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Synthesis and crystal structure of η^3-phosphaallyl-molybdenum and -tungsten complexes

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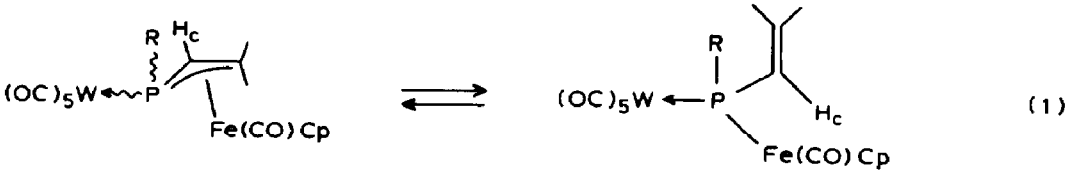
Abstract

The reaction of the (phenyl)(vinyl)chlorophosphine $PW(CO)_5$ complex with $[CpMo(CO)_3]_2$ at 140°C affords, inter alia, the corresponding η^3-phosphaallyl $CpMo(CO)_2$ complex as a mixture of two isomers. In the major isomer the $Mo(CO)_2$ group is sandwiched between the phosphaallyl and cyclopentadienyl units, respectively at 2.0286 and 2.0197 Å. The two planes form an angle of 38°. A permutation between the P–Ph and P–$W(CO)_5$ bonds is observed when comparing this η^3-phosphaallylmolybdenum complex with a previously described η^3-phosphaallyliron complex.

Similar η^3-phosphaallyl $CpW(CO)_2$ complexes are obtained with $NaW(CO)_3Cp$ at 60°C.

Introduction

In previous papers [1,2] we demonstrated that it is possible to prepare stable η^3-phosphaallyliron complexes such as **1**. These complexes are obtained as mixtures of two interconverting isomers **1a** and **1b**. This interconversion probably takes place through a transient 16-electron η^1-phosphaallyliron species **2** (eq. 1).



(1)

(1a (Hc *syn* to W) ;
1b (Hc *anti* to W))

(2)

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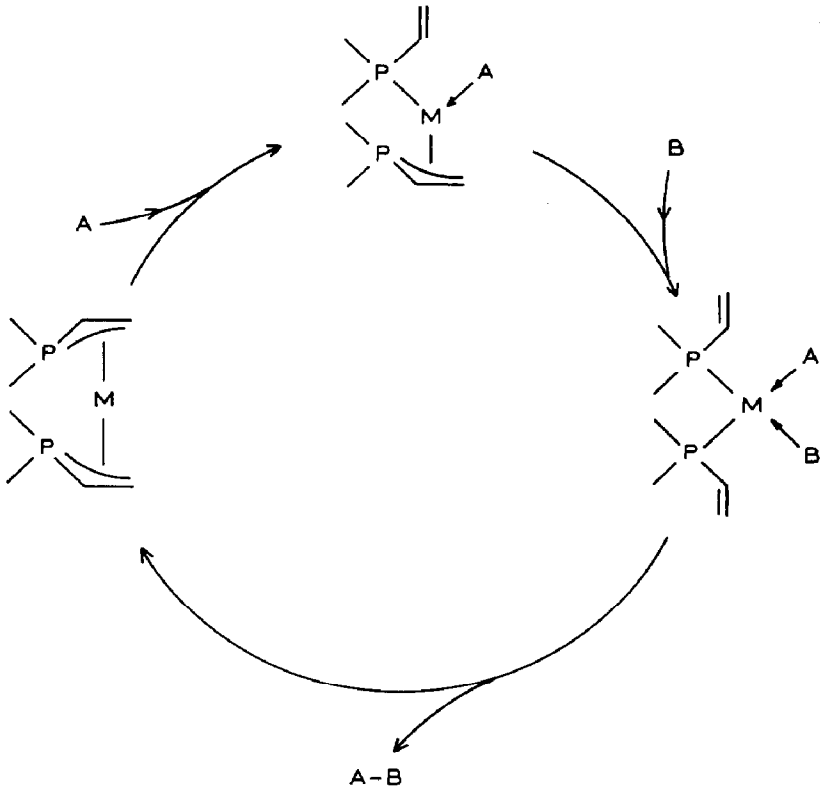


(2)

The existence of this type of equilibrium suggests that it should be possible to use such complexes for catalytic purposes. A tentative general scheme is proposed in eq. 2.

Of course, a requirement for the development of such catalytic processes suppo-
C
ses that it must be possible to adjust the relative stability of the M–P and M– |
C
links within the η^3-phosphaallyl structure and to choose the metallic centre M for its intrinsic ability to catalyse the A–B coupling. In view of this, we decided to study the synthesis of corresponding complexes in the chromic series.

