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Synthesis, characterisation, reactivity and stereochemical studies of heterobimetallic complexes containing an orthometallated cyclopentadienylphosphine bridge

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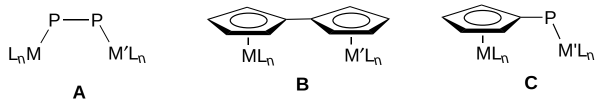
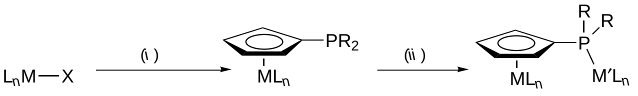
The heterobimetallic diastereoisomer complexes $[X(\eta^5\text{-}C_5H_5)Mo\{(\eta^5\text{-}C_5H_4)PPh(o\text{-}C_6H_4)\}M(CO)_5]$ (X = Cl **1** and **1′** or I **2** and **2′**; M = Cr **a**, Mo **b** or W **c**) containing an orthometallated cyclopentadienylphosphine bridge have been prepared and characterised. They were obtained by reaction of $Li[M(CO)_5(PPh_2)]$ and the corresponding metallocene dichloride in tetrahydrofuran. The crystal structures of **1a** and **2c** showed that the $\eta^5\text{-}C_5H_4PPh\text{-}[M(CO)_5]C_6H_4$ fragment chelates the Mo. Similarly, methylated complexes **3** were prepared when $[Mo(\eta^5\text{-}C_5H_4\text{-}Me)_2Cl_2]$ was used as metallocene dichloride; the 1,3 regioselectivity of these reactions has been assigned on the basis of ^1H and ^{31}P NMR data. Compound **1c** reacted with $LiAlH_4$ to give a dihydride molybdenocene complex $[H(\eta^5\text{-}C_5H_5)Mo(\eta^5\text{-}C_5H_4PPh_2)HW(CO)_4]$. Alkylated diastereoisomers $[R(\eta^5\text{-}C_5H_5)Mo\{(\eta^5\text{-}C_5H_4)PPh(o\text{-}C_6H_4)\}M(CO)_5]$ (R = Me or Et) were obtained by reaction of **1c** with a Grignard reagent; cleavage of the Mo–Me bond with hydrochloric acid has been found to occur with retention of configuration.

Heterobinuclear organometallic complexes and mixed-valence compounds have long been investigated in order to probe the effect of electron delocalisation and metal–metal interactions on physicochemical properties. Moreover, the chemical application of bimetallic complexes to stoichiometric and catalytic reactions is an area of continuing interest. Cyclopentadienyl[1] groups and tertiary phosphines[2] are widely used as ligands due to the large variety of steric and electronic effects that they exert on the reactivities of organometallic complexes. There are three common types of bimetallic compounds that incorporate such ligands (Scheme 1). In type **A** the two metals are bound to the phosphorus atoms of a diphosphane ligand. Diphosphanes can act as two-, three- and four-electron-donor ligands and many examples of such bimetallic systems are known and structurally characterised.[3] In type **B** the metals are co-ordinated to two directly attached cyclopentadienyl rings leading to bis(fulvalene)dimetals or bimetallocenes.[4] This molecular arrangement provides the opportunity of introducing new patterns of physicochemical properties: charge transfer, superconductivity and non-linear optical behaviour. Access to type **C** complexes needs cyclopentadienylphosphines as dissymmetrical bridging ligands. In a first step, the functionalised derivative $[M(\eta^5\text{-}C_5H_4PR_2)L_n]$ has been synthesized by metathesis of $Li[C_5H_4PR_2]$ with the corresponding halogeno complex $[MXL_n]$ and then complexed to the second metallic fragment $M'L_n$[5] (Scheme 2).

In the course of our work on heterobimetallic systems of this type we have recently reported a new synthetic approach involving Group 6 metallocenes.[6] Our synthetic entry point was suggested by a preliminary observation in molybdenum and tungsten chemistry where it was found that anionic metallophosphides $[M(CO)_5(PPh_2)]^-$ (M = Cr, Mo or W) react with $[M(\eta^5\text{-}C_5H_5)_2Cl_2]$ (M = Mo or W) to afford cyclopentadienyl-substituted metallocenes. Formation of these new bimetallic complexes results from an unusual substitution reaction at the cyclopentadienyl ring but not at the metal centre as observed with Group 4 metallocenes[7] and provides a new example of previously reported heterosubstituted molybdenocenes and tungstenocenes.[8] Furthermore, the molybdenum complexes undergo a spontaneous orthometallation reaction yielding a new type of bimetallic complex with a $\eta^5\text{-}C_5H_4P(Ph)[M(CO)_5]\text{-}C_6H_4$ fragment as chelating ligand.



Scheme 1



Scheme 2 (*i*) $Li[C_5H_4PR_2]$; (*ii*) $M'L_n$(thf), where thf = tetrahydrofuran

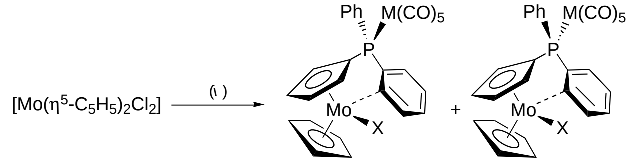
In this paper we describe the synthesis as well as a certain number of reactions of several orthometallated heterobimetallic complexes together with the crystal structure determination of $[I(\eta^5\text{-}C_5H_5)Mo\{(\eta^5\text{-}C_5H_4)PPh(o\text{-}C_6H_4)\}W(CO)_5]$ and stereochemical studies.

Results and Discussion

Synthesis and characterisation of complexes 1, 1′, 2 and 2′

The complex $[Mo(\eta^5\text{-}C_5H_5)_2Cl_2]$ was stirred for 1 h at room temperature with a freshly prepared solution of $Li[M(CO)_5(PPh_2)]$[9] in tetrahydrofuran. The crude product was then purified by chromatography; after evaporating, a large deep purple band gave a dark solid in moderate yield (*ca.* 30%). The structures of complexes **1** and **2** (Scheme 3) were determined by a combination of elemental analysis, field desorption (FD) mass spectrometry, IR, ^1H and ^{13}C NMR spectral data. Their formation results both from a cyclopentadienyl ring substitution and an orthometallation reaction.

The ^1H NMR spectra of complexes **1** showed the presence of two diastereoisomers (about 20 : 1) which result from the phosphorus and molybdenum stereogenic centres. Further attempts to separate the mixture of diastereoisomers by column chromatography were unsuccessful, except for complexes **1c** and **1c′** with M = W. The spectral characteristics of the bimetallic systems with M = Cr or Mo have been obtained from the diastereoisomeric mixtures **1a** + **1a′** and **1b** + **1b′**. The presence of only nine protons in the phenyl as well as in the cyclopentadienyl regions confirms that the complexes are indeed cyclometallated



M	X		
Cr	Cl	**1a**	**1a′**
Mo	Cl	**1b**	**1b′**
W	Cl	**1c**	**1c′**
Cr	I	**2a**	**2a′**
Mo	I	**2b**	**2b′**
W	I	**2c**	**2c′**

Scheme 3 (*i*) Li[Mo(CO)$_5$(PPh$_2$)]

Table 1 Selected interatomic distances (Å) and angles (°) for complexes **1a** and **2c**

	1a (M = Cr, X = Cl)	**2c** (M = W, X = I)
Mo–X	2.476(2)	2.806(5)
Mo–C(6)	2.202(6)	2.194(13)
M–P	2.369(2)	2.501(6)
P–C(5)	1.817(6)	1.836(15)
P–C(22)	1.821(7)	1.801(16)
P–C(7)	1.809(6)	1.767(17)
X–Mo–C(6)	84.2(2)	85.5(4)
C(7)–P–M	114.2(2)	113.4(5)
C(7)–P–C(5)	95.2(3)	96.9(7)
C(5)–P–C(22)	103.8(3)	103.4(7)
C(7)–P–C(22)	103.4(3)	103.8(7)

