Alkyl, Alkynyl, and Olefin Complexes of Bis(π-cyclopentadienyl)-molybdenum or -tungsten: A Reversible Metal-to-ring Transfer of an Ethyl Group

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The compounds $[(\pi\text{-}C_5H_5)_2M(CH_2{=}CHR)H]^+PF_6^-$ where M = Mo, W, R = H; M = W, R = Me, $(\pi\text{-}C_5H_5)_2M(C_2H_4)$, $(\pi\text{-}C_5H_5)_2MoEtCl$, $(\pi\text{-}C_5H_5)_2MMe_2$, $(\pi\text{-}C_5H_5)_2M(C{\equiv}CPh)_2$ have been prepared and studied. The reversible reaction $[(\pi\text{-}C_5H_5)_2M(CH_2{=}CHR)H]^+ \longrightarrow H^+ + (\pi\text{-}C_5H_5)_2MCH_2{=}CHR$ has been demonstrated. With tertiary phosphines the ethyl complex gives the *endo*-ethyl derivatives $(\pi\text{-}C_5H_5)$(1-*endo*-EtC_5H_5)$MoPR_3Cl$. The complex $(\pi\text{-}C_5H_5)$(1-*endo*-EtC_5H_5)$MoPClMe_2Ph$ reacts with thallium tetrafluoroborate to give the ethyl cation $[(\pi\text{-}C_5H_5)_2MoPR_3Et]^+BF_4^-$. This and related cations may also be prepared from the hydridoethylene cations and tertiary phosphine. Mechanisms for these reactions are discussed.

We continue to study the chemistry of the bis(π-cyclopentadienyl)-molybdenum and -tungsten systems in order to unravel factors affecting reactivity and mechanism in organo-transition metal chemistry. For example, the bent bis-π-cyclopentadienyl system provides an opportunity to investigate essentially *cis*-orientated MXR or MR_2 systems, which are relatively rare. Here we describe the often unexpected results of attempts to prepare such complexes. A brief communication of some of this work has been given.[1]

Chemical Studies.—Treatment of the dichloride $(\pi\text{-}C_5H_5)_2MCl_2$ (I; M = Mo) with an excess of ethylaluminium dichloride dimer, followed by ethanolysis gives, in approximately equal yields, garnet crystals (II) and a water soluble cation isolable as a white hexafluorophosphate salt (III). The data in the Table together with a crystal structure determination [2] shows the garnet compound to be the chloroethyl derivative $(\pi\text{-}C_5H_5)_2MoEtCl$ (II). This is soluble in benzene and acetone but only very slightly soluble in light petroleum. Solutions in air show signs of decomposition after a few hours whilst the crystals remain unchanged in air for prolonged periods (days). Pyrolysis *in vacuo* yields ethylene and ethane (*ca.* 5 : 1) as volatile products (g.l.c.). With hydrogen chloride gas, the parent dichloride (II) is formed almost immediately, and with sodium borohydride the ethyl derivative (II) gives the dihydride $(\pi\text{-}C_5H_5)MoH_2$.

Treatment of the ethyl compound (II) with some tertiary phosphines PR_3 (R_3 = Et_3, $MePh_2$, Me_2Ph) gives benzene-soluble, purple-pink, compounds. The data show these to be the 1-*endo*-ethylcyclopentadiene derivatives $(\pi\text{-}C_5H_5)$(1-*endo*-EtC_5H_5)$Mo(PR_3)Cl$ (IV). The formulation as the *endo* isomer is strongly suggested by the observation of strong bands in the i.r. spectra *ca.* 2750 cm^{-1} which are normally characteristic of *exo*-C–H stretching frequencies.[3] The ^1H n.m.r. spectra of the complexes (IV) show that the pairs of hydrogens H_b and H_e or H_c and H_d (for labelling see Scheme 1) are non-equivalent which is to be expected if, as shown in Scheme 1, there is no plane of symmetry in the molecule. In fact, if the EtC_5H_5 ring does not rotate about the

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[1] F. W. S. Benfield, B. R. Francis, and M. L. H. Green, *J. Organometallic Chem.*, 1972, **44**, C13.

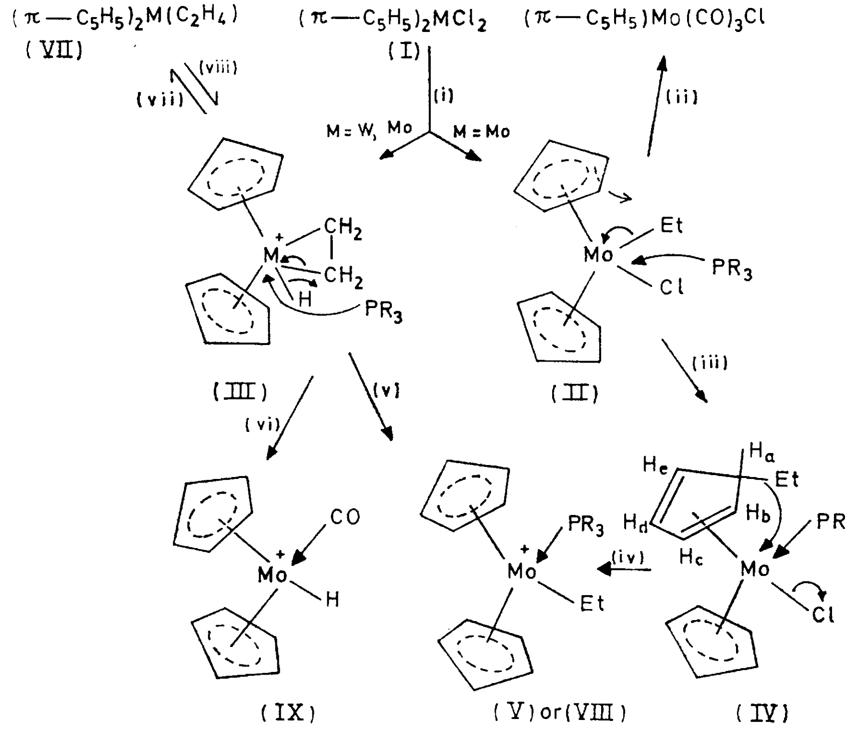
[2] R. A. Forder and C. K. Prout, personal communication.

[3] D. A. White, *Organometallic Chem. Rev. A.*, 1968, **3**, 497.