Results and discussion

We first investigated the reaction of the chlorophosphine complex **3** [2] with $[CpMo(CO)_3]_2$. As expected, it yielded, inter alia, the η^3-complex as a mixture of two isomers **4a** and **b** (eq. 3).

In contrast to the result with the iron complex [1,2], in this case the most stable and abundant product is the *anti* isomer **4b**, in which the H_c–C–P–W dihedral angle is close to 180° and the $^2J(H_c–P)$ coupling close to 0 Hz. The minor *syn* product **4a** on the other hand, in which the H_c–C–P–W dihedral angle is close to 0°, shows a very strong $^2J(H_c–P)$ coupling of 30.7 Hz, as expected [1,2]. As with the iron complexes [2], the $^2J(CH_2–P)$ coupling is higher for the *anti* (12.2 Hz) than for the *syn* isomer (6.3 Hz).

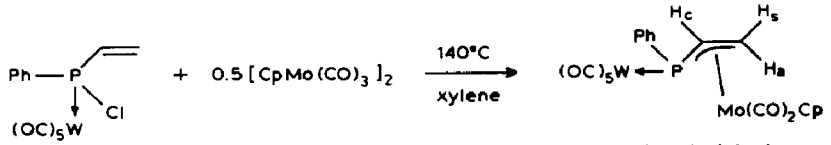
Table 1

Bond distances (Å) and bond angles (°) (Numbers in parentheses are estimated standard deviations in the least significant digits)

W–P	2.5113(7)	O(15)–C(15)	1.153(4)
W–C(16)	2.000(4)	O(16)–C(16)	1.137(5)
W–C(17)	2.021(4)	O(17)–C(17)	1.133(5)
W–C(18)	2.025(4)	O(18)–C(18)	1.128(5)
W–C(19)	2.045(4)	O(19)–C(19)	1.134(5)
W–C(20)	2.037(4)	O(20)–C(20)	1.120(5)
Mo–P	2.5343(8)	C(1)–C(2)	1.397(5)
Mo–C(1)	2.251(3)	C(1)–H(1)	0.89(4)
Mo–C(2)	2.357(3)	C(3)–C(4)	1.398(5)
Mo–C(9)	2.332(4)	C(3)–C(8)	1.392(5)
Mo–C(10)	2.341(5)	C(4)–C(5)	1.376(5)
Mo–C(11)	2.334(5)	C(5)–C(6)	1.363(6)
Mo–C(12)	2.315(4)	C(6)–C(7)	1.379(7)
Mo–C(13)	2.322(4)	C(7)–C(8)	1.383(6)
Mo–C(14)	1.948(5)	C(9)–C(10)	1.331(9)
Mo–C(15)	1.946(4)	C(9)–C(13)	1.391(7)
P–C(1)	1.755(3)	C(10)–C(11)	1.40(1)
P–C(3)	1.811(3)	C(11)–C(12)	1.33(1)
O(14)–C(14)	1.156(5)	C(12)–C(13)	1.367(8)
P–W–C(16)	177.0(1)	P–Mo–C(14)	112.7(1)
P–W–C(17)	89.7(1)	P–Mo–C(15)	72.8(1)
P–W–C(18)	86.5(1)	C(1)–Mo–C(2)	35.2(1)
P–W–C(19)	88.6(1)	C(1)–Mo–C(9)	101.0(2)
P–W–C(20)	92.1(1)	C(1)–Mo–C(10)	86.0(2)
C(16)–W–C(17)	90.6(2)	C(1)–Mo–C(11)	106.0(3)
C(16)–W–C(18)	90.5(2)	C(1)–Mo–C(12)	138.8(2)
C(16)–W–C(19)	91.1(2)	C(1)–Mo–C(13)	135.7(2)
C(16)–W–C(20)	90.9(2)	C(1)–Mo–C(14)	104.1(1)
C(17)–W–C(18)	90.3(2)	C(1)–Mo–C(15)	112.6(1)
C(17)–N–C(19)	178.2(2)	C(2)–Mo–C(9)	99.0(1)
C(17)–W–C(20)	89.4(2)	C(2)–Mo–C(10)	103.2(2)
C(18)–W–C(19)	90.2(2)	C(2)–Mo–C(11)	134.3(3)
C(18)–W–C(20)	178.6(2)	C(2)–Mo–C(12)	155.7(1)
C(19)–W–C(20)	90.1(2)	C(2)–Mo–C(13)	125.8(2)
P–Mo–C(1)	42.51(8)	C(2)–Mo–C(14)	69.9(2)
P–Mo–C(2)	66.84(9)	C(2)–Mo–C(15)	114.2(1)
P–Mo–C(9)	134.4(2)	C(9)–Mo–C(10)	33.1(2)
P–Mo–C(10)	105.2(2)	C(9)–Mo–C(11)	56.8(2)
P–Mo–C(11)	101.1(2)	C(9)–Mo–C(12)	56.7(2)
P–Mo–C(12)	127.1(2)	C(9)–Mo–C(13)	34.8(2)
P–Mo–C(13)	157.8(2)	C(9)–Mo–C(14)	100.7(2)
C(9)–Mo–C(15)	144.9(2)	P–C(1)–C(2)	117.3(2)
C(10)–Mo–C(11)	34.7(3)	P–C(3)–C(4)	119.3(2)
C(10)–Mo–C(12)	56.0(2)	P–C(3)–C(8)	122.1(3)
C(10)–Mo–C(13)	56.3(2)	C(4)–C(3)–C(8)	118.5(3)
C(10)–Mo–C(14)	133.4(3)	C(3)–C(4)–C(5)	120.4(4)
C(10)–Mo–C(15)	136.8(3)	C(4)–C(5)–C(6)	120.9(4)
C(11)–Mo–C(12)	33.3(3)	C(5)–C(6)–C(7)	119.4(4)
C(11)–Mo–C(13)	56.7(2)	C(6)–C(7)–C(8)	120.9(4)
C(11)–Mo–C(14)	145.3(2)	C(3)–C(8)–C(7)	119.8(4)
C(11)–Mo–C(15)	102.2(3)	C(10)–C(9)–C(13)	107.8(5)
C(12)–Mo–C(13)	34.3(2)	C(9)–C(10)–C(11)	109.0(5)
C(12)–Mo–C(14)	113.5(3)	C(10)–C(11)–C(12)	106.5(6)