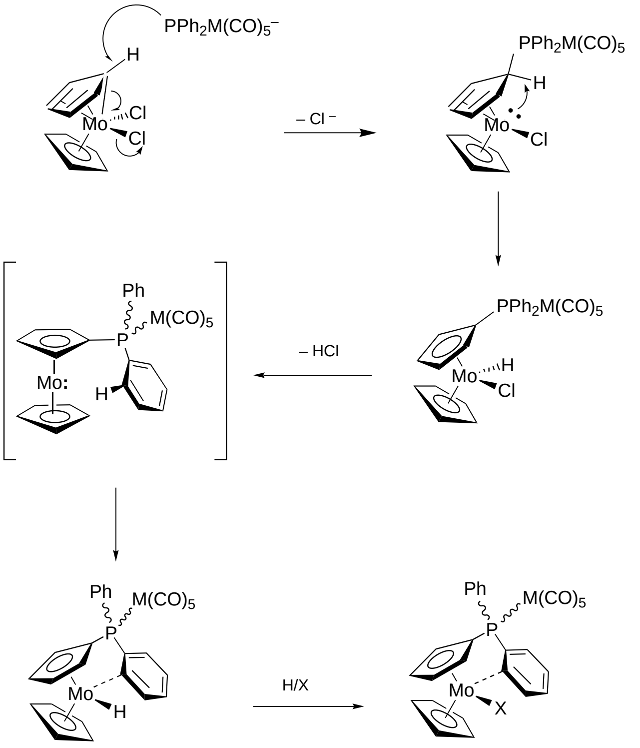
as well as ring substituted. Their spectra contain the four signals expected for the substituted cyclopentadienyl protons in a wide range (*ca.* 2 ppm) and the phenyl region indicates two deshielded signals at *ca.* δ 7.7 and 8.0. Also of interest is the observation that the singlet resonance of the C_5H_5 group protons in major isomers **1** occurs at a high field compared to that of the minor ones **1**′ (Δδ ≈ 0.7 ppm) as these protons are shielded by the ring current of the phenyl group. The ^{13}C NMR spectra of major isomers **1** also provided clear support for the co-ordination mode of these complexes. Indeed this bonding mode was proposed on the basis of the NMR studies before the crystal structure was determined. For compound **1a** the signal of the *ipso*-carbon of the C_5H_4 ring (δ 102.9) is assigned by its coupling constant $^1J_{CP} \approx 36$ Hz; the three phenyl *ipso*-carbons are located near δ 170, 157 and 136. The $^{31}P\text{-}\{^1H\}$ NMR data show an increasing shielding effect from M = Cr to W, and a similar systematically shielded signal is observed for the minor isomers **1**′. The lithium salts Li[M(CO)$_5$(PPh$_2$)] were prepared as an orange solution by treatment of a tetrahydrofuran solution of [M(CO)$_5$(PPh$_2$H)] with 1 equivalent of methyllithium. By using LiMe prepared with iodo- instead of chloro-methane, the iodine-containing complexes **2** and **2**′ were exclusively obtained. These reactions were found to proceed also with a remarkably high diasteoselectivity and the two dark green isomeric complexes were formed in about a 20 : 1 ratio. A chromatographic separation was achieved only for complexes **2a** and **2a**′ (M = Cr). They were analytically and spectroscopically characterised; no drastic changes were observed in their spectroscopic data compared to those of the chlorinated compounds.

As recently observed for the reactions of such metallophosphide anions toward [W(η^5-C$_5$H$_5$)$_2$Cl$_2$],[10] a cyclopentadienyl ring substitution by direct attack of the anion takes place with displacement of a chloride ion (S_N2' type reaction). Formation of complexes **1** or **2** can subsequently result from the sequence in Scheme 4: (*i*) an internal rearrangement involving insertion of the molybdenum moiety into the ring C_{sp^3}–H bond leading to a monohydridomonochloro molybdenocene complex; (*ii*) a formal reductive elimination of a HCl molecule giving a 'molybdenocene' intermediate; (*iii*) an insertion into the phenyl C–H bond;[8i–11] (*iv*) a H for Cl (or I) exchange.

Crystal structures of complexes 1a and 2c

The structure determination of the Mo–Cr bimetallic complex **1a** was described in a preliminary communication.[6a] Suitable crystals of the Mo–W bimetallic complex **2c** for structure determination were grown from a dichloromethane solution. Selected interatomic distances and angles are given in Table 1 and the structure is depicted in Fig. 1.

The two structures consists of a molybdenum atom bonded to a halide (Cl in **1a**, I in **2c**) and a η-C$_5$H$_5$ group which is chelated by a (η^5-C$_5$H$_4$)P(Ph)[M(CO)$_5$]C$_6$H$_4$ fragment through a Mo–C σ bond and a η^5-C$_5$H$_4$ ligand. Crystallographic data for orthometallated complexes which incorporate late transition



Scheme 4 Proposed mechanism for the formation of orthometallated complexes **1** and **2**

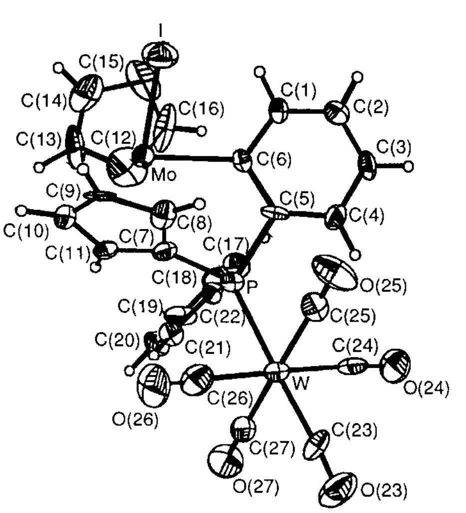
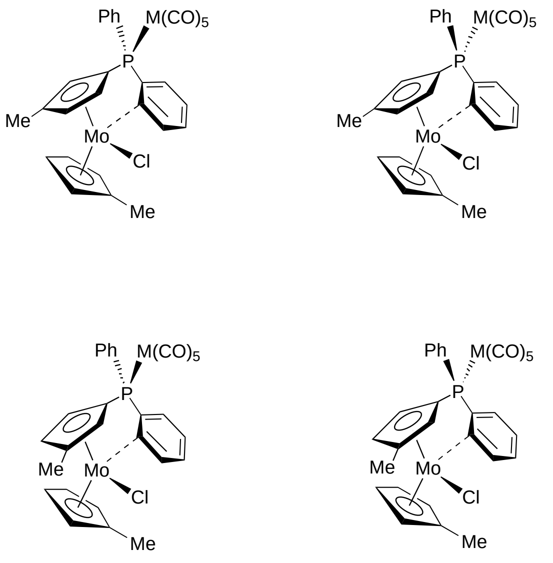
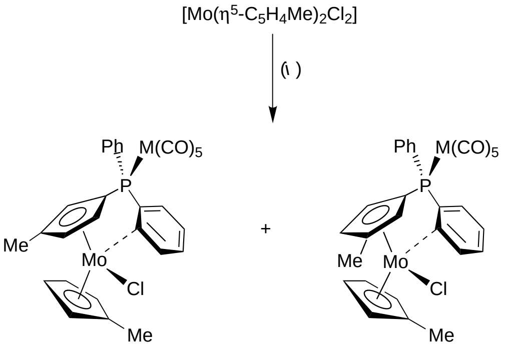