Analytical and i.r. data

	Compound	Colour	M.p.(t/°C) (decomp.)	Analytical data, % Found (Calc.) C	H	Selected i.r. data (mulls)/cm^{-1}
(1)	$(\pi\text{-C}_5\text{H}_5)_2\text{MoEtCl}$	Garnet	106	49·7 (49·6)	5·4 (5·2) [a]	
(2)	$[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\pi\text{-C}_2\text{H}_4)\text{H}]^+\text{PF}_6^-$	White		36·1 (36·0)	4·1 (3·9)	1510w,[b] 1840w[c]
(3)	$[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\pi\text{-C}_2\text{H}_4)\text{H}]^+\text{PF}_6^-$	White		29·4 (29·5)	3·1 (3·2)	1480,[b] 1840w[c]
(4)	$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\pi\text{-C}_2\text{H}_4)$	Orange-brown	150	56·5 (56·8)	5·6 (5·5) [d]	1465w[b]
(5)	$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\pi\text{-C}_2\text{H}_4)$	Orange	176	41·8 (42·2)	4·2 (4·1) [e]	1430w[b]
(6)	$(\pi\text{-C}_5\text{H}_5)\text{Mo}(\textit{endo}\text{-EtC}_5\text{H}_5)\text{ClPMe}_2\text{Ph}$ [g]	Pink-purple	142	55·0 (56·0)	6·1 (6·0)	2965ms, 2920m, 2860m, 2790ms[f]
(7)	$(\pi\text{-C}_5\text{H}_5)\text{Mo}(\textit{endo}\text{-EtC}_5\text{H}_5)\text{ClPMePh}_2$ [g]	Pink-purple	145	60·8 (61·2)	6·1 (5·8)	2960mw, 2930m, 2910sh, 2740m,[f] 2690w,[f] 2650w,[f] 2600w[f]
(8)	$(\pi\text{-C}_5\text{H}_5)\text{Mo}(\textit{endo}\text{-EtC}_5\text{H}_5)\text{ClEt}_3\text{P}$ [g]	Maroon	122	52·8 (52·9)	7·2 (7·4) [h]	2995ms, 2980s, 2960s, 2910sh, 2960sh, 2880ms, 2750m, 2730m,[f] 2710m[f]
(9)	$[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{PMe}_2\text{Ph})\text{Et}]^+\text{BF}_4^-$			49·9 (49·9)	5·4 (5·4)	
(10)	$[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\pi\text{-MeCH=CH}_2)\text{H}]^+\text{PF}_6^-$	Pale yellow		31·2 (31·0)	3·5 (3·4)	1482w,[b] 1970w[c]
(11)	$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\pi\text{-CH}_2\text{=CHMe})$	Orange	115	43·6 (43·8)	4·7 (4·5) [i]	1450w[d]
(12)	$[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{PPh}_3)\text{Et}]^+\text{PF}_6^-$	Orange		55·0 (54·5)	4·5 (4·6)	
(13)	$[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{PPh}_3)\text{Et}]^+\text{PF}_6^-$	Orange		48·5 (48·0)	4·0 (4·0)	
(14)	$[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CO})\text{H}]^+\text{PF}_6^-$	Yellow		33·1 (33·0)	2·6 (2·8)	1870w,[c] 2030s
(15)	$[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{PPh}_3)\text{Pr}^n]^+\text{PF}_6^-$	Orange		38·4 (48·7)	4·2 (4·5)	
(16)	$(\pi\text{-C}_5\text{H}_5)_2\text{MoMe}_2$	Red-orange	180	56·1 (56·4)	6·1 (6·3) [k]	
(17)	$(\pi\text{-C}_5\text{H}_5)_2\text{WMe}_2$	Red-brown	240	41·5 (41·9)	4·7 (4·7) [l]	
(18)	$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{C}\equiv\text{CPh})_2$ [m]	Red-brown				ν(C≡C) 2090
(19)	$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{C}\equiv\text{CPh})_2$	Red-brown		60·9 (60·6)	4·0 (3·4) [n]	ν(C≡C) 2080

[a] Parent ion peak at m/e 292 for ^{98}Mo. [b] ν(C=C). [c] ν(M–H). [d] Parent peak at m/e 256 for ^{98}Mo. [e] Parent ion peak at m/e 342 for ^{184}W. [f] Bands associated with *exo*-C–H stretch. [g] Mass spectrum shows a highest ion at m/e 250 corresponding to $[(\pi\text{-C}_5\text{H}_5)\text{-}^{98}\text{Mo}(\text{C}_5\text{H}_4\text{Et})\text{Cl}]^+$. [h] Cl, 8·6 (8·7); P, 7·4 (7·6); Mo, 23·6 (23·5)%. [i] Parent ion peak at m/e 356 for ^{184}W. [j] ν(C≡O). [k] Parent ion peak at m/e 258 for ^{98}Mo. [l] Parent ion peak at m/e 344 for ^{184}W. [m] Parent ion peak at m/e 430 for ^{98}Mo. [n] Parent ion peak at m/e 516 for ^{184}W.



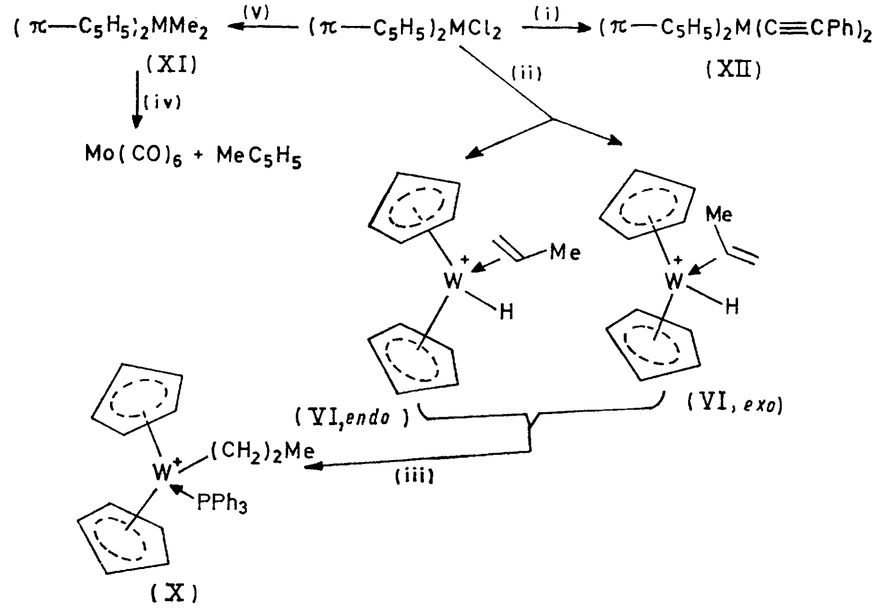
SCHEME 1 (i), $(\text{EtAlCl}_2)_2$, then EtOH–H$_2$O–PF$_6^-$; (ii), CO, 50 atm, 50°; (iii), PR$_3$, R$_3$ = Et$_3$, Me$_2$Ph, MePh$_2$; (iv), Tl$^+$BF$_4^-$; (v), PR$_3$, R$_3$ = Ph$_3$; (vi), CO, 50 atm, 50°; (vii), OH$^-$ or LiPh; (viii), H$_2$O–PF$_6$

ring–Mo axis then geometric isomers may be envisaged. The presence of such isomers is suggested by the occurrence of persistent minor constituents detectable in the ^{1}H n.m.r. spectra.

