Alkyl, Olefin, and Carbonyl Derivatives of Bis(η-cyclopentadienyl)molybdenum and -tungsten

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The compounds $[Mo(\eta\text{-}C_5H_5)_2R(CO)][PF_6]$ (R = Me, $\sigma\text{-}C_3H_5$, CH_2OMe, COMe, CH_2CO_2Me, or CH_2CN) and $[W(\eta\text{-}C_5H_5)_2Me(CO)][PF_6]$, have been prepared by addition of RX to $[Mo(\text{or } W)(\eta\text{-}C_5H_5)_2(CO)]$. Similarly, the compounds $[W(\eta\text{-}C_5H_5)_2(C_2H_4)R''][PF_6]$ (R″ = $\sigma\text{-}C_3H_5$, CH_2CN, and CH_2CO_2Me) have been prepared by addition of R″X to $[W(\eta\text{-}C_5H_5)_2(C_2H_4)]$. Treatment of $[Mo(\eta\text{-}C_5H_5)_2Me(CO)][PF_6]$ with PMe_2Ph gives $[Mo(\eta\text{-}C_5H_5)_2(COMe)(PMe_2Ph)][PF_6]$. The compounds $[W(\eta\text{-}C_5H_5)_2(CH_2CN)Cl]$, $[W(\eta\text{-}C_5H_5)_2(CH_2CN)(PMe_2Ph)][PF_6]$, $[W(\eta\text{-}C_5H_5)_2(\eta\text{-}MeC_2Me)Me][PF_6]$, $[W(\eta\text{-}C_5H_5)_2(O_2CC_6H_4Br\text{-}o)Me]$, and $[W(\eta\text{-}C_5H_5)_2(O_2CC_6H_4OH\text{-}o)Me]$ are also described.

THE addition of an alkyl halide RX to a 16-electron metal centre [M] giving the 18-electron [M]·RX adduct is called an oxidative-addition reaction. The reaction between an 18-electron metal centre [M′] and RX giving the 18-electron product $[M'\text{–}R]^+X^-$ is a closely related reaction which involves a formal increase of the metal valency by two but there is no change in the electron number of the metal centre. The idealised general representation of the latter reaction may be given as (1)

$$MX_xL_l + X_2 \longrightarrow [MX_{x+1}L_l]^+X^- \qquad (1)$$

where L_l represents a number l of two-electron donor ligands, X_x represents a number x of one-electron donor ligands, and M is an 18-electron metal centre. The general reaction $MX_xL_l + X_2 \longrightarrow MX_{x+2}L_{l-1} + L$ involves oxidation of the metal centre, addition of X_2, and replacement of a L ligand by the X_2. We may describe this reaction as oxidative-replacement addition, but oxidation is implicit and we prefer to call the reaction replacement addition. Since the cation $[MX_{x+1}L_l]^+$ is isoelectronic with $MX_{x+2}L_{l-1}$ we may describe (1) similarly as a replacement-addition reaction.

We have studied the replacement-addition reactions of the compounds $[W(\eta\text{-}C_5H_5)_2(C_2H_4)]$ and $[M(\eta\text{-}C_5H_5)_2(CO)]$ (M = Mo or W) with a variety of alkyl halides in order to prepare the alkyl derivatives $[M(\eta\text{-}C_5H_5)_2L(R)]^+$. We were interested in these compounds since they have essentially *cis*-orientated groups L and R and we wished to explore interactions between these groups.