Table 1 (continued)

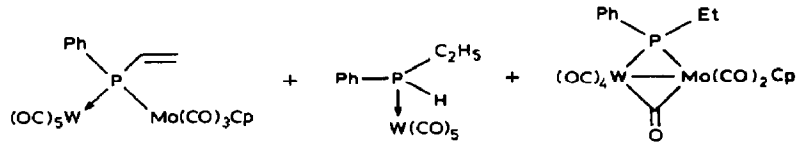
C(12)–Mo–C(15)	89.9(2)	C(11)–C(12)–C(13)	110.2(5)
C(13)–Mo–C(14)	89.5(2)	C(9)–C(13)–C(12)	106.5(5)
C(13)–Mo–C(15)	111.0(2)	Mo–C(14)–O(14)	178.1(4)
C(14)–Mo–C(15)	81.5(2)	Mo–C(15)–O(15)	177.9(3)
W–P–Mo	131.42(3)	W–C(16)–O(16)	177.2(4)
W–P–C(1)	122.3(1)	W–C(17)–O(17)	178.3(4)
W–P–C(3)	117.4(1)	W–C(18)–O(18)	177.4(4)
Mo–P–C(1)	60.1(1)	W–C(19)–O(19)	178.8(4)
Mo–P–C(3)	106.4(1)	W–C(20)–O(20)	178.7(5)
C(1)–P–C(3)	104.7(2)		



(3)

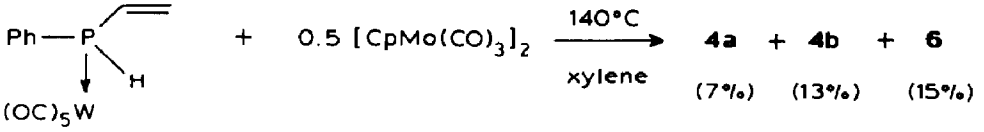
(4a (*syn*) (12%) ;
4b (*anti*) (24%))

(3)



(5 (9%)) (6 (15%)) (7 (7%))

These η^3-phosphaallylmolybdenum complexes can also be obtained from the secondary vinylphosphine complex **8** [3] (eq. 4).



(8) (4)

In this case, the yields of **4a** and **4b** are lower owing to the easier formation of the saturated side-product **6**. The reduction of the vinyl bond of **8** (→ **6**) was also observed with iron [1]. Finally, it must be mentioned that the *syn* and *anti* isomers under rapid equilibration in boiling toluene (equilibrium ratio *anti*/*syn* = 90/10).