The *endo* ethyl derivatives (IV; R$_3$ = Me$_2$Ph) show an interesting and unexpected reaction with thallium tetrafluoroborate. The cation product, isolated as the tetrafluoroborate salt, is shown by the data in the Table and the Experimental section to be the ethyl derivative $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{PMe}_2\text{Ph})\text{Et}]^+\text{BF}_4^-$ (V). Complexes analogous to (V) may be prepared by an alternative route described below. The ethyl compound (II) also reacts with carbon monoxide (50 atm, 50°) giving the well known tricarbonyl compound $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Cl}$ in good yield.

The white salt (III), described above, is shown by the data to be the hydrido-ethylene compound $[(\pi\text{-}C_5H_5)_2Mo(C_2H_4)H]^+PF_6^-$ (III; M = Mo). This is soluble in acetone and solutions are largely decomposed in air within a few minutes. The cation (III) may also be readily prepared starting from the chloroethyl derivative (II) by treatment with thallium hexafluorophosphate or with an excess of ethylaluminium dichloride dimer. The tungsten analogue (III; M = W) is prepared from the dichloride (I; M = W) and ethylaluminium dichloride dimer and there was no evidence for the formation of the tungsten analogue of the ethyl derivative (II) during this reaction.

The ^1H n.m.r. spectra at room temperature of the hydridoethylene complexes (III) each show a single resonance due to the ethylene hydrogens. This apparent equivalence may be due either to a sufficiently rapid rotation of the ethylene about the ethylene–metal axis or to a rapid on–off equilibrium of either the proton or the ethylene. The spectra of the complexes (III) were determined at —90° in acetone and only a slight relative broadening of the ethylene resonance was observed of dubious validity. Treatment of the dichloride (I; M = W) with isopropylmagnesium chloride followed by addition of ammonium hexafluorophosphate to the aqueous extract of the hydrolysed reaction product gave pale yellow crystals. The data shows these to be the hydridopropene cation (VI). This is soluble in acetone and dimethyl sulphoxide and the solutions are decomposed within a few hours.



SCHEME 2 (i), LiC≡CPh; (ii), Pr^iMgCl, then $H_2O\text{–}PF_6$; (iii), PPh_3; (iv), CO, 50 atmos., 50°; (v), MeMgBr

The ^1H n.m.r. spectrum of the cation (VI) shows two high field lines at τ 16·79 and 16·65 assignable to two W–H systems and two symmetrical doublets in the region τ 3·98—4·09 due to $\pi\text{-}C_5H_5$ resonances. Assuming that the W(C=C)H system of the cation (VI) is approximately planar, then two isomers, *exo*- and *endo*-methyl may be envisaged, see Scheme 2. The ^1H n.m.r. spectrum may be readily assigned on this basis assuming that the two isomers exist in the relative ratios *ca.* 4 : 3. Raising the temperature to 50° caused no appreciable change in the relative intensities of the bands assigned to the two isomers.

The hydrido-ethylene (III) and -propene (VI) cations react readily with aqueous base forming the previously reported neutral olefin derivatives $(\pi\text{-}C_5H_5)_2M(CH_2{=}CHR)$ (VII; M = Mo, R = H; M = W, R = H, Me).[1] The ethylene derivatives have been independently described by Thomas.[4] The propene derivative (VII; M = W, R = Me) forms orange-red crystals soluble in benzene and light petroleum and the solutions are very sensitive to oxidation by air. The ^1H n.m.r. spectrum shows that the two $\pi\text{-}C_5H_5$ groups are non-equivalent and therefore in-plane rotation of the propene, if any, is slow on the n.m.r. time-scale. Also, a rigid MC_2 system may be assumed for the neutral ethylene derivatives (VII) since metal–ethylene bonding is thought to be normally slightly stronger than that in propene.

The complex (VII; M = Mo, R = H) may also be prepared by treatment of the ethyl derivative (II) with an excess of phenyl-lithium.

The neutral olefin compounds (VII) are readily protonated by dilute hydrochloric acid or even as a result of addition of aqueous hexafluorophosphate to acetone solutions of (VII).

Treatment of the hydridoethylene cations (III) with triphenylphosphine causes an internal insertion reaction and the orange, air-stable ethyl derivatives $[(\pi\text{-}C_5H_5)_2M(PPh_3)Et]^+PF_6^-$ (VIII; M = Mo or W) are formed. These are soluble in acetone and dimethyl sulphoxide. Solutions slowly darken on exposure to air (hours). In apparent contrast to this reaction, treatment of the ethylene cation (III; M = Mo) with carbon monoxide

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[4] J. L. Thomas, *J. Amer. Chem. Soc.*, 1973, **95**, 1838.

yields the carbonylhydride $[(\pi\text{-}C_5H_5)_2Mo(CO)H]^+PF_6^-$ (IX). Under analogous conditions the tungsten cation (III; M = W) reacted only slowly with carbon monoxide and no new tractable products were obtained. The cation (III; M = W, R = H) with carbon tetrachloride gives the dichloride $(\pi\text{-}C_5H_5)_2WCl_2$. The corresponding dibromide $(\pi\text{-}C_5H_5)MoBr_2$ is similarly prepared using bromoform and the cation (III; M = Mo, R = H).

The sole isolated product of the reaction of the isomeric mixture of the cation (III; M = W, R = Me) with triphenylphosphine was the n-propyl derivative $[(\pi\text{-}C_5H_5)_2W(PPh_3)Pr^n]^+[PF_6]^-$ (X) although both n- and isopropyl products might have been expected.

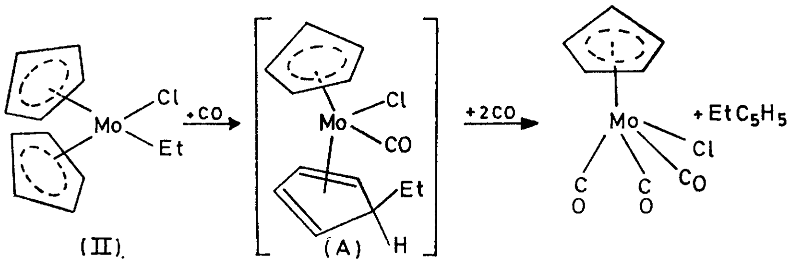
Treatment of the dichlorides $(\pi\text{-}C_5H_5)_2MCl_2$ (I; M = Mo or W) with an excess of methylmagnesium chloride in ether yields sublimable waxy red brown crystals which the data in the Table and the Experimental section show to be the briefly reported [5] dimethyl derivatives $(\pi\text{-}C_5H_5)_2MMe_2$ (XI). They are soluble in light petroleum and solutions are decomposed in air within a few minutes. Treatment of benzene solutions with hydrogen chloride reforms the parent dichlorides (I) and methane is evolved (i.r.). Toluene solutions of (XI) were exposed to carbon monoxide (50 atm, 50 °C) giving the corresponding hexacarbonyls $M(CO)_6$ and methylcyclopentadiene (i.r.). The methyl derivatives (XI) have been independently prepared by Thomas.[4]

The dichlorides (I) react with phenylethynyl lithium giving red-brown crystals which the data shows to be the bis-π-phenylethynyl derivatives $(\pi\text{-}C_5H_5)M(C{\equiv}CPh)_2$ (XII; M = Mo or W). The tungsten compound was formed in *ca.* 60% yield, whilst the molybdenum derivative was obtained in very small yields and has been only partially characterised, by i.r. and mass spectral data. The complexes (XII) appear stable in air but solutions in dichloromethane slowly decompose.