Fig. 1 An ORTEP[12] plot and atom-labelling scheme for complex **2c**. Small circles indicate hydrogen positions



Scheme 5 Regioisomers 1–3 of complexes **3** (only one enantiomer is shown)



	M
3a, 3a'	Cr
3c, 3c'	W

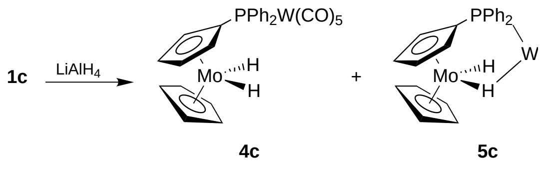
Scheme 6 (*i*) Li[M(CO)$_5$(PPh$_2$)]

elements are quite common,[13] but examples of such compounds with early transition metals are scarce and concern monocyclopentadienyl complexes of Ti[14] and Mo.[15] These major diastereoisomers are stereochemically alike [using the priority sequences: Cl (or I) > η^5-C$_5$H$_4$Me > η^5-C$_5$H$_5$ > σ-C$_6$H$_4$ around molybdenum and Cr (or W) > η^5-C$_5$H$_4$Me > σ-C$_6$H$_4$ > σ-C$_6$H$_5$ around phosphorus[16]] and the bulky group M(CO)$_5$ is in an expected *exo* position; the minor complexes will be unlike isomers.

The structures exhibit a non-planar five-membered heterocyclic [Mo,C(7),P,C(5),C(6)] array. The phosphorus atom is approximately tetrahedrally co-ordinated with P−C(5) and P−C(7) distances 1.817(6) and 1.809(6) Å, respectively (for **1a**). As expected, the C(5)− P−C(7) angle within the five-membered ring is smaller [95.2 °(3) for **1a**] than the idealised tetrahedral value. The P−Cr distance [2.369(2) Å] is longer than that reported for dibridged [H(η-C$_5$H$_5$)$_2$Ta(μ-H)(μ-PPh$_2$)Cr(CO)$_5$] [2.284(3) Å][17] but notably shorter than that of the phosphido-bridged [{(MeO)$_3$P}(η-C$_5$H$_5$)$_2$Nb(PPh$_2$)Cr(CO)$_5$] [2.549(2) Å].[18] The Mo−C(6) distance [2.202(6) Å in **1a** and 2.194(13) Å in **2c**] is similar to metal–carbon bond lengths in molybdenum σ-aryl complexes[19] or in a Mo−σ-C(sp^2) complex.[15,20]

Synthesis of methylated complexes 3

From our investigations on metallocene complexes we are aware of the influence which is exerted by the substitution degree of the cyclopentadienyl ligands on the nature of the products as well as by the metal employed.[21] Indeed, these observations were confirmed when [W(η^5-C$_5$H$_5$)$_2$Cl$_2$] was treated with metallophosphide anions leading to cyclopentadienyl-substituted bimetallic compounds but without further formation of orthometallated complexes.[10] In this regard it was of interest to test the reactivity of Li[M(CO)$_5$(PPh$_2$)] (M = Cr or W) towards the electron-donor substituted [Mo(η^5-C$_5$H$_4$Me)$_2$-Cl$_2$] molybdenocene complex by employing the basic synthetic methodology used to prepare complexes **1**.



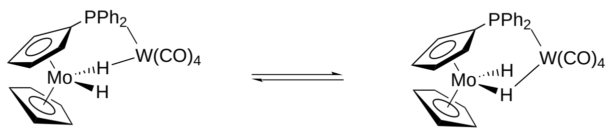
Scheme 7

The presence of the methyl groups did not have any influence on the reactivity of metallophosphide anions towards [Mo-(η^5-C$_5$H$_4$Me)$_2$Cl$_2$] *vs.* [Mo(η^5-C$_5$H$_5$)$_2$Cl$_2$]; two cyclopentadienyl-substituted and orthometallated isomers (ratio about 1 : 1) were isolated after chromatographic work-up. However, the ring substitution now occurred at a prochiral cyclopentadienyl ligand in 1–2 or 1–3 positions: thus, four racemic 1–2 and four racemic 1–3 regeoisomers (Scheme 5) could theoretically be obtained. The structures of isomers **3** and **3′** (Scheme 6) have been clearly established by IR, ^{1}H and ^{31}P NMR data. The ring substitution together with the presence of chiral elements was evidenced by the proton NMR spectrum: complex **3a′**, for example which exhibits two singlets (3 H, Me protons) at δ 1.90 and 2.06 and a set of seven multiplets (C$_5$H$_4$Me protons). The 1–3 regioselectivity of this reaction was proposed on the basis of ^{1}H NMR homodecoupling experiments: irradiation of the signal at δ 2.06 led to modification of the resonances of two cyclopentadienyl protons (at δ 5.68 and 4.03) and a similar result was obtained on irradiation of the second methyl proton signal at δ 1.90 (signals at δ 4.58 and 4.47 are modified). The ^{31}P NMR data for complexes **3a**, **3a′** and **1a** (δ 62.9, 63.2 and 63.6 respectively) on the one hand,and **3c**, **3c′** and **1c** (δ 22.3, 22.8 and 22.6 respectively) on the other, are very similar. This feature has made it possible to propose for isomers **3** and **3′** the configurations represented in Scheme 5 which retain a like arrangement of the molybdenum and phosphorus chiral centres. However, the relative 3 position of the methyl group could not be established.

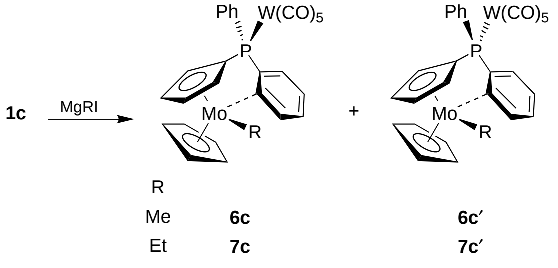
Reactivity of complex 1c

Halides co-ordinated to transition metals can readily be displaced when treated with metal hydrides or Grignard reagents. Attempts were thus made to synthesize new hydride or alkylated orthometallated complexes. After hydrolysis, treatment of **1c** with an excess of LiAlH$_4$ gave a mixture of the two complexes **4c** and **5c**. Since **4c** did not survive on silica gel chromatography, only pure **5c** could be isolated. These reactions resulted in the formation of an orange solid involving unexpected Mo−C bond breaking and characterised by means of IR and NMR spectroscopy as a dihydride molybdenocene compound with a hydride group that functions as a bridging ligand (Scheme 7).

The IR spectrum of complex **5c** has shown four CO absorptions (at 2014, 1943, 1894 and 1843 cm^{-1}) characteristic of the W(CO)$_4$ fragment *cis* disubstituted. The C_s symmetry of this molecule has clearly been established from the ^{1}H NMR data: only two signals were observed for the four substituted cyclopentadienyl protons and one high-field doublet (δ −10.93; $^2J_{PH}$ = 2.9 Hz, accompanied by tungsten satellites $^1J_{WH}$ = 16.2 Hz) for the two equivalent hydrides. Equivalence of these hydrides results from two equally populated enantiomeric states (Scheme 8). Moreover, this complex is structurally analogous to



Scheme 8 The two enantiomeric forms for complex **5c**



Scheme 9

the recently reported[10] tungstenocene hydride-bridged bimetallic complex crystallographically characterised but synthesized differently.

