[Mo(\eta\text{-}C_5H_5)_2]^+$; 218 $[^{98}Mo(\eta\text{-}C_5H_5)_2]^+$.

Reactions of the Adduct [(II)•MgMeI].—(a) *With carbon monoxide.* The adduct (1.0 g) in thf (50 cm^3) was treated with a stream of carbon monoxide at 3.5 atm for 24 h at room temperature. The mixture became green. Methanol (10 cm^3) then water (10 cm^3) were added and after stirring benzene (60 cm^3) was added. The yellow-green benzene layer was separated, concentrated under reduced pressure, and chromatographed as described for (III). Two bands developed and they were shown to contain the dihydride (II) (30%) and the monocarbonyl $[W(\eta\text{-}C_5H_5)_2(CO)]$ (10%).

(b) *With benzyl bromide.* The adduct (0.9 g) in thf (50 cm^3) at −80 °C was treated with benzyl bromide (1.0 g) in thf (10 cm^3). Analysis of the supernatant gas showed methane to be present (g.l.c.). After 24 h the reaction mixture was green and green crystals had separated. These were identified (i.r.) as the compound $[WBr_2(\eta\text{-}C_5H_5)_2]$ (0.45 g).

(c) *With methyl iodide.* The reaction was carried out as described in (b). Methane was found in the vapour above the reaction mixture. After 12 h green crystals separated from the mixture and they were shown to be $[W(\eta\text{-}C_5H_5)_2I_2]$ (0.79 g from 1.14 g of adduct).

Reactions of the Adduct [(II)•MgBrPr^i].—(a) *With methyl iodide.* The adduct (0.7 g) in thf (30 cm^3) at −80 °C was treated with iodomethane (1.0 g). The mixture was allowed to warm to room temperature and dark green crystals separated. The supernatant vapour was found to contain propane and methane (g.l.c.). The green crystals were shown to be $[W(\eta\text{-}C_5H_5)_2I_2]$ (0.55 g).

(b) *With carbon monoxide.* The adduct (0.56 g) in thf (50 cm^3) was treated with a stream of carbon monoxide at room temperature for 18 h. The initially yellow solution became red then, after 12 h, green. Following hydrolysis and chromatography the dihydride (II) and $[W(\eta\text{-}C_5H_5)_2(CO)]$ (0.3 g) were isolated.

(c) *With allyl bromide.* The adduct (0.7 g) in thf (80 cm^3) was treated with allyl bromide (0.5 cm^3) in thf (20 cm^3) at −80 °C. After 2 h at −80 °C the mixture was allowed to warm to room temperature. A red-orange colour developed and after 1 h water (25 cm^3) and light petroleum (b.p. 100—120 °C, 100 cm^3) were added. The red aqueous layer was separated and treated with aqueous $[NH_4][PF_6]$ giving a red precipitate. This was shown to be the compound $[W(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)_2][PF_6]$ (0.7 g) identified by comparison of its i.r. spectrum with that of an authentic sample. The compound $[W(\eta\text{-}C_5H_5)_2H_2]$, (II), was isolated from the organic layer.

(d) *With benzophenone.* The adduct (0.6 g) in thf (100 cm^3) at −80 °C was treated with benzophenone (0.35 g) in thf (50 cm^3) and the mixture was warmed to room temperature. After 2 d the resulting red solution was hydrolysed, and extraction with benzene gave an orange solution. This was concentrated under reduced pressure and treated with light petroleum (b.p. 30—40 °C). Deep red crystals separated leaving a red-yellow supernatant layer, from which the dihydride (II) could be isolated. The red crystals were collected, washed with light petroleum (b.p. 30—40 °C), and dried under reduced pressure giving pure $[W(\eta\text{-}C_5H_5)_2(C_6H_4COPh\text{-}p)H]$, (XIV), which was identified by comparison of the i.r. and ^{1}H n.m.r. spectra with those of an authentic sample (0.12 g), yield *ca.* 25% from $[W(\eta\text{-}C_5H_5)_2H_2]$.

We thank the S.R.C. for a grant and for support (to G. A. M. and D. M. R.).

[5/2446 *Received*, 15*th December*, 1975]