RESULTS

Chemical Studies.—Treatment of the monocarbonyl $[Mo(\eta\text{-}C_5H_5)_2(CO)]$ (1) with RX (RX = MeI, $CH_2{=}CHCH_2Br$, PhBr, $CH_2{=}CHBr$, $MeOCH_2Cl$, MeCOCl, $MeOCOCH_2Br$, or $NCCH_2Cl$) gives, with the exceptions of RX = PhBr and $CH_2{=}CHBr$, smooth reactions, and after addition of hexafluorophosphate the salts $[Mo(\eta\text{-}C_5H_5)_2R(CO)][PF_6]$ [R = Me (2), $CH_2{=}CHCH_2$ (3), CH_2OMe (4), COMe (5), CH_2CO_2Me (6), or CH_2CN (7)] were isolated in good yields. The new compounds (2)—(7) are fully characterised by the data in the Table. They are moderately stable in air. The tungsten compound $[W(\eta\text{-}C_5H_5)_2(CO)]$ also reacts readily with iodomethane giving $[W(\eta\text{-}C_5H_5)_2Me(CO)][PF_6]$.

Treatment of (2) with dimethylphenylphosphine at 80 °C gives the acyl derivative $[Mo(\eta\text{-}C_5H_5)_2(COMe)(PMe_2Ph)][PF_6]$ (8). Reduction of (2) with $Na[AlH_2(OCH_2CH_2OMe)_2]$ led to the isolation of (1). Attempts to protonate the acyl CO group in (8) using concentrated hydrochloric acid or pure CF_3CO_2H were unsuccessful and the starting material was recovered unchanged.

Compound (4) was treated with hydrogen chloride in an attempt to cleave the methoxy-group. However, no tractable products could be isolated. Compound (6) was treated with concentrated hydrochloric acid in an attempt to hydrolyse the ester group to give the corresponding carboxylic acid derivative. However, no reaction was observed and (6) was recovered unchanged. Similarly, there was no reaction between (6) and concentrated K[OH] at 70 °C. Attempts to protonate the nitrogen of the CH_2CN group in (7) with hydrogen chloride gas gave no reaction and the starting material was recovered unchanged.

The ethylene compound $[W(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)]$ (9) was treated with RX = $ClCH_2CN$, $MeOCOCH_2Br$, and $CH_2{=}CHCH_2Br$, giving the compounds $[W(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)R][PF_6]$ [R = CH_2CN (10), CH_2CO_2Me (11), or $CH_2CH{=}CH_2$ (12)]. Reaction of (9) with $ClCH_2CN$ also gave the neutral compound $[W(\eta\text{-}C_5H_5)_2(CH_2CN)Cl]$ (13).

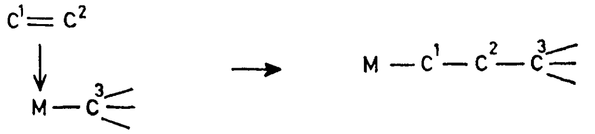
Treatment of compound (10) with PMe_2Ph followed by addition of hexafluorophosphate gives $[W(\eta\text{-}C_5H_5)_2(CH_2CN)(PMe_2Ph)][PF_6]$ (14). Compound (11) showed no reaction with either concentrated hydrochloric acid or concentrated potassium hydroxide.

The diethyl sulphide compound $[W(\eta\text{-}C_5H_5)_2(SEt_2)Me][PF_6]$ was treated with but-2-yne giving $[W(\eta\text{-}C_5H_5)_2(MeC_2Me)Me][PF_6]$ (15). This compound did not react with PMe_2Ph even at 90 °C for 48 h.

Treatment of $[W(\eta\text{-}C_5H_5)_2Me_2]$ with *o*-bromobenzoic acid or *o*-hydroxybenzoic acid gives the compounds $[W(\eta\text{-}C_5H_5)_2(O_2CC_6H_4Br\text{-}o)Me]$ (16) and $[W(\eta\text{-}C_5H_5)_2(O_2CC_6H_4OH\text{-}o)Me]$ (17), respectively. They are moderately sensitive to oxidation.