The addition of an excess (30%) of MgMeI to complex **1c** at room temperature gave a bright orange solution (Scheme 9). After chromatographic work-up, two isomers **6c** and **6c**′ were separated (ratio 1:1); complexes **7c** and **7c**′ were obtained in the same way, starting from MgEtBr and fully characterised. The close resemblance of the ^1H and ^{31}P NMR spectra of **6c** and **7c** to those of **1c** suggests analogous diastereomeric structures with the bulky $W(CO)_5$ group in an *exo* position: in particular, complexes **6c**, **7c** and **1c**, compared to **6c**′, **7c**′ and **1c**′, present a more shielded ^1H NMR C_5H_5 signal and a more deshielded ^{31}P NMR signal.

Compound **6c** was also treated with hydrochloric acid in toluene solution in the hope of recovering the chloride complex by substitution of the alkylmetal group. As shown by the ^1H NMR spectrum of the crude material, only the diasteroisomer **1c** was formed during this reaction. Diastereoisomer **1c**′ was formed when **6c**′ was treated in a similar way. Therefore, hydrochloric acid cleavage of the Mo–Me bond is stereospecific with respect to the chiral metal centre and occurs with retention of configuration. This feature contrasts with the previously reported HCl cleavage of the Ti–Me bond of $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)Me(C_6F_5)]$ which results in epimerisation at the titanium atom.[22]

Conclusion

The spectroscopic and crystallographic data reported indicate that metallophosphide anions allow direct nucleophilic cyclopentadienyl substitution of molybdenocene dichloride; they act as chelating ligands and provide an interesting new way to obtain diastereomeric binuclear complexes by an orthometallation reaction. Different aspects of their reactivity have been studied. To the best of our knowledge, the first insight into the stereochemical process of a substitution reaction at molybdenum has been obtained from the systematic correlation of the NMR data for various diastereomeric pairs.

Experimental

Nuclear magnetic resonance spectra were recorded on a Bruker AC 200 instrument at 200 MHz for ^1H, 50 MHz for ^{13}C and 81 MHz for ^{31}P. The chemical shifts are reported in ppm relative to $SiMe_4$ (^1H and ^{13}C) and external H_3PO_4 ($^{31}P\text{-}\{^1H\}$). Infrared spectra were obtained with a Nicolet 250 spectrometer, with the sample in solution in thf. Field desorption and electron ionisation (EI) mass spectra were recorded respectively on a Finnigan-MAT 311A apparatus and a Kratos Concept 32S apparatus. Elemental analyses were performed by the CNRS microanalytical laboratory. Structural assignments are based on ^1H, $^{13}C\text{-}\{^1H\}$, $^{31}P\text{-}\{^1H\}$ NMR, IR, FD or EI mass spectra and elemental analysis.

Preparations

All reactions were carried out under an atmosphere of purified argon using standard Schlenk-line techniques and conventional glass vessels. The solvents were dried over suitable reagents and freshly distilled under argon before use. The lithium reagent $Li[M(CO)_5(PPh_2)]$[9] and $[Mo(\eta^5\text{-}C_5H_5)_2Cl_2]$[23] were prepared according to literature procedures.

Syntheses

$[Cl(\eta^5\text{-}C_5H_5)Mo\{(\eta^5\text{-}C_5H_4)PPh(o\text{-}C_6H_4)\}M(CO)_5]$ 1 and 1′. A thf solution (5 cm^3) of $Li[M(CO)_5(PPh)_2]$ (M = Cr, Mo or W) (1.45 mmol), prepared with low-chloride methyllithium (Janssen), was rapidly added to a suspension of $[Mo(\eta^5\text{-}C_5H_5)_2Cl_2]$ (0.430 g, 1.45 mmol) in thf (20 cm^3). The brown solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the resulting oily brown residue washed with pentane (10 cm^3) and dried *in vacuo*. The solid was chromatographed over a silica gel (70–230 mesh) column. Impurities were first eliminated by eluting with toluene. Elution with toluene–thf (9:1) gave a large deep purple band corresponding to the mixture of **1** and **1**′ (95:5). These two diastereoisomers have only been separated in the case where M = W: the mixture was then rechromatographed with toluene–thf (95:5) as eluent, giving two fractions corresponding respectively to minor diastereoisomer **1c**′ and major diastereoisomer **1c**. In every case, each product was recrystallised from CH_2Cl_2. Black analytically pure crystals were obtained.

$[Cl(\eta^5\text{-}C_5H_5)Mo\{(\eta^5\text{-}C_5H_4)PPh(o\text{-}C_6H_4)\}Cr(CO)_5]$ **1a** and **1a**′: yield *ca.* 0.280 g (30%) (Found: C, 51.1; H, 2.8; Cl, 5.6; P, 4.9%; M^+, 638.0. $C_{27}H_{18}ClCrMoO_5P$ requires C, 50.9; H, 2.85; Cl, 5.5; P, 4.85%; *M*, 637.9). Fourier-transform IR (thf, cm^{-1}): 2061m and 1941s (sh) (ν_{CO}). NMR ($CDCl_3$): **1a**, ^1H, δ 8.06–8.01 (m, 1 H, C_6H_5), 7.74–7.63 (m, 1 H, C_6H_5), 7.39–7.35 (m, 3 H, C_6H_5), 7.29–7.07 (m, 4 H, C_6H_5), 5.93 (m, 1 H, C_5H_4), 5.67 (m, 1 H, C_5H_4), 5.13 (m, 1 H, C_5H_4), 4.65 (s, 5 H, C_5H_5) and 4.10 (m, 1 H, C_5H_4); $^{13}C\text{-}\{^1H\}$, δ 221.8 (d, $J_{CP} = 7.2$, 1 C, CO *trans*), 217.1 (d, $J_{CP} = 12.6$, 4 C, CO *cis*), 170.7 (d, $J_{CP} = 5.4$, 1 C, C_6H_5 *ipso*), 157.4 (d, $J_{CP} = 48.5$, 1 C, C_6H_5 *ipso*), 145.9 (d, $J_{CP} = 9.0$, 1 C, C_6H_5), 136.0 (d, $J_{CP} = 32.3$, 1 C, C_6H_5 *ipso*), 133.9 (d, $J_{CP} = 25.1$, 1 C, C_6H_5), 131.1 (d, $J_{CP} = 1.8$, 1 C, C_6H_5), 130.4 (d, $J_{CP} = 9.0$, 2 C, C_6H_5), 129.7 (d, $J_{CP} = 1.8$, 1 C, C_6H_5), 129.3 (d, $J_{CP} = 9.0$, 2 C, C_6H_5), 124.3 (d, $J_{CP} = 14.4$, 1 C, C_6H_5), 116.5 (d, $J_{CP} = 5.4$, 1 C, C_5H_4), 102.9 (d, $J_{CP} = 35.9$, 1 C, C_5H_4 *ipso*), 101.8 (d, $J_{CP} = 14.4$, 1 C, C_5H_4), 97.9 (d, $J_{CP} = 5.4$, 1 C, C_5H_4), 97.7 (s, 5 C, C_5H_5) and 91.1 (d, $J_{CP} = 3.6$, 1 C, C_5H_4); $^{31}P\text{-}\{^1H\}$, δ 63.6 (s); **1a**′, ^1H, δ 5.37 (s, 5 H, C_5H_5); $^{31}P\text{-}\{^1H\}$, δ 50.1 (s).