The *anti* isomer **4b** crystallizes well and we decided to carry out an X-ray diffraction study, since only *syn* structures have been studied with iron [1]. The overall geometry of the phosphaallyl skeleton appears to be closely similar in the molybdenum and iron cases; P–C(1): 1.755(3) vs. 1.761(5) Å, C(1)–C(2): 1.397(5) vs. 1.380(7) Å, P–C(1)–C(2): 117.3(2) vs. 119.6(4)°. In each case, the carbonyls on

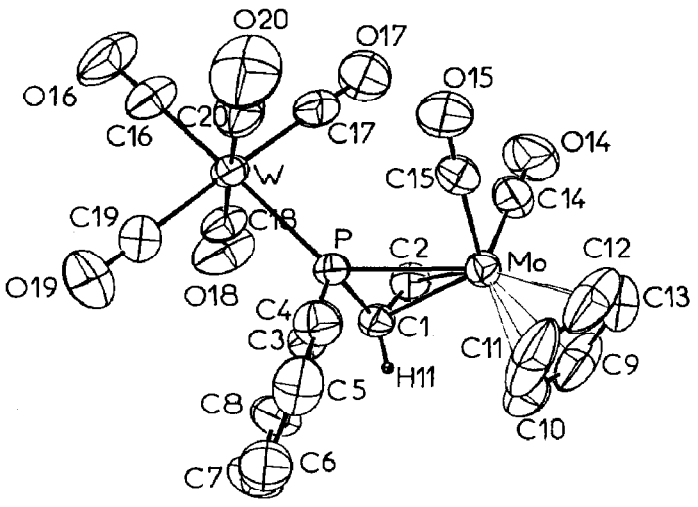


Fig. 1. ORTEP drawing of a molecule of **4b**. Vibrational ellipsoids are drawn to enclose 50% of the electron density. Hydrogen atoms are omitted except for HC(1). Principal bond distances (Å): W–P 2.5113(7), Mo–P 2.5343(8), P–C(1) 1.755(3), P–C(3) 1.811(3), C(1)–C(2) 1.397(5), Mo–C(1) 2.251(3), Mo–C(2) 2.357(3), Mo–C(14) 1.949(5), Mo–C(15) 1.946(4), Mo–C(Cp) 2.315(4) to 2.341(5). Selected bond angles (°): W–P–C(1) 122.3(1), W–P–C(3) 117.4(1), W–P–Mo 131.42(3), C(1)–P–C(3) 104.7(3), C(3)–P–Mo 106.4(1), P–C(1)–C(2) 117.3(2), P–Mo–C(14) 112.7(1), P–Mo–C(15) 72.8(1), C(2)–Mo–C(14) 69.9(2), C(2)–Mo–C(15) 114.2(1), C(14)–C(15) 81.5(2).

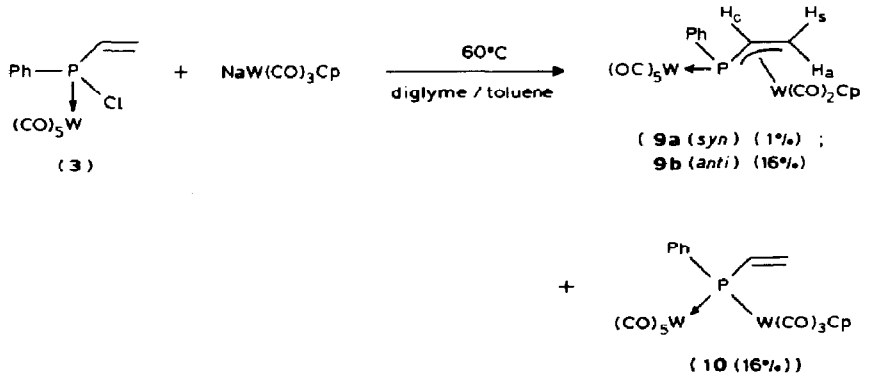
molybdenum or iron are directed towards the inside of the phosphaallyl unit. The molybdenum atom is sandwiched between the phosphaallyl and the cyclopentadienyl planes, at 2.0286 and 2.0197 Å, respectively from these planes. The angle between the two planes is 38.25(0.36)°. The main differences between the molybdenum *anti* and the iron *syn* structures are found at phosphorus. As expected, the H_c–C–P–W dihedral angle is in the present case very large (144.1(3)°), whereas it is very low in the iron derivative (2.0°).

The molybdenum *anti* structure can be related to the iron *syn* structure by interchanging the PPh and $PW(CO)_5$ substituents at phosphorus. In the molybdenum complex, the P–Ph bond lies practically in the plane of the phosphaallyl unit, whereas $W(CO)_5$ is above this plane (opposite to molybdenum). The reverse is found for the *syn* iron structure, as indicated by the following data: C(2)–C(1)–P–W = 178° (Fe), 55.2° (Mo); C(2)–C(1)–P–C(Ph) = 45.6° (Fe), 191.9° (Mo). The other significant data are collected in the caption of Fig. 1 and in Table 1.