DISCUSSION

The new compounds (2)—(15) were prepared and studied for several different reasons. It has long been implicit in the literature that the ligand-transfer insertion reaction (or ligand-transfer reaction) (2) could readily



(2)

occur, and, indeed, it is this insertion reaction which is postulated to be the key step in the Ziegler–Natta polymerisation of olefins.[1] It is certainly well established that ethylene will readily insert into metal–hydrogen systems, *e.g.*[2] reaction (3). Also, it has been

$$[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\eta\text{-}\mathrm{C_2H_4})\mathrm{H}][\mathrm{PF_6}] + \mathrm{PMe_2Ph} \longrightarrow [\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Et}(\mathrm{PMe_2Ph})][\mathrm{PF_6}] \quad (3)$$

widely demonstrated that carbon monoxide may insert into transition-metal–alkyl bonds, an example being the formation of (8) from (2) with dimethylphenylphosphine.

Analytical and spectroscopic data

	Compound	Colour	Analysis (%) [a]		Selected i.r. data (cm^{-1})	^{1}H N.m.r. data [b]
			C	H		
(1)	$[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Me(CO)}][\mathrm{PF_6}]$	Orange	28.9 (28.7)	2.6 (2.6)	1 960s [ν(CO)]	4.78, **10**, *s*, $(\eta\text{-}\mathrm{C_5H_5})_2$; 9.50, **3**, *s* [satellites $J(^{183}\mathrm{W\text{-}H})$ 5.5], Me [c]
(2)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Me(CO)}][\mathrm{PF_6}]$	Orange	35.0 (34.8)	3.3 (3.2)	2 010s [ν(CO)]	4.20, **10**, *s*, $(\eta\text{-}\mathrm{C_5H_5})_2$; 9.34, **3**, *s*, Me [c]
(3)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{CH_2CH{=}CH_2})(\mathrm{CO})][\mathrm{PF_6}]$	Orange	37.9 (38.2)	3.4 (3.4)	2 128s [ν(CO)]	4.20, **2**, *s*, $(\eta\text{-}\mathrm{C_5H_5})_2$ + CH; 5.33, **2**, *c*, $=\mathrm{CH_2}$; 8.05, **2**, *d* (*J* 9), $-\mathrm{CH_2}$ [c]
(4)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{CH_2OMe})(\mathrm{CO})][\mathrm{PF_6}]$	Yellow	34.8 (35.2)	3.3 (3.4)	2 020s [ν(CO)]	4.26, **10**, *s*, $(\eta\text{-}\mathrm{C_5H_5})_2$; 5.80, **2**, *s*, $\mathrm{CH_2}$; 6.50, **3**, *s*, Me [c]
(5)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{COMe})(\mathrm{CO})][\mathrm{PF_6}]$	Yellow	35.6 (35.4)	2.9 (2.9)	2 020s, 1 675s [ν(CO)]	4.00, **10**, *s*, $(\eta\text{-}\mathrm{C_5H_5})_2$; 7.34, **3**, *s*, Me [c]
(6)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{CH_2CO_2Me})(\mathrm{CO})][\mathrm{PF_6}]$	Orange	36.0 (35.6)	3.1 (3.2)	2 020, 1 692 [ν(CO)]	4.02, **10**, *s*, $(\eta\text{-}\mathrm{C_5H_5})_2$; 6.44, **3**, *s*, Me; 8.36, **2**, *s*, $\mathrm{CH_2}$ [c]
(7)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{CH_2CN})(\mathrm{CO})][\mathrm{PF_6}]$	Orange	35.7 (35.7)	2.8 (2.7)	2 230 [ν(CN)] 2 045s [ν(CO)]	3.90, **10**, *s*, $(\eta\text{-}\mathrm{C_5H_5})_2$; 8.53, **2**, *s*, $\mathrm{CH_2}$ [c]