$[Cl(\eta^5\text{-}C_5H_5)Mo\{(\eta^5\text{-}C_5H_4)PPh(o\text{-}C_6H_4)\}Mo(CO)_5]$ **1b** and **1b**′: yield *ca.* 0.290 g (29%) (Found: C, 49.4; H, 2.7; Cl, 5.4; P, 4.7. $C_{27}H_{18}ClMo_2O_5P$ requires C, 47.7; H, 2.7; Cl, 5.2; P, 4.55%). Fourier-transform IR(thf, cm^{-1}): 2071m and 1947s (sh) (ν_{CO}). NMR ($CDCl_3$): **1b**, ^1H, δ 8.04–7.98 (m, 1 H, C_6H_5), 7.70–7.58 (m, 1 H, C_6H_5), 7.39–7.30 (m, 3 H, C_6H_5), 7.24–7.07 (m, 4 H, C_6H_5), 5.92 (m, 1 H, C_5H_4), 5.63 (m, 1 H, C_5H_4), 5.13 (m, 1 H, C_5H_4), 4.67 (s, 5 H, C_5H_5) and 4.03 (m, 1 H, C_5H_4); $^{31}P\text{-}\{^1H\}$, δ 43.2 (s); **1b**′, ^1H, δ 5.36 (s, 5 H, C_5H_5); $^{31}P\text{-}\{^1H\}$, δ 21.0 (s).

$[Cl(\eta^5\text{-}C_5H_5)Mo\{(\eta^5\text{-}C_5H_4)PPh(o\text{-}C_6H_4)\}W(CO)_5]$ **1c**: yield *ca.* 0.440 g (39%) (Found: C, 44.1; H, 2.4; Cl, 4.8; P, 4.2. $C_{27}H_{18}ClMoO_5PW$ requires C, 42.2; H, 2.35; Cl, 4.6; P, 4.0%). Fourier-transform IR (thf, cm^{-1}): 2070m and 1939s (sh) (ν_{CO}). NMR ($CDCl_3$): ^1H, δ 8.03–7.99 (m, 1 H, C_6H_5), 7.69–7.57 (m, 1 H, C_6H_5), 7.40–7.39 (m, 3 H, C_6H_5), 7.25–7.12 (m, 4 H, C_6H_5), 5.93 (m, 1 H, C_5H_4), 5.65 (m, 1 H, C_5H_4), 5.13 (m, 1 H, C_5H_4), 4.67 (s, 5 H, C_5H_5) and 4.05 (m, 1 H, C_5H_4); $^{13}C\text{-}\{^1H\}$, δ 199.8 (d, $J_{CP} = 20.3$, 1 C, CO *trans*), 197.6 (d, $J_{CP} = 7.2$, $^1J_{WC} = 125.1$, 4 C, CO *cis*), 171.2 (d, $J_{CP} = 6.1$, 1 C, C_6H_5 *ipso*), 157.7 (d,

$J_{CP} = 52.9$, 1 C, C_6H_5 *ipso*), 146.0 (d, $J_{CP} = 10.5$, 1 C, C_6H_5), 136.2 (d, $J_{CP} = 37.0$, 1 C, C_6H_5 *ipso*), 134.3 (d, $J_{CP} = 27.1$, 1 C, C_6H_5), 131.2 (d, $J_{CP} = 1.8$, 1 C, C_6H_5), 130.5 (d, $J_{CP} = 10.8$, 2 C, C_6H_5), 129.9 (d, $J_{CP} = 1.8$, 1 C, C_6H_5), 129.3 (d, $J_{CP} = 9.0$, 2 C, C_6H_5), 124.4 (d, $J_{CP} = 14.6$, 1 C, C_6H_5), 116.2 (d, $J_{CP} = 6.0$, 1 C, C_5H_4), 104.2 (d, $J_{CP} = 40.9$, 1 C, C_5H_4 *ipso*), 101.9 (d, $J_{CP} = 13.8$, 1 C, C_5H_4), 97.8 (d, $J_{CP} = 5.7$, 1 C, C_5H_4), 97.7 (s, 5 C, C_5H_5) and 90.9 (d, $J_{CP} = 4.0$, 1 C, C_5H_4); $^{31}P\text{-}\{^1H\}$, δ 22.6 (s, $^1J_{WP} = 234$ Hz).

$[Cl(\eta^5\text{-}C_5H_5)Mo\{(\eta^5\text{-}C_5H_4)PPh(o\text{-}C_6H_4)\}W(CO)_5]$ **1c′**: yield *ca.* 0.033 g (3%). Fourier-transform IR (thf, cm^{-1}): 2070m and 1939s (sh) (ν_{CO}). NMR ($CDCl_3$): ^1H, δ 8.02–7.14 (m, 9 H, C_6H_5), 5.88 (m, 1 H, C_5H_4), 5.72 (m, 1 H, C_5H_4), 5.37 (s, 5 H, C_5H_5), 4.98 (m, 1 H, C_5H_4) and 4.77 (m, 1 H, C_5H_4); $^{31}P\text{-}\{^1H\}$, δ 11.2 (s, $^1J_{WP} = 210$ Hz).

$[I(\eta^5\text{-}C_5H_5)Mo\{(\eta^5\text{-}C_5H_4)PPh(o\text{-}C_6H_4)\}M(CO)_5]$ 2 and 2′. The procedure described above for complex **1** was performed but using LiMe prepared from iodomethane. The crude product was chromatographed over a silica gel column. Elution with toluene gave two red and a large green band. The solvent was removed under reduced pressure from the last band, giving a green powder of **2** and **2′** (95:5). These two diastereoisomers have only been separated in the case where M = Cr: the mixture was then rechromatographed with toluene as eluent, giving two fractions corresponding respectively to the minor diastereoisomer **2a′** and the major diastereoisomer **2a**. In every case, each product was recrystallised from CH_2Cl_2. Dark green analytically pure crystals were obtained.

$[I(\eta^5\text{-}C_5H_5)Mo\{(\eta^5\text{-}C_5H_4)PPh(o\text{-}C_6H_4)\}Cr(CO)_5]$ **2a**: yield *ca.* 0.411 g (39%) (Found: C, 44.5; H, 2.5%; M^+, 730.1. $C_{27}H_{18}CrIMoO_5P$ requires C, 44.5; H, 2.5%; *M*, 729.8). Fourier-transform IR (thf, cm^{-1}): 2061m and 1941s (sh) (ν_{CO}). NMR ($CDCl_3$): ^1H, δ 8.56–8.54 (m, 1 H, C_6H_5), 7.70–7.59 (m, 1 H, C_6H_5), 7.41–7.37 (m, 3 H, C_6H_5), 7.17–7.07 (m, 4 H, C_6H_5), 6.44 (m, 1 H, C_5H_4), 5.22 (m, 1 H, C_5H_4), 5.05 (m, 1 H, C_5H_4), 4.67 (s, 5 H, C_5H_5) and 4.36 (m, 1 H, C_5H_4); $^{13}C\text{-}\{^1H\}$, δ 221.7 (d, $J_{CP} = 7.1$, 1 C, CO *trans*), 217.1 (d, $J_{CP} = 12.7$, 4 C, CO *cis*), 169.4 (d, $J_{CP} = 5.5$, 1 C, C_6H_5 *ipso*), 157.4 (d, $J_{CP} = 47.8$, 1 C, C_6H_5 *ipso*), 151.2 (d, $J_{CP} = 10.0$, 1 C, C_6H_5), 136.2 (d, $J_{CP} = 31.7$, 1 C, C_6H_5 *ipso*), 134.1 (d, $J_{CP} = 25.7$, 1 C, C_6H_5), 131.1 (s, 1 C, C_6H_5), 130.6 (d, $J_{CP} = 10.0$, 2 C, C_6H_5), 129.6 (s, 1 C, C_6H_5), 129.3 (d, $J_{CP} = 9.0$, 2 C, C_6H_5), 124.1 (d, $J_{CP} = 14.5$, 1 C, C_6H_5), 111.7 (d, $J_{CP} = 6.0$, 1 C, C_5H_4), 101.6 (d, $J_{CP} = 36.0$, 1 C, C_5H_4 *ipso*), 97.5 (d, $J_{CP} = 13.0$, 1 C, C_5H_4), 95.4 (s, 5 C, C_5H_5), 94.3 (d, $J_{CP} = 5.4$, 1 C, C_5H_4) and 91.8 (d, $J_{CP} = 4.1$ Hz, 1 C, C_5H_4); $^{31}P\text{-}\{^1H\}$, δ 62.3 (s).