We then tried to extend this chemistry to chromium and tungsten. All our experiments with chromium involving treatment of either $NaCr(CO)_3Cp$ or $[CpCr(CO)_3]_2$ with **3** failed. However, we were successful with tungsten, although the yields of η^3-complexes were lower (eq. 5).

No reduction products similar to **6** and **7** were formed, probably because we used a lower temperature. The preference for the *anti* structure appeared to be even stronger then in the case of molybdenum.

This new series of experiments shows that formation of η^3-phosphaallyl complexes can occur with a variety of metallic centres, and that a delicate balance exists between *syn* and *anti* structures, although we are unable, at the moment, to establish what factors determine the relative stabilities of the isomers.



Experimental

All reactions were performed under argon. NMR spectra were recorded on multinuclear WP80 SY and AC 200 SY Bruker spectrometers operating at 80.13 and 200.13 (^{1}H), 20.15 and 50.32 (^{13}C), and 32.44 (^{31}P) MHz; chemical shifts are in ppm downfield from internal TMS (^{1}H and ^{13}C) or external 85% H_3PO_4 (^{31}P), and coupling constants are in Hz. Mass spectra are recorded on a Shimadzu GC-MS QP 1000 instrument at 70 eV under electronic impact. Infrared spectra were obtained with a Perkin–Elmer model 297 spectrometer. Elemental analyses were performed by the Service Central de Microanalyse du CNRS, France.

General data

Chromatographic separations were carried on with silica gel columns (70–230 mesh, Merck). $[CpMo(CO)_3]_2$ was a commercial sample used without further purification. $NaW(CO)_3Cp$ was obtained by reaction of $W(CO)_6$ with NaCp in refluxing diglyme.

Procedure for the synthesis of:

$[\eta^3$-$(OC)_5WPPh(CH{=}CH_2)]Mo(CO)_2Cp$	***(4a,4b)***
$[\eta^1$-$(OC)_5WPPh(CH{=}CH_2)]Mo(CO)_3Cp$	***(5)***
$(OC)_5W[PhPEtH]$	***(6)***
$(OC)_4W[\mu_2$-$PhPEt](\mu_2$-$CO)Mo(CO)_2Cp$	***(7)***

A solution of 2.47 g (5 mmol) of $(OC)_5W[PhP(CH{=}CH_2)Cl]$ in 10 ml of dry xylene was heated under reflux with 1.17 g (2.5 mmol) of $[Mo(CO)_3Cp]_2$ for 1.5 h. After filtration and evaporation of the solution, the residue was chromatographed. Elution with hexane gave 350 mg (15%) of **6**, then with hexane/CH_2Cl_2 (90/10), 240 mg (7%) of **7** are obtained. Further elution with hexane/CH_2Cl_2 (80/20) yielded, first 410 mg (12%) of **4a**, second 320 mg (9%) of **5**, and third 810 mg (24%) of **4b**. Bright yellow crystals of **4b** are readily obtained from hexane/CH_2Cl_2 (50/50).

4a; yellow oil; ^{1}H NMR (C_6D_6): δ 1.30 (m, $^2J(H_a{-}H_s) \cong 2$ Hz, $^3J(H_a{-}H_c) \cong {}^3J(H_a{-}P) \cong 11$ Hz, H_a), 2.46 (m, $^3J(H_s{-}P) = 29.4$, $^3J(H_s{-}H_c) = 8.3$ Hz, H_s), 3.79 (m, $^2J(H_c{-}P) = 30.7$ Hz, H_c), 4.65 (s, Cp), 6.7–7.5 (m, Ph); ^{13}C NMR (C_6D_6): δ

43.76 (d, ^2J(C–P) = 6.3 Hz, CH_2), 59.29 (d, ^{1}J(C–P) = 9.5 Hz, CH), 92.92 (s, Cp), 128.30–132.01 (Ph), 197.44 (d, ^2J(C–P) = 7.5 Hz, *cis* W-CO), 229.52 ($Mo(CO)_2$); ^{31}P NMR (C_6D_6): δ −14.12, $^1J(^{31}P-^{183}W)$ = 239 Hz; IR (decalin): ν(CO) 2070m, 1980m, 1970s, 1945vs, 1930s, 1905m cm^{-1}.