(8)	$[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{COMe})(\mathrm{PMe_2Ph})][\mathrm{PF_6}]$	Yellow	43.3 (43.5)	4.1 (4.3)	1 604s [ν(CO)]	2.45, **5**, *c*, Ph; 4.53, **10**, *d* [*J*(P–H) 2.0], $(\eta\text{-}\mathrm{C_5H_5})_2$; 7.49, **3**, *s*, Me; 8.11, **6**, *d* [*J*(P–H) 9.5], $\mathrm{Me_2}$ [c]
(10)	$[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\eta\text{-}\mathrm{C_2H_4})(\mathrm{CH_2CN})][\mathrm{PF_6}]$	Yellow-brown	31.8 (31.9)	(3.0) (3.1) [d]	2 220s [ν(CN)]	4.18, **10**, *s*, $(\eta\text{-}\mathrm{C_5H_5})_2$; 7.01, **2**, *t*, $=\mathrm{CH_2}$; 7.68, **2**, *s*, $\mathrm{CH_2CN}$; 7.81, **2**, *t*, $=\mathrm{CH_2}$ [c]
(11)	$[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\eta\text{-}\mathrm{C_2H_4})(\mathrm{CH_2CO_2Me})][\mathrm{PF_6}]$	Yellow	32.3 (32.2)	3.4 (3.4)	1 672s [ν(CO)]	4.25, **10**, *s*, $(\eta\text{-}\mathrm{C_5H_5})_2$; 6.33, **3**, *s*, Me; 7.04, **2**, *c*, $=\mathrm{CH_2}$; 7.13, **2**, *s*, $\mathrm{CH_2O}$; 7.50, **2**, *c*, $=\mathrm{CH_2}$ [c]
(12)	$[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\eta\text{-}\mathrm{C_2H_4})(\mathrm{CH_2CH{=}CH_2})][\mathrm{PF_6}]$	Orange	34.2 (34.1)	3.6 (3.6)	1 615s [ν(C=C)]	3.73, **1**, *c*, $-\mathrm{CH}=$; 4.36, **10**, *s*, $(\eta\text{-}\mathrm{C_5H_5})_2$; 5.10, **2**, *c*, $=\mathrm{CH_2}$; 7.22, **4**, *c*, $-\mathrm{CH_2}-$, $=\mathrm{CH_2}$; 8.07, **2**, *t*, $=\mathrm{CH_2}$
(13)	$[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{CH_2CN})\mathrm{Cl}]$	Red-purple	37.2 (37.1)	3.1 (3.1) [e]	2 215s [ν(CN)]	4.85, **10**, *s*, $(\eta\text{-}\mathrm{C_5H_5})_2$; 8.70, **2**, *s*, $\mathrm{CH_2}$ [c]
(14)	$[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{CH_2CN})(\mathrm{PMe_2Ph})][\mathrm{PF_6}]$	Orange	37.4 (37.7)	3.5 (3.6) [f]	2 205s [ν(CN)]	2.25, **5**, *c*, Ph; 5.17, **10**, br *s*, $(\eta\text{-}\mathrm{C_5H_5})_2$; 7.12, **2**, *s*, $\mathrm{CH_2}$; 7.77, **6**, *d* [*J*(P–H) 13.5], $\mathrm{PMe_2}$ [c]
(15)	$[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\eta\text{-}\mathrm{MeC_2Me})\mathrm{Me}][\mathrm{PF_6}]$	White	34.2 (34.1)	3.6 (3.6)	2 230s [ν(C≡C)]	4.09, **10**, *s*, $(\eta\text{-}\mathrm{C_5H_5})_2$; 6.93, **3**, *q*, MeC; 7.53, **3**, *q*, CMe; 8.21, **3**, *s*, WMe [g]
(16)	$[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{O_2CC_6H_4Br}\text{-}o)\mathrm{Me}]$	Red-brown	41.4 (40.9)	3.4 (3.2) [h]	1 650s [ν(CO)]	2.61, **4**, *c*, $\mathrm{C_6H_4}$; 4.75, **10**, *s*, $(\eta\text{-}\mathrm{C_5H_5})_2$; 9.59, **3**, *s*, Me [i]
(17)	$[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{O_2CC_6H_4OH}\text{-}o)\mathrm{Me}]$	Red-brown	46.3 (46.4)	4.05 (3.9)	1 630 [ν(CO)]	2.95, **4**, *c*, $\mathrm{C_6H_4}$; 4.95, **10**, *s*, $(\eta\text{-}\mathrm{C_5H_5})_2$; 5.97, **1**, *s*, (br), OH; 9.62, **3**, *s*, Me [c]