$[I(\eta^5\text{-}C_5H_5)Mo\{(\eta^5\text{-}C_5H_4)PPh(o\text{-}C_6H_4)\}Cr(CO)_5]$ **2a′**: yield *ca.* 0.031 g (3%) (Found: M^+, 730.1. $C_{27}H_{18}CrIMoO_5P$ requires *M*, 729.8). Fourier-transform IR (thf, cm^{-1}): 2063m and 1942s (sh) (ν_{CO}). NMR ($CDCl_3$): ^1H, δ 8.44–8.42 (m, 1 H, C_6H_5), 7.62–7.52 (m, 2 H, C_6H_5), 7.37–7.03 (m, 6 H, C_6H_5), 6.32 (m, 1 H, C_5H_4), 5.38 (s, 5 H, C_5H_5), 5.27 (m, 2 H, C_5H_4) and 4.98 (m, 1 H, C_5H_4); $^{13}C\text{-}\{^1H\}$, δ 220.8 (d, $J_{CP} = 7.0$, 1 C, CO *trans*), 217.2 (d, $J_{CP} = 13.0$, 4 C, CO *cis*), 161.0 (d, $J_{CP} = 48.7$, 1 C, C_6H_5 *ipso*), 160.8 (d, $J_{CP} = 7.2$, 1 C, C_6H_5 *ipso*), 150.9 (d, $J_{CP} = 12.0$, 1 C, C_6H_5), 141.0 (d, $J_{CP} = 33.2$, 1 C, C_6H_5 *ipso*), 132.1 (d, $J_{CP} = 20.0$, 1 C, C_6H_5), 130.5 (d, $J_{CP} = 10.0$, 2 C, C_6H_5), 130.2 (s, 1 C, C_6H_5), 129.2 (d, $J_{CP} = 9.0$, 2 C, C_6H_5), 128.8 (s, 1 C, C_6H_5), 124.1 (d, $J_{CP} = 12.0$, 1 C, C_6H_5), 110.6 (d, $J_{CP} = 3.6$, 1 C, C_5H_4), 103.4 (d, $J_{CP} = 38.0$, 1 C, C_5H_4 *ipso*), 99.2 (d, $J_{CP} = 1.8$, 1 C, C_5H_4), 95.7 (s, 5 C, C_5H_5), 95.3 (d, $J_{CP} = 19.0$, 1 C, C_5H_4) and 94.8 (d, $J_{CP} = 7.5$, 1 C, C_5H_4); $^{31}P\text{-}\{^1H\}$, δ 49.5 (s).

$[I(\eta^5\text{-}C_5H_5)Mo\{(\eta^5\text{-}C_5H_4)PPh(o\text{-}C_6H_4)\}Mo(CO)_5]$ **2b** and **2b′**: yield *ca.* 0.350 g (31%) (Found: M^+, 772.5. $C_{27}H_{18}IMo_2O_5P$ requires *M*, 771.8). Fourier-transform IR (thf, cm^{-1}): 2071m and 1947s (sh) (ν_{CO}). NMR ($CDCl_3$): **2b**, ^1H, δ 8.56–8.50 (m, 1 H, C_6H_5), 7.65–7.54 (m, 1 H, C_6H_5), 7.41–7.37 (m, 3 H, C_6H_5), 7.17–7.07 (m, 4 H, C_6H_5), 6.43 (m, 1 H, C_5H_4), 5.19 (m, 1 H, C_5H_4), 5.06 (m, 1 H, C_5H_4), 4.69 (s, 5 H, C_5H_5) and 4.29 (m, 1 H, C_5H_4); $^{13}C\text{-}\{^1H\}$, δ 210.4 (d, $J_{CP} = 21.3$, 1 C, CO *trans*), 206.1 (d, $J_{CP} = 8.8$, 4 C, CO *cis*), 170.0 (d, $J_{CP} = 4.7$, 1 C, C_6H_5 *ipso*), 158.1 (d, $J_{CP} = 47.3$, 1 C, C_6H_5 *ipso*), 151.2 (d, $J_{CP} = 9.7$, 1 C, C_6H_5), 136.4 (d, $J_{CP} = 30.3$, 1 C, C_6H_5 *ipso*), 134.1 (d, $J_{CP} = 28.5$, 1 C, C_6H_5), 130.9 (d, $J_{CP} = 5.0$, 2 C, C_6H_5), 130.7 (s, 1 C, C_6H_5), 129.5 (s, 1 C, C_6H_5), 129.2 (d, $J_{CP} = 8.4$, 2 C, C_6H_5), 124.1 (d, $J_{CP} = 14.5$, 1 C, C_6H_5), 111.1 (d, $J_{CP} = 6.8$, 1 C, C_5H_4), 103.1 (d, $J_{CP} = 35.7$, 1 C, C_5H_4 *ipso*), 97.5 (d, $J_{CP} = 14.7$, 1 C, C_5H_4), 95.3 (s, 5 C, C_5H_5), 94.2 (d, $J_{CP} = 5.1$, 1 C, C_5H_4) and 91.8 (d, $J_{CP} = 3.4$ Hz, 1 C, C_5H_4); $^{31}P\text{-}\{^1H\}$, δ 42.3 (s); **2b′**, ^1H, δ 5.36 (s, 5 H, C_5H_5); $^{31}P\text{-}\{^1H\}$, δ 22.0 (s).

$[I(\eta^5\text{-}C_5H_5)Mo\{(\eta^5\text{-}C_5H_4)PPh(o\text{-}C_6H_4)\}W(CO)_5]$ **2c** and **2c′**: yield *ca.* 0.340 g (27%) (Found: C, 37.3; H, 2.7%; M^+, 860.6. $C_{27}H_{18}IMoO_5PW$ requires C, 37.7; H, 2.1%; *M*, 861.8). Fourier-transform IR (thf, cm^{-1}); 2071m and 1942s (sh) (ν_{CO}). NMR ($CDCl_3$): **2c**, ^1H, δ 8.56–8.49 (m, 1 H, C_6H_5), 7.64–7.52 (m, 1 H, C_6H_5), 7.42–7.38 (m, 3 H, C_6H_5), 7.17–7.07 (m, 4 H, C_6H_5), 6.44 (m, 1 H, C_5H_4), 5.19 (m, 1 H, C_5H_4), 5.06 (m, 1 H, C_5H_4), 4.69 (s, 5 H, C_5H_5) and 4.30 (m, 1 H, C_5H_4); $^{13}C\text{-}\{^1H\}$, δ 199.7 (d, $J_{CP} = 19.7$, 1 C, CO *trans*), 197.6 (d, $J_{CP} = 5.4$, $^1J_{WC} = 125.0$, 4 C, CO *cis*), 170.0 (d, $J_{CP} = 6.9$, 1 C, C_6H_5 *ipso*), 157.8 (d, $J_{CP} = 52.7$, 1 C, C_6H_5 *ipso*), 151.3 (d, $J_{CP} = 10.4$, 1 C, C_6H_5), 136.2 (d, $J_{CP} = 36.3$, 1 C, C_6H_5 *ipso*), 134.4 (d, $J_{CP} = 26.9$, 1 C, C_6H_5), 131.2 (s, 1 C, C_6H_5), 130.7 (d, $J_{CP} = 11.0$, 2 C, C_6H_5), 129.8 (s, 1 C, C_6H_5), 129.2 (d, $J_{CP} = 9.0$, 2 C, C_6H_5), 124.2 (d, $J_{CP} = 14.5$, 1 C, C_6H_5), 111.2 (d, $J_{CP} = 6.5$, 1 C, C_5H_4), 102.9 (d, $J_{CP} = 40.9$, 1 C, C_5H_4 *ipso*), 97.5 (d, $J_{CP} = 14.1$, 1 C, C_5H_4), 95.4 (s, 5 C, C_5H_5), 94.3 (d, $J_{CP} = 5.5$, 1 C, C_5H_4) and 91.8 (d, $J_{CP} = 4.5$, 1 C, C_5H_4); $^{31}P\text{-}\{^1H\}$, δ 21.7 (s, $^1J_{WP} = 238$); **2c′**, ^1H, δ 5.37 (s, 5 H, C_5H_5); $^{31}P\text{-}\{^1H\}$, δ 11.2 (s, $^1J_{WP} = 220$ Hz).