4b: yellow crystals, m.p. 223 °C (dec); ^{1}H NMR (CD_2Cl_2): δ 1.54 (m, $^2J(H_a-H_s)$ = 2.3, $^3J(H_a-H_c)$ = 2.1, $^3J(H_a-P)$ ≃ 12 Hz, H_a), 3.24 (m, $^3J(H_s-P)$ = 41.4, $^3J(H_s-H_c)$ = 8.9 Hz, H_s), 4.87 (m, $^2J(H_c-P)$ ≃ 0 Hz, H_c), 5.10 (s, Cp), 7.3–7.7 (m, Ph); ^{13}C NMR (CD_2Cl_2): δ 41.58 (d, ^2J(C–P) = 12.2 Hz, CH_2), 62.38 (d, ^1J(C–P) = 13.7 Hz, CH), 94.04 (s, Cp), 128.76–129.71 (Ph), 196.74 (d, ^2J(C–P) = 9.6 Hz, *cis* W-CO); ^{31}P NMR (CD_2Cl_2): δ −33.24, $^1J(^{31}P-^{183}W)$ = 246.6 Hz; IR (CH_2Cl_2): ν(CO) 2065m, 1975s, 1945vs cm^{-1}; MS (EI, 70 eV, ^{184}W): *m/z* (relative intensity) 676 (*M*, 31), 480 (*M* − 7CO, 100); Anal. Found: C, 35.47; H, 1.94. $C_{20}H_{13}MoO_7PW$ calc: C, 35.53; H, 1.94%.

5: yellow-brown oil; ^{1}H NMR (C_6D_6): δ 4.45 (d, ^3J(P–H) ≅ 0.5 Hz, Cp), 5.45 (m, $^2J(H_a-H_s)$ = 1.2, $^3J(H_a-H_c)$ = 17.7 Hz, H_a), 5.64 (m, $^3J(H_s-H_c)$ = 11.1 Hz, H_s), 6.46 (m, H_c), 7.0–7.7 (m, Ph); ^{13}C NMR (C_6D_6): δ 94.97 (s, Cp), 126.0 (s, CH_2), 127.5–131.8 (m, Ph), 141.78 (d, ^2J(C–P) = 13.3 Hz, CH), 199.6 (*cis*-W-CO); ^{31}P NMR (C_6D_6): δ −44.68, $^1J(^{31}P-^{183}W)$ = 205.1 Hz; IR (decalin): ν(CO) 2070w, 2030w, 1950m.br, 1940s.br, 1920m,br cm^{-1}; MS (EI, 70 eV, ^{184}W): *m/z* (relative intensity) 677 (*M* − CO + H, 8), 478 (*M* − 8CO − 2H, 100).

6: pale pink oil; ^{1}H NMR (C_6D_6): δ 0.5–0.7 (m, CH_3), 1.4–1.6 (m, CH_2), 5.08 (dm, ^1J(H–P) = 350.5 Hz, PH), 6.9–7.3 (m, Ph); ^{13}C NMR (C_6D_6): δ 11.75 (d, ^2J(C–P) = 4.7 Hz, CH_3), 23.15 (d, ^1J(C–P) = 27.1 Hz, CH_2), 129–134 (m, Ph), 196.66 (d, ^2J(C–P) = 7.2 Hz, *cis* W-CO), 199.45 (d, ^2J(C–P) = 20.2 Hz, *trans*-W-CO); ^{31}P NMR (C_6D_6): δ −21.6, $^1J(^{31}P-^{183}W)$ = 224.6 Hz; IR (decalin): ν(CO) 2070m, 1930–1940s.br cm^{-1}; MS (EI, 70 eV, ^{184}W): *m/z* (relative intensity) 462 (*M*, 23), 320 (M − 5CO − 2H, 100).

7: dark red oil; two isomers are obtained; ^{1}H NMR (C_6D_6): δ 1.0–1.16 (m, CH_3), 2.5–3.5 (m, CH_2), 4.62 and 4.87 (Cp), 6.8–7.8 (m, Ph); ^{13}C NMR (C_6D_6): δ 12.44 and 14.12 (s, CH_3), 32.94 and 35.40 (d, ^1J(C–P) = 23.4 and 27.4 Hz, CH_2), 92.40 and 93.21 (s, Cp), 127.5–143.2 (m, Ph), 198.15 and 198.84 (s, *cis* W-CO); ^{31}P NMR (C_6D_6): δ 180.21 and 180.96, $^1J(^{31}P-^{183}W)$ = 195.3 Hz; IR (decalin): ν(CO) 2070m, 1975m, 1960s.br, 1955s.br, 1880w cm^{-1}; MS (EI, 70 eV, ^{184}W): *m/z* (relative intensity) 678 (*M*, 32), 478 (*M* − 7CO − 2H, 100).