[a] Calculated values are given in parentheses. [b] Given as: chemical shift (τ), **relative intensity**, *multiplicity*, assignment; *J* values in Hz. [c] In $(\mathrm{CD_3})_2\mathrm{CO}$. [d] N, 2.7 (2.7%). [e] N, 3.3 (3.6%). [f] N, 2.5 (2.2%). [g] In $\mathrm{C_6D_5NO_2}$. [h] Br, 15.5 (15.2%). [i] In $(\mathrm{CD_3})_2\mathrm{SO}$.

These two examples clearly indicate that these common insertion reactions occur as well with the $[\mathrm{M}(\eta\text{-}\mathrm{C_5H_5})_2]$ (M = Mo or W) system as with more familiar examples.

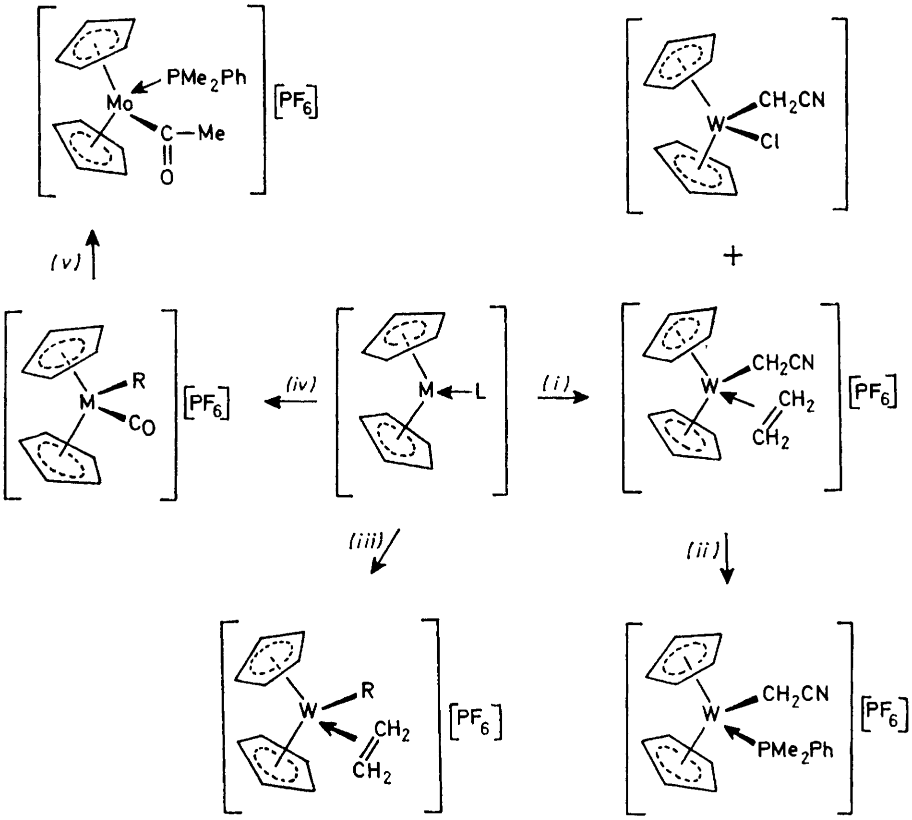
One objective in preparing the $[\mathrm{M}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{olefin})(\mathrm{alkyl})]^+$ system was to try to obtain a simple example where an olefin-alkyl transition-metal compound reacted to give the insertion (or ligand-transfer) product. For example, it might have been expected that treatment of the compound $[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\eta\text{-}\mathrm{C_2H_4})\mathrm{Me}][\mathrm{PF_6}]$ with tertiary phosphine would give the n-propyl derivative $[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{CH_2CH_2Me})(\mathrm{PMe_2Ph})][\mathrm{PF_6}]$. However, this reaction does not occur as is discussed in detail elsewhere.[3] We note, however, that the anticipated n-propyl product $[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{CH_2CH_2Me})(\mathrm{PPh_3})][\mathrm{PF_6}]$ is in fact readily formed by treatment of $[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{MeCH{=}CH_2})\mathrm{H}][\mathrm{PF_6}]$ with $\mathrm{PPh_3}$ showing that n-propyl compounds are stable to isolation.[2]