The i.r. spectra of the complexes (XII; M = Mo or W) show a band assignable to $\nu(C{\equiv}C)$ at 2090 and 2080 cm^{-1}, for M = Mo or W respectively.

DISCUSSION

In the light of the ethyl migration reaction, whereby the complexes (IV) are formed from complex (II), the following mechanism for the formation of $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$ from (II) and carbon monoxide can be envisaged. The contrasting observation that the tertiary phosphine complexes (IV) do not further react with an excess of tertiary phosphine giving $(\pi\text{-}C_5H_5)Mo(PR_3)_3Cl$ may reflect the difference of ligand properties of carbon monoxide and PR_3. The net effect of attachment of carbon monoxide to an electron-rich metal is withdrawal of electron density, whereas tertiary-alkylphosphines normally cause an increase of electron density on the metal.



(II) (A)

The removal of electron density by the carbonyl group in the proposed intermediate (A) would cause reduction of back donation to the EtC_5H_5 group and hence weakening of the $Mo\text{–}EtC_5H_5$ bond. In contrast this bond would be relatively stronger in the compound (IV). Since the complexes $[C_6H_6Mo(PPh_2Me)_3H_2]^{2+}$ are known [6] it seems unlikely that steric overcrowding would restrict formation of the complexes $(\pi\text{-}C_5H_5)M(PR_3)_3Cl$.

Thomas has described the ethylene complex (VII; R = H) and related derivatives.[4] He shows that with hydrogen chloride the ethylene complex evolves ethane and he suggests that the reaction is indicative of a metallocyclopropane structure for the MoC_2H_4 system. However the formation of ethane may well proceed *via* the intermediate hydridoethylene cation (III; M = Mo), as follows:

$$[\mathrm{Mo}](C_2H_4) \xrightarrow{+H^+} \{[\mathrm{Mo}](C_2H_4)H\}^+ \xrightarrow{+Cl^-}$$

$$[\mathrm{M}]\Big\langle{}^{\mathrm{Et}}_{\mathrm{Cl}} \xrightarrow{+H^+} [\mathrm{M}]^+\Big\langle\begin{smallmatrix}\mathrm{H}\\ \mathrm{Et}\\ \mathrm{Cl}\end{smallmatrix} \xrightarrow{+Cl^-} [\mathrm{M}]\Big\langle{}^{\mathrm{Cl}}_{\mathrm{Cl}} + C_2H_6$$

Therefore, ethane formation is not a criterion of metal–ethylene bond type.

There exists a continuum of energetic possibilities between the two hypothetical extreme descriptions of the metal–ethylene bond, namely with σ-symmetry interactions only, $M \longleftarrow \begin{smallmatrix}C\\ \Vert\\ C\end{smallmatrix}$, or with π-symmetry interactions only, $M\Big\langle\begin{smallmatrix}C\\ \vert\\ C\end{smallmatrix}$. Transition metals will always give rise to contributions from both symmetry types. Therefore it is not normally useful to discuss differences of contributions from the σ- and π-symmetry interactions in terms of valence bond representations, *i.e.* the disposition of ' black lines ' between the metal and olefin carbons. In terms of writing reaction mechanism *via* putative electron shifts using the ' curly arrow ' convention it seems more explicit if a metallocyclopropane representation is used. This is demonstrated in Scheme 1. In this context, we have written an electron-

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[5] M. L. H. Green and P. J. Knowles, *J.C.S. Chem. Comm.*, 1970, 1677.

[6] M. L. H. Green, J. Knight, L. C. Mitchard, G. G. Roberts, and W. E. Silverthorn, *Chem. Comm.*, 1971, 1620.

shift mechanism for the alkyl transfer reaction. The addition of the ethyl group to the metal, when complex (II) gives the product (IV), is an 'internal oxidative-addition reaction' of a C–C bond, akin to well known C–H oxidative addition reactions. Clearly the formation of (V) from (IV) is an 'internal reductive-elimination reaction' of a C–C system.

Finally, the formation of $M(CO)_6$ from the dimethyl derivatives (XI) may be envisaged to involve two successive methyl-to-ring steps giving intermediate *endo*-methylcyclopentadiene species.

EXPERIMENTAL

All preparations and purifications were carried out in the absence of oxygen. Where required, solvents were dried by refluxing over, and distillation from, calcium hydride. Light petroleum is AnalaR, b.p. 30—40 °C. I.r. spectra were measured on mulls using a Perkin-Elmer 457 instrument calibrated with polystyrene. Low-resolution mass spectra were determined using a MS9 spectrometer. The compounds $(\pi\text{-}C_5H_5)_2MH_2$, M = Mo or W,[7] and $(\pi\text{-}C_5H_5)_2MCl_2$, M = Mo or W,[8] were prepared as previously described.

Choroethylbis(π-cyclopentadienyl)molybdenum and Hydridoethylenebis(π-cyclopentadienyl)molybdenum Hexafluorophosphate.—The dichloride $(\pi\text{-}C_5H_5)_2MoCl_2$ (2 g, 6·75 mmol) was added, in portions, to a benzene solution of commercial ethylaluminium dichloride (40 mmol, 30 ml of 170 g l^{-1} solution) in benzene (30 ml). A dark oil was formed below a green solution after 10—15 min. The mixture was stirred for 12 h at room temperature by which time the originally green solution above the oil was colourless. The supernatant liquid was decanted and the residual oil was dried *in vacuo*, cooled to −196°, and cooled ethanol (*ca.* 30 ml) was cautiously added over a period of 10 min. The mixture was allowed to warm slowly to room temperature giving a red-brown solution. Solvent was removed *in vacuo* to give a red-brown solid which was extracted with water to give a pale red-brown extract and an insoluble crystalline garnet residue. The extract was filtered to give a pale red-brown filtrate. The insoluble crystalline residue was dried *in vacuo*.