$[Cl(\eta^5\text{-}C_5H_4Me)Mo\{(\eta^5\text{-}C_5H_3Me\text{-}3)PPh(o\text{-}C_6H_4)\}M(CO)_5]$ 3 and 3′. The procedure described above for complex **1** was performed but starting from $[Mo(\eta^5\text{-}C_5H_4Me)Cl_2]$ (0.455 g, 1.40 mmol) instead of $[Mo(\eta^5\text{-}C_5H_5)_2Cl_2]$. The crude product, obtained after removal of solvent, was chromatographed over a silica gel (70–230 mesh) column. Impurities were first eliminated by eluting with toluene. Elution with toluene–thf (9:1) gave a large brown band corresponding to the mixture of **3** and **3′** (1:1). These two diastereoisomers were then rechromatographed on three connected Merck-Lobar columns [240 × 10 mm; LiChroprep Si-60 (40–63 μm)]. Elution with toluene–chloroform (7:3) gave two distinct brown bands corresponding respectively to diastereoisomers **3** and **3′**. Each product was recrystallised from CH_2Cl_2.

$[Cl(\eta^5\text{-}C_5H_4Me)Mo\{(\eta^5\text{-}C_5H_3Me\text{-}3)Ph(o\text{-}C_6H_4)\}Cr(CO)_5]$ **3a** and **3a′**: yield *ca.* 0.250 g (27%) (Found: C, 50.7; H, 3.5%; M^+, 665.9. $C_{29}H_{22}ClCrMoO_5P$ requires C, 52.4; H, 3.3%; *M*, 665.9). Complex **3a**: yield *ca.* 0.110 g (12%). NMR ($CDCl_3$): ^1H, δ 8.12–8.09 (m, 1 H, C_6H_5), 7.74–7.62 (m, 1 H, C_6H_5), 7.37–7.35 (m, 3 H, C_6H_5), 7.21–7.10 (m, 4 H, C_6H_5), 5.05 (m, 1 H), 4.73 (m, 1 H), 4.53 (m, 1 H), 4.39 (s, 1 H), 4.18 (m, 1 H), 4.02 (m, 1 H), 3.83 (m, 1 H) (C_5H_4 or C_5H_3), 1.96 (s, 3 H, CH_3) and 1.82 (s, 3 H, CH_3); $^{31}P\text{-}\{^1H\}$, δ 62.9 (s). Complex **3a′**: yield *ca.* 0.100 g (10%). NMR ($CDCl_3$): ^1H, δ 7.89–7.83 (m, 1 H, C_6H_5), 7.72–7.61 (m, 1 H, C_6H_5), 7.37–7.35 (m, 3 H, C_6H_5), 7.21–7.16 (m, 4 H, C_6H_5), 5.68 (m, 1 H), 5.03 (m, 1 H), 4.58 (m, 1 H), 4.47 (s, 1 H), 4.03 (m, 1 H), 3.92 (m, 1 H), 3.60 (m, 1 H) (C_5H_4 or C_5H_3), 2.06 (s, 3 H, CH_3) and 1.90 (s, 3 H, CH_3); $^{31}P\text{-}\{^1H\}$, δ 63.2 (s).

$[Cl(\eta^5\text{-}C_5H_4Me)Mo\{(\eta^5\text{-}C_5H_3Me\text{-}3)PPh(o\text{-}C_6H_4)\}W(CO)_5]$ **3c** and **3c′**: yield *ca.* 0.330 g (29%). Complex **3c**: yield *ca.* 0.120 g (11%). NMR ($CDCl_3$): ^1H, δ 8.09–8.05 (m, 1 H, C_6H_5) 7.58–7.56 (m, 1 H, C_6H_5), 7.39–7.33 (m, 3 H, C_6H_5), 7.21–7.10 (m, 4 H, C_6H_5), 5.04 (m, 1 H), 4.77 (m, 1 H), 4.53 (m, 1 H), 4.43 (s, 1 H), 4.14 (m, 1 H), 4.03 (m, 1 H), 3.83 (m, 1 H) (C_5H_4 or C_5H_3), 1.96 (s, 3 H, CH_3) and 1.84 (s, 3 H, CH_3); $^{31}P\text{-}\{^1H\}$, δ 22.3 (s, $^1J_{WP} = 237$ Hz). Complex **3c′**: yield *ca.* 0.110 g (10%). NMR ($CDCl_3$): ^1H, δ 7.85–7.80 (m, 1 H, C_6H_5), 7.64–7.55 (m, 1 H, C_6H_5), 7.41–7.35 (m, 3 H, C_6H_5), 7.20–7.15 (m, 4 H, C_6H_5), 5.69 (m, 1 H), 5.03 (m, 1 H), 4.62 (m, 1 H), 4.48 (s, 1 H), 3.99 (m, 2

Table 2 Crystal structure data for complex **2c**

Empirical formula	$C_{27}H_{18}IMoO_5PW$
M	860.10
Crystal size/mm	0.10 × 0.20 × 0.45
Space group	$P2_1/c$ (no. 14)
a/Å	12.03(2)
b/Å	14.60(2)
c/Å	14.74(1)
β/°	92.2(1)
U/Å^3	2587
Z	4
μ(Mo-Kα)/cm^{-1}	62.9
D_c/g cm^{-3}	2.21
F(000)	1616
Radiation (λ/Å)	Mo-Kα (0.710 69)
2θ Limits/°	3.0–45.0
hkl Ranges	0–13, 0–16, −16 to 16
Scan mode	θ–2θ
Total unique data with $I > 2.5\sigma(I)$	2258
No. observations (*n*)	3561
No. variables (*p*)	326
Weighting scheme, w^{-1}	$\sigma^2(F)$
Maximum, minimum peaks in final difference map/e Å^{-3}	0.92, −0.97
Root-mean-square shift/e.s.d. in final least-squares cycle	0.013
$R(F)$[a]	0.047
$R'(F)$[b]	0.034
Goodness of fit[c]	1.46

[a] $R(F) = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$. [b] $R'(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{\frac{1}{2}}$. [c] $[\Sigma(w|F_o - F_c|^2)/(n - p)]^{\frac{1}{2}}$.

H), 3.60 (m, 1 H) (C_5H_4 or C_5H_3), 2.05 (s, 3 H, CH_3) and 1.87 (s, 3 H, CH_3); ^{31}P-{^{1}H}, δ 22.8 (s, $^1J_{WP}$ = 233 Hz).

[H_2(η^5-C_5H_5)Mo(η^5-$C_5H_4PPh_2$)W(CO)$_5$] 4c and [H(η^5-C_5H_5)-Mo(η^5-$C_5H_4PPh_2$)HW(CO)$_4$] 5c. To a thf solution (20 cm^3) of complex **1c** (0.200 g, 0.26 mmol), was slowly added $LiAlH_4$ (30% excess) at 0 °C. The mixture was stirred for 3 h at room temperature. The excess of $LiAlH_4$ was filtered off. After hydrolysis of the filtrate, the solvent was removed under reduced pressure to give a crude product which was extracted with diethyl ether. The resulting red powder was a mixture of complexes **4c** and **5c** (1 : 5). Chromatography over a silica gel column (elution with toluene) gave only **5c**, as an orange powder.