We conclude that we have failed to find any simple example of the insertion of ethylene into transition-metal–alkyl bonds in our bis(cyclopentadienyl)-tungsten or -molybdenum derivatives, despite the fact that they readily exhibit the related insertions of CO into metal–alkyl or of olefin into metal–hydrogen bonds. We also observe that there are relatively few, if any, simple examples of insertion of a co-ordinated olefin into a metal–carbon bond where the alkyl group is attached to the same metal. This might seem surprising in view of the very large number of different systems which can act as catalysts for the oligomerisation of mono-olefins if they proceed *via* the insertion step that is normally postulated.

We are left with two alternatives. We can assume that there are some special reasons why our compounds $[\mathrm{M}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{olefin})(\mathrm{alkyl})]^+$ do not undergo the insertion reaction, and we can also assume that it is chance that no other simple olefin-alkyl compounds have been shown to undergo the expected insertion step. Alternatively, we can postulate that the insertion of an olefin into a metal–alkyl bond is, unlike insertion of olefins into M–H, not a ready or common reaction. This postulate implies that the mechanisms for olefin polymerisation might not be correct and, in view of this we have recently proposed elsewhere an alternative mechanism for the stereospecific polymerisation of olefins by Ziegler–Natta catalysts.[4]

EXPERIMENTAL

All the reactions and manipulations were carried out under dinitrogen or *in vacuo*. The solvents were dried and distilled. The compounds $[M(\eta\text{-}C_5H_5)_2(CO)]$ (M = Mo or W),[5] $[W(\eta\text{-}C_5H_5)_2(C_2H_4)]$,[2] and $[W(\eta\text{-}C_5H_5)_2(SEt_2)Me][PF_6]$ [6] were prepared as described. Hydrogen-1 n.m.r. spectra were recorded using Bruker (90 MHz) or JEOL (60 MHz) instruments. Microanalyses were by A. Bernhardt or by the microanalytical department of this laboratory. Infrared spectra were recorded as mulls on a Perkin-Elmer 457 instrument and were calibrated with polystyrene film. Mass spectra were obtained using an A.E.I. M.S.9 spectrometer.



SCHEME Some replacement-addition reactions and related chemistry of bis(η-cyclopentadienyl)-molybdenum and -tungsten compounds. (*i*) L = C_2H_4, $ClCH_2CN$, room temperature (r.t.); (*ii*) PMe_2Ph, r.t.; (*iii*) L = C_2H_4, RX = $MeOCOCH_2Br$ or $CH_2{=}CHCH_2Br$, 60 °C, 15 min, then aqueous $[NH_4][PF_6]$; (*iv*) L = CO, RX = MeI, $CH_2{=}CHCH_2Br$, $MeOCH_2Cl$, $MeOCOCH_2Br$, or $ClCH_2CN$, r.t., M = Mo; for M = W, RX = MeI. Then aqueous $[NH_4][PF_6]$; (*v*) PMe_2Ph, 78 °C for 72 h