A saturated aqueous solution of ammonium hexafluorophosphate was added to the filtrate to give a slightly off-white precipitate which was collected, washed with water until the washings were very pale in colour, and dried *in vacuo*. The off-white precipitate was extracted with acetone and the extract was filtered to give a pale green filtrate. Ethanol was added and solvent was slowly removed *in vacuo* to give white crystals which were collected, washed with a little ethanol and dried *in vacuo*. A further recrystallisation from acetone–ethanol or acetone–ether gave white crystals of the pure $[(\pi\text{-}C_5H_5)_2MoH(C_2H_4)]^+PF_6^-$, *ca.* 20%. The water-insoluble garnet solid was extracted with benzene and the solution was filtered giving a deep red filtrate. This was slowly concentrated *in vacuo* and light petroleum was slowly added and the mixture was allowed to stand for 15 min. The garnet crystals precipitated and were collected by filtration, washed with several aliquots of light petroleum, and dried *in vacuo*, giving the pure compound, *ca.* 20% yield.

The tungsten compound $[(\pi\text{-}C_5H_5)_2W(C_2H_4)H]^+PF_6^-$ was similarly prepared from the dichloride $(\pi\text{-}C_5H_5)_2WCl_2$ (0·79 g, 2·06 mmol) and ethylaluminium dichloride (20 mmol) in toluene (25 ml) for 24 h, *ca.* 60% yield. None of the neutral chloroethyl complex $(\pi\text{-}C_5H_5)_2WEtCl$ was detected.

Reactions of the Hydridoethylene Complexes $[(\pi\text{-}C_5H_5)_2MH(C_2H_4)]^+PF_6^-$.—(a) *With carbon tetrachloride.* The complex $[(\pi\text{-}C_5H_5)_2W(C_2H_4)H]^+PF_6^-$ (0·25 g, 0·51 mmol) in acetone (AnalaR, 10 ml) gave a colourless solution and carbon tetrachloride (AnalaR, 0·8 mmol) was added. After about 1 h a purple tinge was perceptible. The mixture was allowed to stand overnight giving a deep purple solution. After 3 days dark coloured crystals precipitated and the solution was red-brown. The crystals were collected, washed with a little acetone, and then dried *in vacuo*. The i.r. spectrum of the green-black crystals was compared with that of an authentic sample of the dichloride $(\pi\text{-}C_5H_5)_2WCl_2$ and found to be identical.

A similar reaction between the molybdenum hydridoethylene complex $[(\pi\text{-}C_5H_5)_2Mo(C_2H_4)H]^+PF_6^-$ and bromoform yielded greenish crystals identified as the dibromide $(\pi\text{-}C_5H_5)_2MoBr_2$ by comparison of their i.r. spectrum with that of an authentic sample.

(b) *With carbon monoxide.* The complex $[(\pi\text{-}C_5H_5)_2Mo(C_2H_4)H]^+PF_6^-$ (0·32 g) in acetone (50 ml, AnalaR) was refluxed with simultaneous passage of carbon monoxide. The solution slowly became orange. After 8 h solvent was removed *in vacuo* to give a brown solid. This was extracted with acetone and the extract filtered to yield an orange filtrate. An equal volume of ethanol was added to the filtrate and solvent was slowly removed *in vacuo* to yield small brown crystals which were dissolved in aqueous acetone, containing ammonium hexafluorophosphate, and solvent was slowly removed *in vacuo* to give small yellow crystals. These were collected, washed with water, and finally recrystallised from hot water to give yellow crystals which were washed with a little cold water and dried *in vacuo*. Comparison of their i.r. spectrum with that of an authentic sample of the hydridocarbonyl complex $[(\pi\text{-}C_5H_5)_2Mo(CO)H]^+PF_6^-$ showed that they were identical.

A similar reaction was repeated with the tungsten analogue $[(\pi\text{-}C_5H_5)_2W(C_2H_4)H]^+PF_6^-$ and after 15 h off-white crystals were obtained after crystallisation from acetone–ethanol. Examination of their i.r. spectrum showed a weak band at 2020 cm^{-1} assignable to a carbonyl stretching frequency but there were other bands in the spectrum which could be assigned to starting material. It appeared that only very slow displacement of the ethylene was occurring. The reaction was not further studied.

Hydrido(π-propene)bis(π-cyclopentadienyl)tungsten Hexafluorophosphate.—A suspension of the dichloride $(\pi\text{-}C_5H_5)_2WCl_2$ (0·67 g, 1·74 mmol) in toluene (15 ml) was treated with an excess of isopropylmagnesium bromide (6 mmol) in ether and the mixture was stirred at room temperature for two days. The solvent was removed from the resulting brown reaction product under reduced pressure. The residue was cooled to −196° and ethanol was added (5 ml). The mixture was allowed to warm to room temperature and the solvent was removed under reduced pressure. The residue was extracted with water (15 ml) giving an orange-brown solution. This was filtered and aqueous ammonium hexafluorophosphate was added giving yellow-brown crystals. These were washed with water and dried *in vacuo*. Recrystallisation from acetone–ethanol gave pale yellow crystals of the pure compound, *ca.* 30% yield.

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Ethyl(triphenylphosphine)bis(π-cyclopentadienyl)molybdenum Hexafluorophosphate.—The ethylenehydride $[(\pi\text{-}C_5H_5)_2Mo(C_2H_4)H]^+PF_6^-$ (0·3 g, 0·75 mmol) in acetone (50 ml) was treated with triphenylphosphine (1·2 g, 4 mmol) and mixture was refluxed for 20 h. A red solution developed then solvent was removed *in vacuo* to give a red-brown oil which was washed with benzene (3 × 40 ml) and the light petroleum (2 × 50 ml) to yield a red-brown solid which was dried *in vacuo*. The solid was extracted with acetone to give a red-brown solution and a brown insoluble residue; after filtration toluene was added to the filtrate. Solvent was slowly removed *in vacuo* giving small orange crystals which were collected, washed with toluene then ether, and dried *in vacuo*. Recrystallisation from acetone–aqueous ammonium hexafluorophosphate then acetone–water gave orange crystals of the pure compound, *ca*. 30% yield.

Ethyl(triphenylphosphine)bis(π-cyclopentadienyl)tungsten Hexafluorophosphate.—The ethylenehydride $[(\pi\text{-}C_5H_5)_2W(C_2H_4)H]^+PF_6^-$ (0·4 g, 0·98 mmol) in acetone (50 ml) was treated with triphenylphosphine (1·2 g, 4 mmol) and the mixture was refluxed for 6 days. A deep red-amber solution developed. The solvent was removed *in vacuo* to give a partially solidified red oil which was washed with benzene (3 × 50 ml) and light petroleum (2 × 20 ml) yielding an orange crystalline solid which was dried *in vacuo*. This was extracted with acetone and the extract filtered to give an orange-red solution. A volume of toluene equal to half the volume of filtrate was added. The solvent was slowly removed *in vacuo* and white crystals precipitated. These were collected by filtration and identified from their i.r. spectrum as starting material. The red mother liquor was further concentrated *in vacuo* and orange crystals were precipitated, collected by filtration, washed with toluene, and dried *in vacuo*. They were recrystallised twice from acetone–water and dried *in vacuo*. Their ^1H n.m.r. spectrum indicated that they were contaminated with starting material. The crystals were finally purified by chromatography on an alumina column made up in acetone, the sample being introduced to the column in acetone. Elution with acetone–ethanol (1 : 1) gave an orange band which was collected. Solvent was removed very slowly *in vacuo* and white crystals separated; the solution was cooled to 0° and the red mother liquor was separated by filtration and re-chromatographed on alumina in acetone. Elution with ethanol afforded an orange band which was collected and concentrated *in vacuo* to yield orange crystals which were separated, washed with ethanol, and dried *in vacuo*. The crystals were recrystallised from acetone–water, washed with water, and dried *in vacuo*, *ca*. 20% yield.