Complex **4c**: ^{1}H NMR (C_6D_6) δ −8.56 (s, MoH); only this characteristic could be obtained from the spectrum of the crude material.

Complex **5c**: yield *ca.* 0.028 g (15%). Fourier-transform IR (thf, cm^{-1}): 2014m, 1943s, 1894vs and 1843s (ν_{CO}). NMR (C_6D_6): ^{1}H, δ 7.86–6.96 (m, 10 H, C_6H_5), 4.58 (m, 2 H, C_5H_4), 4.18 (s, 5 H, C_5H_5), 3.72 (m, 2 H, C_5H_4) and −10.93 (d, $^2J_{PH}$ = 2.9, $^1J_{WH}$ = 16.2 Hz, 2 H, MoH); ^{31}P-{^{1}H}, δ 3.1 (s, $^1J_{WP}$ masked).

[Me(η^5-C_5H_5)Mo{(η^5-C_5H_4)PPh(*o*-C_6H_4)}W(CO)$_5$] 6c and 6c′. To a thf solution (15 cm^3) of complex **1c** (0.340 g, 0.44 mmol) was added an excess (30%) of MgMeI (in ether solution). The mixture was stirred for 1 h at room temperature. Removal of the solvent under reduced pressure gave an orange powder, which was purified by column chromatography. Elution with toluene afforded a pure red-orange mixture of complexes **6c** and **6c′** (1 : 1). This was rechromatographed on three connected Merck-Lobar columns [240 × 10 mm; LiChroprep Si 60 (40–63 μm)]. Elution with toluene–pentane (1 : 1) gave two bands: a yellow one and an orange one corresponding respectively to diastereoisomers **6c′** and **6c** (Found: C, 44.3; H, 3.4%; M^+, 748.2. $C_{28}H_{21}MoO_5PW$ requires C, 44.95; H, 2.85%; *M*, 749.9).

Complex **6c**: yield *ca.* 0.075 g (22%). Fourier-transform IR (thf, cm^{-1}): 2070m and 1939s (sh) (ν_{CO}). NMR (C_6D_6): ^{1}H δ 7.79–6.90 (m, 9 H, C_6H_5), 4.78 (m, 1 H, C_5H_4), 4.36 (s, 5 H, C_5H_5), 4.33 (m, 1 H, C_5H_4), 3.89 (m, 1 H, C_5H_4), 3.73 (m, 1 H, C_5H_4) and 0.14 (s, 3 H, Mo−CH_3); ^{31}P-{^{1}H}, δ 19.8 (s, $^1J_{WP}$ = 232 Hz).

Complex **6c′**: yield *ca.* 0.080 g (24%). Fourier-transform IR (thf, cm^{-1}): 2070m and 1938s (sh) (ν_{CO}). NMR (C_6D_6): ^{1}H, δ 7.95–6.87 (m, 9 H, C_6H_5), 4.41 (m, 1 H, C_5H_4), 3.94 (m, 1 H, C_5H_4), 3.85 (m, 2 H, C_5H_4), 3.68 (s, 5 H, C_5H_5) and 0.19 (s, 3 H, Mo−CH_3); ^{31}P-{^{1}H}, δ 8.2 (s, $^1J_{WP}$ = 232 Hz).

[Et(η^5-C_5H_5)Mo{η^5-C_5H_4)PPh(*o*-C_6H_4)PPh}W(CO)$_5$] 7c and 7c′. The procedure described above for complexes **6c** and **6c′** was utilised but starting from MgEtBr instead of MgMeI (Found: C, 45.6; H, 3.3%; M^+, 764. $C_{29}H_{23}MoO_5PW$ requires C, 45.7; H, 3.05%; *M*, 763.9).

Complex **7c**: yield *ca.* 0.074 g (22%). Fourier-transform IR (thf, cm^{-1}): 2070m and 1939s (sh) (ν_{CO}). NMR (C_6D_6): ^{1}H, δ 7.97–6.88 (m, 9 H, C_6H_5), 4.56 (m, 1 H, C_5H_4), 3.89 (m, 3 H, C_5H_4), 3.71 (s, 5 H, C_5H_5) and 1.21–0.87 (m, 5 H, Mo−CH_2CH_3); ^{13}C-{^{1}H}, δ 200.0 (d, J_{CP} = 19.3, 1 C, CO *trans*), 198.1 (d, J_{CP} = 7.3, 4 C, CO *cis*); 180.5–122.7 (m, C_6H_5), 103.8 (d, 1 C, J_{CP} = 6.4, C_5H_4), 98.1 (d, 1 C, J_{CP} = 14.7, C_5H_4), 95.2 (d, J_{CP} = 46.8, 1 C, C_5H_4 *ipso*), 90.8 (s, 5 C, C_5H_5), 90.2 (d, J_{CP} = 6.4, 1 C, C_5H_4), the last C_5H_4 masked, 23.4 (s, 1 C, CH_3) and 7.9 (s, 1 C, CH_2); ^{31}P-{^{1}H}, δ 20.7 (s, $^1J_{WP}$ = 232 Hz).

Complex **7c′**: yield *ca.* 0.077 g (23%). Fourier-transform IR (thf, cm^{-1}): 2070m and 1938s (sh) (ν_{CO}). NMR (C_6D_6): ^{1}H, δ 7.77–6.96 (m, 9 H, C_6H_5), 4.75 (m, 1 H, C_5H_4), 4.56 (m, 1 H, C_5H_4), 4.39 (s, 5 H, C_5H_5), 3.98 (m, 1 H, C_5H_4), 3.75 (m, 1 H, C_5H_4) and 1.16–0.83 (m, 5 H, Mo−CH_2CH_3); ^{13}C-{^{1}H}, δ 199.1 (d, J_{CP} = 20.2, 1 C, CO *trans*), 198.0 (d, J_{CP} = 7.3, 4 C, CO *cis*), 170.4 (d, J_{CP} = 17.5, 1 C, C_6H_5 *ipso*), 161.7 (d, J_{CP} = 63.4, 1 C, C_6H_5 *ipso*), 142.8 (d, J_{CP} = 12.9, 1 C, C_6H_5), 131.4–122.7 (m, C_6H_5), 105.8 (s, 1 C, C_5H_4), 97.7 (s, 1 C, C_5H_4), 94.6 (d, J_{CP} = 19.3, 1 C, C_5H_4), 93.1 (d, J_{CP} = 51.4, 1 C, C_5H_4 *ipso*), 91.4 (s, 5 C, C_5H_5), 90.0 (d, J_{CP} = 8.1, 1 C, C_5H_4), 23.4 (s, 1 C, CH_3) and 6.8 (s, 1 C, CH_2); ^{31}P-{^{1}H}, δ 9.0 (s, $^1J_{WP}$ = 236 Hz).

Crystallography

Black single crystals of complex **2c** were grown from a dichloromethane solution at low temperature. Suitable ones for X-ray diffraction studies were mounted on a Syntex R3 diffractometer. Quantitative data were obtained at room temperature. All experimental parameters used are given in Table 2. A systematic search in reciprocal space showed that the crystals belong to the monoclinic space group. The resulting data set was transferred to a Micro VAX II computer and the SHELXTL PLUS[24] program was used for all subsequent calculations. The structure was solved and refined by conventional three-dimensional Patterson, Fourier-difference and full-matrix least-squares methods based on *F*. An empirical absorption correction was applied. All non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were located in Fourier–difference maps. These were assigned a fixed *U* = 0.08 Å^2 and their coordinates were not refined.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/409.

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