Carbonylbis(η-cyclopentadienyl)methylmolybdenum Hexafluorophosphate, (2).—The compound $[Mo(\eta\text{-}C_5H_5)_2(CO)]$ (0.5 g, 1.98 mmol) in dry toluene (50 cm^3) was treated with iodomethane (0.06 cm^3, 1.97 mmol). A yellow precipitate appeared immediately. This was extracted with water and aqueous ammonium hexafluorophosphate was added giving a yellow precipitate. This was collected, washed with water (2 × 15 cm^3), and the residue was dissolved in acetone (20 cm^3). After filtration, water (10 cm^3) was added to the filtrate and the solution was slowly concentrated under reduced pressure giving orange crystals. These were collected, washed with water, and dried *in vacuo*, yield 0.65 g (80%). The compound $[W(\eta\text{-}C_5H_5)_2Me(CO)][PF_6]$ was prepared similarly in 75% yield from $[W(\eta\text{-}C_5H_5)_2(CO)]$.

Acetylbis(η-cyclopentadienyl)(dimethylphenylphosphine)-molybdenum Hexafluorophosphate, (8).—Compound (2) (0.5 g, 1.2 mmol) in acetone 50 cm^3) was treated with dimethylphenylphosphine (0.23 g, 1.7 mmol) and the mixture was warmed to 78 °C for 72 h. The solvent was removed under reduced pressure giving an oily red residue. This was washed with light petroleum–diethyl ether (3 × 25 cm^3) to remove excess of the tertiary phosphine. The residue was extracted with tetrahydrofuran and diethyl ether was added slowly. Yellow crystals separated, which were collected, washed with diethyl ether, and dried *in vacuo*, yield 0.4 g (65%).

Allylcarbonylbis(η-cyclopentadienyl)molybdenum Hexafluorophosphate (3).—The compound $[Mo(\eta\text{-}C_5H_5)_2(CO)]$ (0.49 g, 1.96 mmol) in toluene (50 cm^3) was treated with allyl bromide (0.17 cm^3, 1.97 mmol). The resulting yellow precipitate was dissolved in water and ammonium hexafluorophosphate was added.

The following compounds were prepared as described for (2): *carbonylbis(η-cyclopentadienyl)(methoxymethyl)molybdenum hexafluorophosphate*, (4), starting with $[Mo(\eta\text{-}C_5H_5)_2(CO)]$ (0.53 g, 2.0 mmol) and dry, distilled, acid-free bis(chloromethyl) ether (0.15 cm^3, 2.0 mmol), yield 0.3 g (60%); *acetylcarbonylbis(η-cyclopentadienyl)molybdenum hexafluorophosphate*, (5), starting with $[Mo(\eta\text{-}C_5H_5)_2(CO)]$ (0.49 g, 2 mmol) and dry distilled acetyl chloride (0.14 cm^3, 2.0

mmol), yield 0.64 g (70)%; *carbonylbis(η-cyclopentadienyl)(methoxycarbonylmethyl)molybdenum hexafluorophosphate*, (6), starting with $[Mo(\eta\text{-}C_5H_5)_2(CO)]$ (0.52 g, 2.0 mmol) and methyl bromoacetate (0.2 cm^3, 2 mmol), yield 0.72 g (75%); and *carbonyl(cyanomethyl)bis(η-cyclopentadienyl)molybdenum hexafluorophosphate*, (7), starting from $[Mo(\eta\text{-}C_5H_5)_2(CO)]$ (0.65 g, 2.7 mmol) and chloromethyl cyanide (0.2 cm^3, 2.7 mmol), yield 0.79 g (70%).

Cyanomethylbis(η-cyclopentadienyl)ethylenetungsten Hexafluorophosphate, (10), *and Chloro(cyanomethyl)bis(η-cyclopentadienyl)tungsten*, (13).—The compound $[W(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)]$ (9) (0.3 g, 0.87 mmol) in toluene (25 cm^3) was treated with chloromethyl cyanide (0.05 cm^3, 0.87 mmol) and the mixture was warmed to 60 °C for 1 h. A brown-yellow solid precipitated which was collected and washed with toluene. The residue was extracted with water (25 cm^3), and aqueous ammonium hexafluorophosphate was added giving a brown-yellow precipitate. This was collected and recrystallised from acetone–water, yield 0.3 g (65%).