Reactions of Ethylchlorobis(π-cyclopentadienyl)molybdenum.—(a) *With ethylaluminium dichloride*. The compound $(\pi\text{-}C_5H_5)_2MoEtCl$ (0·25 g, 0·86 mmol) in benzene (10 ml) was treated with ethylaluminium dichloride (4·5 mmol) in benzene (15 ml). A rapid reaction occurred and a dark oil was formed below a very pale yellow supernatant liquid. The supernatant liquid was decanted and remaining solvent was removed *in vacuo*. The resulting oil was decomposed at −196° with ethanol and the mixture allowed to warm slowly to room temperature when solvent was removed *in vacuo* to yield a light brown residue. This was extracted with water to give a pale red-brown extract which was filtered to give a clear pale red-brown filtrate. Addition of a saturated aqueous solution of ammonium hexafluorophosphate gave a copious white precipitate. This was collected, washed with water, and dried *in vacuo*, *ca*. 65% yield. Comparison of the i.r. spectrum of the white crystals with that of the hydridoethylene hexafluorophosphate $[(\pi\text{-}C_5H_5)_2Mo(C_2H_4)H]^+PF_6^-$ showed them to be identical.

(b) *With sodium borohydride*. $(\pi\text{-}C_5H_5)_2MoEtCl$ (0·2 g, 0·7 mmol) in ethanol (25 ml) was treated with sodium borohydride (an excess, *ca*. 0·1 mmol). The mixture was stirred at room temperature for 12 h giving an orange solution. Solvent was removed *in vacuo* and the orange residue was washed with water then dried *in vacuo*. Recrystallisation from toluene at low temperature (−20°) yielded yellow crystals which were collected, washed with a little cold toluene, and dried *in vacuo*. The product was identified as the dihydride $(\pi\text{-}C_5H_5)_2MoH_2$ by the i.r. spectrum.

(c) *With phenyl-lithium*. $(\pi\text{-}C_5H_5)_2MoEtCl$ (0·3 g, 1·0 mmol) was suspended in ether (20 ml) and phenyl-lithium in ether (1·1 mmol) was added. An orange solution immediately formed and after 15 min solvent was removed *in vacuo* to give a brownish residue. This was extracted with light petroleum and the extract filtered to give an orange filtrate from which solvent was removed *in vacuo*. The residue was treated with ethanol at −78° to free it from any traces of the organolithium reagent and the mixture allowed to warm slowly to room temperature and solvent was removed *in vacuo* giving an orange solid. Extraction with light petroleum followed by filtration yielded an orange filtrate which was concentrated *in vacuo* and then slowly cooled to −78°. Red-orange crystals precipitated which were collected by filtration, washed with a little cold light petroleum and dried, *in vacuo*. Comparison of the i.r. and ^1H n.m.r. spectra with those of an authentic sample showed the product to be the neutral ethylene complex $(\pi\text{-}C_5H_5)_2Mo(C_2H_4)$.

(d) *With carbon monoxide*. The compound $(\pi\text{-}C_5H_5)_2MoEtCl$ (0·26 g) in toluene (25 ml) was placed in a glass bomb-liner within a bomb under carbon monoxide (50 atm, 50°). After 45 h the bomb was allowed to cool and cautiously vented. The liner was removed; it contained an orange solution and a little orange solid. Solvent was removed *in vacuo* to yield orange needle crystals which were washed with light petroleum to free them from a small amount of contaminating oil. The crystals were then dissolved in toluene and the solution filtered to give a clear orange filtrate. This was concentrated *in vacuo*, light petroleum was added until crystals began to form, and then the solution was cooled slowly to −78°. The resulting orange crystals were collected, washed with light petroleum, and dried *in vacuo*. They were identified as the known complex $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$ by comparison of i.r. spectrum with the literature, and by the ^1H n.m.r. and mass spectra and elemental analysis (Found: C, 34·3; H, 1·8%. Required for $C_8H_5ClO_3Mo$: C, 34·2; H, 1·7%).

*Chloro(triethylphosphine)(*endo*-ethylcyclopentadiene)(π-cyclopentadienyl)molybdenum*.—The compound $(\pi\text{-}C_5H_5)_2MoEtCl$ (0·89 mmol) in toluene (10 ml) was treated with triethylphosphine (0·4 ml, 3·3 mmol). The solution was heated at 80° for 24 h. A red solution was formed and removal of solvent *in vacuo* yielded an oily pink solid. The oil was removed by repeated washing with cold light petroleum (−78°). The resulting pink solid was dissolved in the minimum quantity of petrol (b.p. 100—120°) at 80° and the solution filtered hot giving a deep red filtrate which was allowed to cool slowly to room temperature and then gradually cooled to −78°. The resulting maroon needles were separated from the mother liquor by filtration, washed several times with cold light petroleum (−78°), and dried *in vacuo*. A second crop of crystals was obtained by concentration of the mother liquor by removal of solvent *in vacuo*, and slow cooling to −78° as before, *ca.* 60% yield.

The reaction was repeated under the same conditions with the phosphines PMe_2Ph and $PMePh_2$, giving the corresponding products $(\pi\text{-}C_5H_5)(\textit{endo}\text{-}Et\text{-}C_5H_4)Mo(PR_3)Cl$, $R_3 = Me_2Ph$ or $MePh_2$, respectively.