Procedure for the preparation of:

$[\eta^3$-$(OC)_5WPPh(CH=CH_2)]W(CO)_2Cp$ ***(9a,9b)***
$[\eta^1$-$(OC)_5WPPh(CH=CH_2)]W(CO)_3Cp$ ***(10)***

To a solution of $(OC)_5W[PhP(CH=CH_2)Cl]$ (2.97 g, 6 mmol) in 5 ml of dry toluene was added 17 ml of 0.52 *M* $NaW(CO)_3Cp$ (9 mmol) in diglyme. The mixture was kept at 50 °C for 0.5 h and the solvent then removed at 60 °C under vacuum. The crude product was washed with hexane and chromatographed. Elution with hexane/CH_2Cl_2 (80/20) gave 50 mg (1%) of **9a**, then 760 mg (16%) of **10**, and with elution with hexane/CH_2Cl_2 (60/40) finally gave 730 mg of **9b**. **9b** crystallizes very well from hexane/CH_2Cl_2 (50/50).

9a: only mixture of **9a** with **9b** and **10** was available for analyses due to the low yield; ^{1}H NMR (CD_2Cl_2): δ 1.26 (p.t, $^2J(H_a-H_s)$ = 2.9, $^3J(H_a-H_c)$ = 9.8, $^3J(H_a-P)$

$\simeq$ 14 Hz, H_a), 2.89 (d*d*d, $^3J(H_s-H_c) = 8.0$, $^3J(H_s-P) = 30.0$ Hz, H_s), 4.05 (d*d*d, $^2J(H_c-P) = 29.4$ Hz, H_c), 5.59 (s, Cp), 7.2–7.7 (m, Ph); ^{13}C NMR (CD_2Cl_2): δ 92.3 (s, Cp), 128–132 (m, Ph); ^{31}P NMR (CD_2Cl_2): δ −42.57; IR (decalin) 2070m, 1975m, 1945s cm^{-1}.

9b: yellow bright crystals, slightly soluble in CD_2Cl_2, m.p. 232°C (dec); ^{1}H NMR (CD_2Cl_2): δ 1.56 (p.t, $^2J(H_a-H_s) = 2.9$, $^3J(H_a-H_c) \cong 9$, $^3J(H_a-P) \cong 11.3$ Hz, H_a), 2.99 (d*d*d, $^3J(H_s-H_c) = 8.6$, $^3J(H_s-P) = 41.8$ Hz, H_s), 4.42 (p.t, $^2J(H_c-P) =$ 2.3 Hz, H_c), 5.22 (s, Cp), 7.2–7.7 (m, Ph); ^{13}C NMR (CD_2Cl_2): $\delta \cong 32$ (CH_2), $\cong 53$ (CH), 92.8 (s, Cp), 128.8–129.6 (m, Ph), 196.8 (d, $^2J(C-P) = 7.6$ Hz, *cis* $W(CO)_5$); ^{31}P NMR (CD_2Cl_2): δ −64.17 ($^1J(^{31}P-^{183}W) = 244.1$ Hz, $W(CO)_5$), $^1J(^{31}P-^{183}W)$ $\cong 37$ Hz, $W(CO)_2$); IR (CH_2Cl_2): ν(CO) 2070m, 1990w, 1975m, 1945s cm^{-1}; MS (EI, 70 eV, ^{184}W): m/z (relative intensity) 763 ($M-H$, 10), 283 (100); Anal. Found: C, 31.50; H, 1.87. $C_{20}H_{13}O_7PW_2$ calc: C, 31.44; H, 1.71%.

Table 2

Positional parameters and their estimated standard deviations [a]

Atom	x	y	z	B (Å^2)
W	0.30307(1)	0.25292(1)	0.64419(1)	3.309(2)
Mo	0.11352(3)	0.57213(3)	0.80905	3.343(5)
P	0.29232(8)	0.50562(7)	0.71522(5)	2.93(1)
C(14)	−0.2011(4)	0.2949(4)	0.7664(3)	7.53(9)
O(15)	0.2370(4)	0.3740(3)	0.9283(2)	6.72(7)
O(16)	0.3037(4)	−0.0633(3)	0.5395(3)	9.0(1)
O(17)	−0.0022(4)	0.0850(4)	0.7017(3)	8.0(1)
O(18)	0.0966(4)	0.2426(4)	0.4236(2)	7.75(9)
O(19)	0.6119(4)	0.4376(4)	0.5925(3)	8.2(1)
C(20)	0.5025(4)	0.2679(4)	0.8693(3)	9.7(1)
C(1)	0.1515(3)	0.5599(3)	0.6486(2)	3.35(6)
C(2)	−0.0047(4)	0.4594(4)	0.6241(3)	4.03(7)
C(3)	0.4728(3)	0.6770(3)	0.7581(2)	3.40(6)
C(4)	0.5780(4)	0.7144(4)	0.8588(3)	4.20(7)
C(5)	0.7144(4)	0.8456(4)	0.8939(3)	4.99(9)
C(6)	0.7519(4)	0.9391(4)	0.8308(4)	5.4(1)
C(7)	0.6508(5)	0.9022(4)	0.7300(3)	5.9(1)
C(8)	0.5118(4)	0.7722(4)	0.6932(3)	4.72(8)
C(9)	0.0347(5)	0.7738(4)	0.8294(3)	7.0(1)
C(10)	0.1814(7)	0.8347(5)	0.8281(4)	9.0(1)
C(11)	0.2781(6)	0.8215(6)	0.9162(5)	9.5(1)
C(12)	0.1864(6)	0.7542(5)	0.9702(4)	8.0(1)
C(13)	0.0348(5)	0.7221(5)	0.9196(3)	6.9(1)
C(14)	−0.0835(4)	0.3968(4)	0.7808(3)	5.09(9)
C(15)	0.1926(4)	0.4474(4)	0.8826(3)	4.59(7)
C(16)	0.3057(5)	0.0514(4)	0.5799(4)	5.7(1)
C(17)	0.1073(4)	0.1430(4)	0.6802(3)	4.93(9)
C(18)	0.1729(4)	0.2458(4)	0.5013(3)	4.58(8)
C(19)	0.5023(4)	0.3704(4)	0.6111(3)	5.13(9)
C(20)	0.4327(5)	0.2644(5)	0.7896(3)	5.74(9)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
$(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