When the above reaction was carried out in the presence of an excess of chloromethyl cyanide (2 cm^3), after filtration of the yellow-brown precipitate a red mother liquor was obtained. After allowing this to stand for several days red-purple crystals separated. These were filtered off, washed with water, and dried *in vacuo*, yield *ca.* 10%.

(Cyanomethyl)bis(η-cyclopentadienyl)(dimethylphenylphosphine)tungsten Hexafluorophosphate, (14).—Compound (10) (0.25 g, 0.47 mmol) in acetone (30 cm^3) was treated with PMe_2Ph (0.13 g, 0.8 mmol). The initially yellow solution turned orange within a few minutes. After 1 h the solvent was removed under reduced pressure and the orange residue was washed with light petroleum to remove excess of PMe_2Ph. The residue was crystallised from dichloromethane–diethyl ether at −78 °C giving orange crystals, yield 0.15 g (50%).

Bis(η-cyclopentadienyl)(ethylene)(methoxycarbonylmethyl)tungsten Hexafluorophosphate, (11).—The compound $[W(\eta\text{-}C_5H_5)_2(C_2H_4)]$ (0.74 g, 2.3 mmol) in toluene (50 cm^3) was treated with methyl bromoacetate (0.21 cm^3, 2.3 mmol). Within a few minutes a yellow precipitate appeared and after 15 min this was collected and extracted with water (20 cm^3). Aqueous ammonium hexafluorophosphate was added and the resulting yellow precipitate was collected and recrystallised from acetone–water as yellow crystals (0.76 g, 76%).

Allylbis(η-cyclopentadienyl)(ethylene)tungsten Hexafluorophosphate, (12).—Compound (9) (0.24 g, 0.64 mmol) in toluene (25 cm^3) was treated with allyl bromide (0.02 cm^3, 0.66 mmol) and the mixture was warmed to 60 °C for 15 min. The hexafluorophosphate salt was isolated in the manner described above, yield 0.26 g (70%).

But-2-ynebis(η-cyclopentadienyl)methyltungsten Hexafluorophosphate, (15).—The compound $[W(\eta\text{-}C_5H_5)_2(SEt_2)Me][PF_6]$ (0.5 g, 0.88 mmol), prepared as described,[6] was treated in acetone (60 cm^3) with but-2-yne (0.1 g, 1.8 mmol) and the mixture was warmed to 60 °C for 4 h. The initial red colour changed steadily through purple to almost colourless. The solvent was removed under reduced pressure and the white residue was washed with water and finally recrystallised from acetone–water, yield 0.28 g (70%).

o-*Bromobenzoatobis(η-cyclopentadienyl)methyltungsten*.—The compound $[W(\eta\text{-}C_5H_5)_2Me_2]$ (0.45 g, 1.31 mmol), prepared as described,[2] in light petroleum (b.p. 100—120 °C, 25 cm^3) was treated with *o*-bromobenzoic acid (0.20 g, 1.31 mmol) The solution changed from orange-red to deep red over 1 h. The solution was then concentrated under reduced pressure giving red-brown crystals. These were collected, washed with light petroleum, and recrystallised from diethyl ether–light petroleum, yield 0.57 g (82%).

*Bis(η-cyclopentadienyl)(*o*-hydroxybenzoato)methyltungsten Hexafluorophosphate*.—The compound $[W(\eta\text{-}C_5H_5)_2Me_2]$ (0.35 g, 1.02 mmol) in toluene (25 cm^3) was treated with *o*-hydroxybenzoic acid (0.14 g, 1.02 mmol) and the mixture was warmed to 60 °C. The solution changed from orange to deep red. After 30 min the solvent was removed under reduced pressure giving red-brown crystals. These were washed with light petroleum, dissolved in diethyl ether, and addition of light petroleum gave red-brown crystals which were collected, washed, and dried *in vacuo*, yield 0.38 g (80%).

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