Ethyl(triphenylphosphine)bis(π-cyclopentadienyl)molybdenum Hexafluorophosphate.—The compound $(\pi\text{-}C_5H_5)(1\text{-}\textit{endo}\text{-}EtC_5H_5)Mo(PMe_2Ph)Cl$ (0·33 g, 0·77 mmol) in acetone (AnalaR, 30 ml) was treated with dry, finely-ground, thallium(I) tetrafluoroborate (0·33 g, 1·0 mmol). A flocculent precipitate settled from the initially deep-red solution leaving an orange-yellow solution. After stirring for 12 h the mixture was filtered and solvent was removed from the orange-red filtrate under reduced pressure. The residual oily solid was washed with cold water (0°) giving a brown powder which was extracted with hot water (25 ml). After filtration the filtrate was allowed to cool slowly and orange crystals separated. These were collected, washed with cold water (2 × 3 ml), and dried *in vacuo*. Yield, *ca.* 30%.

n-Propyl(triphenylphosphine)bis(π-cyclopentadienyl)tungsten Hexafluorophosphate.—The propenehydride $[(\pi\text{-}C_5H_5)_2W(C_3H_6)H]^+PF_6^-$ (0·32 g, 0·61 mmol) in acetone (50 ml) was treated with triphenylphosphine (1·2 g, 4·5 mmol) and the mixture was refluxed for 5 days. A deep orange solution was formed and removal of solvent *in vacuo* gave an oily orange crystalline mass. This was washed with benzene (2 × 5 ml) and light petroleum (2 × 20 ml) and the resulting orange crystals were dried *in vacuo*. Extraction with acetone and filtration gave an orange filtrate and a dark brown insoluble residue. A volume of toluene equal to half the volume of the filtrate was added to it and solvent was slowly removed *in vacuo* to give orange crystals. These were separated, washed with a little toluene, and dried *in vacuo*. Recrystallisation from acetone–ether and acetone–water yielded orange crystals of the pure compound, *ca.* 40% yield.

Ethylenebis(π-cyclopentadienyl)molybdenum.—The ethylenehydride $[(\pi\text{-}C_5H_5)_2Mo(C_2H_4)H]^+PF_6^-$ (0·2 g) in acetone (10 ml) gave a colourless solution to which was added water (1 ml) and potassium hydroxide (0·9 g). The mixture was stirred at room temperature and rapidly turned orange. After 10 min solvent was removed *in vacuo* giving orange-brown crystals which were thoroughly dried *in vacuo*. These were extracted with light petroleum to give an orange solution and a white residue. The extract was filtered giving an orange filtrate which was concentrated by slow removal of solvent *in vacuo* and then slowly cooled to −78°. Orange-brown needles separated and were collected, washed with a little cold light petroleum, and dried *in vacuo*. A second crop was obtained from the mother liquor by further removal of solvent *in vacuo* and then cooling to −78° as before, *ca.* 90% yield.

The analogous complexes $(\pi\text{-}C_5H_5)_2W(C_2H_3R)$ (R = H, Me) were similarly prepared in high yields from the hydrides $[(\pi\text{-}C_5H_5)_2W(C_2H_3R)H]^+PF_6^-$.

Reactions of the Neutral Ethylene Complexes $(\pi\text{-}C_5H_5)_2M(C_2H_4)$.—(a) *With hydrogen chloride*. The complex $(\pi\text{-}C_5H_5)_2W(C_2H_4)$ (0·3 g) in benzene (25 ml) was treated with hydrogen chloride. A grey-white precipitate immediately formed and the solution became colourless. An excess of hydrogen chloride was removed *in vacuo*. The supernatant liquid was filtered from the precipitate which was dried *in vacuo* to give a white powder. This was dissolved in water and a few drops of aqueous ammonium hexafluorophosphate were added giving a white precipitate which was collected, washed with water, and recrystallised from acetone–water by slow removal of solvent *in vacuo*, and finally dried *in vacuo*. The resulting white crystals were identified as the hydridoethylene cation $[(\pi\text{-}C_5H_5)_2W(C_2H_4)H]^+PF_6^-$ by comparison of the i.r. spectrum with that of a fully characterised sample.

A similar experiment with the molybdenum analogue $(\pi\text{-}C_5H_5)_2Mo(C_2H_4)$ led to very similar observations and isolation of the hydridoethylene cation $[(\pi\text{-}C_5H_5)_2Mo(C_2H_4)H]^+PF_6^-$ identified by comparison of the i.r. spectrum with that of an authentic sample.

Rapid protonation of the complexes $(\pi\text{-}C_5H_5)_2M(C_2H_4)$ (M = Mo and W) was also affected by 65% hexafluorophosphoric acid in acetone solution giving identical products.

(b) *With triphenyl- and dimethylphenyl-phosphine*. The complexes $(\pi\text{-}C_5H_5)_2M(C_2H_4)$ (M = Mo or W) (0·1 g) were heated with an excess of triphenylphosphine (0·3 g) at 90° for 3 days. A red melt resulted which solidified on cooling. The resulting solid was powdered and washed with cold light petroleum several times. Crystallisation from light petroleum by slow cooling gave orange crystals identified from the ^1H n.m.r. spectrum as the starting complex in each case.

Dimethylbis(π-cyclopentadienyl)molybdenum. The dichloride $(\pi\text{-}C_5H_5)_2MoCl_2$ (2·0 g, 6·7 mmol) was added in aliquot portions to a stirred ethereal solution of methylmagnesium chloride (20 mmol; 0·10 ml in 20 ml Et_2O) and the suspension stirred until no starting material remained, and a red-orange solution was formed. The solvent was removed *in vacuo* and the resulting sticky red oil was repeatedly extracted with dry light petroleum until the extracts were colourless. The petroleum extracts were combined and solvent removed *in vacuo* giving a waxy red-orange solid. Sublimation of the solid at 80°, 10^{-2} Torr, yielded waxy red-orange crystals of the pure product, *ca.* 30% yield.

The tungsten analogue was similarly prepared from the dichloride $(\pi\text{-}C_5H_5)_2WCl_2$. The pure product was obtained by sublimation at 120°, 10^{-3} Torr, *ca.* 30% yield.

Reactions of the Complexes $(\pi\text{-}C_5H_5)_2MMe_2$.—(a) *With hydrogen chloride*. The compound $(\pi\text{-}C_5H_5)_2MoMe_2$ (0·1 g) in benzene (5 ml) gave a deep red solution which was treated with hydrogen chloride for a few seconds. A vigorous reaction occurred in which a dark precipitate was formed with evolution of a gas. The gaseous product of the reaction was identified as methane and contained no ethane.

The organometallic product was collected by filtration, washed with ether, and recrystallised from liquid sulphur dioxide–ether and identified as the dichloride $(\pi\text{-}C_5H_5)_2MoCl_2$ by comparison of the i.r. spectrum with that of an authentic sample.

The above experiment was repeated with the tungsten analogue $(\pi\text{-}C_5H_5)_2WMe_2$ and reaction was observed to occur as with the molybdenum compound. The gaseous product was identified from its i.r. spectrum as methane, no ethane being formed. The organometallic product was the dichloride $(\pi\text{-}C_5H_5)_2WCl_2$.

(b) *With carbon monoxide*. $(\pi\text{-}C_5H_5)_2MoMe_2$ (0·25 g) in benzene (25 ml) was placed in a glass liner within a high pressure vessel and treated with carbon monoxide (60 atm at 50°). After 2 days the bomb was allowed to cool to room temperature and the liner removed. The liner contained a red solution and some dark insoluble residue. The solution was filtered to give a red filtrate from which solvent was concentrated *in vacuo*. When white crystals precipitated, the oily red mother liquor was decanted, the crystals washed with a little benzene, and dried *in vacuo*. Comparison of the i.r. and mass spectra of the white crystals with those of an authentic sample showed the product to be the hexacarbonyl, $Mo(CO)_6$.