10: yellow solid, m.p. 145°C; ^{1}H NMR (CD_2Cl_2): δ 5.4 (s, Cp), 5.7 (m, $^2J(H_a-H_s) \cong 1$ Hz, $^3J(H_a-H_c) = 17.3$ Hz, H_a), 5.8 (m, $^3J(H_s-H_c) = 11.5$ Hz, H_s), 6.6 (m, $^2J(H_c-P) \cong 17.3$ Hz, H_c), 7.1–7.7 (m, Ph); ^{13}C NMR (CD_2Cl_2): δ 94.3 (s, Cp), 127.0 (s, CH_2), 128.5–131.3 (m, Ph), 141.3 (d, $^1J(C-P) = 16.0$ Hz, CH), 199.7 (d, $^2J(C-P) = 5.3$ Hz, *cis* $W(CO)_5$), 201.9 (d, $^2J(C-P) = 20.0$ Hz, *trans* $W(CO)_5$), 216.7–220.8 ($W(CO)_3$); ^{31}P NMR (CD_2Cl_2): δ −75.09 ($^1J(^{31}P-^{183}W) = 210.0$ Hz, $W(CO)_5$), ($^1J(^{31}P-^{183}W) = 90.3$ Hz, $W(CO)_3$); IR (decalin): ν(CO) 2070w, 2020w, 1975w, 1945–1935s, 1930–1910s cm^{-1}; MS (EI, 70 eV, ^{184}W): *m/z* (relative intensity) 792 (*M*, 2), 283 (100); Anal. Found: C, 32.09; H, 1.92. $C_{21}H_{13}O_8PW_2$ calc: C, 31.85; H, 1.65%.

X-Ray data collection and processing

Crystals of complex **4b** are triclinic, space group $P\bar{1}$ with cell parameters *a* 9.653(1), *b* 9.699(1), *c* 13.417(2) Å, α 100.42(2), β 102.51(2), γ 110.93(2)°, *V* 1098.5(8) Å^3, $Z = 2$, d_c 1.86 g cm^{-3}. A crystal fragment having dimensions of $0.3 \times 0.2 \times 0.16$ mm was used for collection of intensity data on a Enraf–Nonius CAD4 diffractometer. Data were collected at room temperature in the $\theta/2\theta$ scan mode with Mo-K_α. A total of 6402 reflections were measured in the range $1 < \theta < 30$ degrees; of 5047 had $\sigma I > 3\sigma(I)$, and were used in all subsequent calculations. The crystal structure was determined by use of the Enraf–Nonius SDP structure determination package used with a Digital Equipment Micro-Vax II computer. All heavy atoms were refined using anisotropic temperature factors. Most hydrogen atom positions were determined from a final difference Fourier map and were assigned a fixed isotropic thermal parameter equal to 1.3 times the equivalent *B* of the attached carbon atom. The cyclopentadienyl hydrogen atoms were introduced at fixed positions and not refined. An extinction coefficient was included in the final least-squares cycles and converged to a value of 2.38(3)E − 7. The least-squares refinement converged to $Rf = 0.021$, $Rwf = 0.029$, unit weight agreement factor = 1.08, with $p = 0.04$ in $\sigma^2(F^2) = \sigma^2\text{counts} + (pI)^2$.

Positional parameters are collected in Table 2.

Supplementary material

Tables of positional parameters for hydrogens, thermal displacement parameters for heavy atoms, observed and computed structure factor amplitudes can be obtained from the authors.

References

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