The above experiment was repeated with the tungsten analogue $(\pi$-$C_5H_5)_2WMe_2$. Similar observations were made and the organometallic product was identified as the hexacarbonyl $W(CO)_6$ from the i.r. and mass spectra.

Diphenylethynylbis(π-cyclopentadienyl)tungsten.— Dichlorobis(π-cyclopentadienyl)tungsten (2 g, 5·2 mmol) was added to an ethereal solution of phenylethynyl-lithium (*ca.* 15 mmol) and the mixture refluxed for 20 h. The solvent was removed *in vacuo* and the resulting brown residue washed with ether (3 × 10 ml) and extracted with acetone until the extracts were very pale in colour. After filtration the solvent was removed *in vacuo* yielding red-brown crystals. These were recrystallised from dichloromethane–ether, washed with ether, and dried *in vacuo* giving red-brown crystals of the pure compound, *ca.* 60% yield.

The preparation of the molybdenum analogue was attempted by the same method. A small yield of a red-brown product was obtained (*ca.* 4%).

^1H *N.M.R. Data*.—Determined on a Varian Associates instrument at 100 MHz, unless otherwise stated. Data given as: compound number (Table); **chemical shift** (τ), *rel. intensity*, **multiplicity** (J/Hz), assignment, *etc.*

(1) 5·42;[a] 8·37, *2*, **q** [$J(CH_2,Me)$ 7·5] CH_2; 8·61, *3*, **t** [$J(Me,CH_2)$ 7·5] Me In C_6D_6 at 270 MHz

(2) 4·50;[a] 7·82, *4*, **s**, C_2H_4; 15·00, *1*, **s**, Mo–H In $(CD_3)_2CO$

(3) 3·91;[a] 7·82, *4*, **s**, C_2H_4; 16·58, *1*, **s**, W–H $(CD_3)_2CO$

(4) 5·90;[a] 8·50, *4*, **s**, C_2H_4 $(CD_3)_2CO$

(5) 5·90;[a] 9·10, *4*, **s**, C_2H_4 C_6D_6

(6)[b] 2·51—2·84, *5*, **c**, Ph; 4·68, *1*, **c**, H_c or H_d; 4·90, *6*, **d** [J(P,H) 1·15] π-C_5H_5 and H_d or H_c; 5·84, *1*, **c**, H_b or H_e; 6·61, *1*, **c**, H_e or H_b; 8·37, *5*, **d** [J(PMe) 7·5] MeP and quartet [$J(Me,CH_2)$ 7·5] CH_2; 8·53, *1*, **c**, H_a; 8·70, *3*, **d** [J(P,Me) 7·5] Me; 8·95, *3*, **t** (J 7·5) CMe C_6D_6

(7)[b] 2·53—2·84, *10*, **c**, Ph_2; 4·38, *1*, **c**, H_c or H_d; 4·92, *6*, **d** [J(P,H) 1·15] π-C_5H_5 and H_d or H_c; 5·95, *1*, **c**, H_b or H_e; 6·59, *1*, **c**, H_e or H_b; 7·96, *3*, **d** [J(P,Me) 7·52] PMe; 8·26, *1*, **c**, H_a; 8·47, *2*, **c**, CH_2; 9·04, *3*, **t** [$J(Me,CH_2)$ 6·85] CMe C_6D_6

(8)[b] 4·48, *1*, **c**, H_c or H_d; 4·75, *1*, **c**, H_d or H_c; 4·88, *5*, **d** [J(P,H) 1·14] π-C_5H_5; 5·39, *1*, **c**, H_b or H_e; 6·68, *1*, **c**, H_e or H_b, 8·33, *6*, **c**, $(CH_2)_3$; 8·50, *2*, **c**, *endo*-CH_2; 8·86, *3*) **t** (J 7·5), *endo*-Me; 9·06, *9*, **doublet of triplets** [J(P,Me) 12·75, J (CH_2,Me) 7·5] Me_3 C_6D_6

(9) 2·08, *5*, **c**, Ph; 4·51, *10*, **d** [$J(P,\pi$-$C_5H_5)$ 2·25] $(\pi$-$C_5H_5)_2$; 7·58, *6*, **d** [$J(P,Me_2)$ 10·25] Me_2; *ca.* 8·5, *5*, **c**, Et $(CD_3)_2SO$

(10) 3·98, 4·03, and 5·05, 4·09 (of rel. intens. 4 : 3), *10*, each a singlet, π-C_5H_5; 7·67, *6*, **c**, C_3H_6; 16·65, 16·79 (of rel. intens. 4 : 3), *1*, each a singlet, W–H of isomers $(CD_3)_2SO$

(11) 5·95, *5*. **s**, π-C_5H_5; 6·00, *5*, **c**, π-C_5H_5; 8·23, *3*, **d** [J(Me,H) 6·0] Me; 8·41, *1*, **c**, H_1; 8·73, *1*, **doublet of doublets** [$J(H_2, H_3)$ 6·0, J $(H_1, H_2$, or $H_3)$ 10·5] H_2 or H_3; 9·16, *1*, **doublets of doublets** [$J(H_2,H)$ 6, J $(H_1, H_3$, or $H_2)$ 10·5] H_3 or H_2 In C_6D_6 at 270 MHz

(12) 2·10, *15*, **c**, Ph_3; 4·50, *10*, **d** [$J(P,\pi$-$C_5H_5)$ 1·9] $(\pi$-$C_5H_5)_2$; 8·40, *5*, **c**, Et $(CD_3)_2SO$

(13) 2·20, *15*, **c**, Ph_3; 4·40, *10*, **d**, [$J(P,\pi$-$C_5H_5)$ 1·5] $(\pi$-$C_5H_5)_2$; 8·17, *5*, **c**, Et $(CD_3)_2SO$

(14) 4·26;[a] 18·10, *1*, **s**, Mo–H $(CD_3)_2SO$

(15) 2·00, *15*, **c**, Ph_3; 4·40, *10* **d** [$J(P,\pi$-$C_5H_5)$ 2·0] $(\pi$-$C_5H_5)_2$; 8·20, *4*, **c**, $(CH_2)_2$; 8·60, *3*, **c**, Me $(CD_3)_2SO$

(16) 5·80;[a] 9·81, *6*, **s**, Me_2 C_6D_6

(17) 5·80;[a] 9, 76, *6*, **t** [$J(^{183}W,H)$ 6·0] Me_2 C_6D_6

(19) 2·15, *10*, **c**, Ph_2; 4·20[a] $CDCl_3$

[a] As *10*, **s**, $(\pi$-$C_5H_5)_2$. [b] The spectrum also shows evidence of an inseparable minor constituent (2—3%) which has a spectrum very similar to that of the assigned major components. This may be an isomer (see the text).

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