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## Heterobimetallic group 6 rhodium complexes

### I. Formation of tribridged derivatives

$[(OC)_3M(\mu-Cl)(\mu-CO)(\mu-dppm)Rh(NBD)]$  ( $M = Mo, W$ )  
 by ring opening of  $[(OC)_4M(dppm-PP)]$ . Crystal structure  
 of  $[(OC)_3Mo(\mu-Cl)(\mu-CO)(\mu-dppm)Rh(NBD)]$

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#### Abstract

Heterobimetallic complexes of the type  $[(OC)_3M(\mu-Cl)(\mu-CO)(\mu-dppm)Rh(NBD)]$  ( $M = Mo, W$ ,  $dppm = Ph_2PCH_2PPh_2$ ) have been prepared in high yield by ring opening of the co-ordinatively saturated compound  $[(OC)_4M(dppm-PP)]$  with the dimeric complex  $[RhCl(NBD)]_2$  in dichloromethane, and an X-ray diffraction study of the molybdenum derivative has been carried out. The Mo–Rh bond length, 2.945 Å, is consistent with the presence of a single Mo–Rh bond. Additionally, the two metal centres are asymmetrically bridged by  $dppm$ , carbonyl and chloride ligands. Different behaviour in solution is proposed for the compounds. The new compounds were characterized by elemental analysis, and infrared and  $^1H$ -,  $^{31}P$ - and  $^{13}C$ -NMR spectroscopy.

#### Introduction

Heterobimetallic complexes are of much current interest because of the catalytic potential of such bifunctional systems. Complexes containing constraining ligands such as  $Ph_2PCH_2PPh_2$  (bis(diphenylphosphino)methane,  $dppm$ ) are of special interest since proximity effects involved in bridging behaviour can be used to favour formation of the metal–metal bond [1].

The diphosphine ligand  $dppm$  can act as a chelating ligand to give four-membered rings but is particularly important as a bridging group. It has been reported that ring opening of the four-membered rings in some  $\eta^2-Ph_2PCH_2PPh_2$  complexes of metals with  $d^8$ -electron configuration provides an excellent method of producing

bimetallic systems containing  $M(\mu\text{-dppm})_2M'$  moieties, where M denotes  $\text{Pt}^{\text{II}}$ ,  $\text{Pd}^{\text{II}}$ ,  $\text{Ir}^{\text{II}}$ , or  $\text{Rh}^{\text{I}}$  and  $M'$  one of a variety of metals. Many examples of this type, in a variety of stereochemistries, are known [2–7]. In contrast, there are very few bimetallic complexes containing a single bridging dppm ligand, and most of these are homobimetallic species. It is noteworthy that, except  $[(\text{OC})_4\text{Fe}(\mu\text{-dppm})\text{Fe}(\text{OC})_4]$ , they all contain a metal–metal bond and at least one strongly bridging ligand in addition to dppm.

We reasoned that the known, co-ordinatively saturated compounds  $[(\text{OC})_4M(\text{dppm-PP})]$  ( $M = \text{Mo}, \text{W}$ ) might be useful in the synthesis of heterobimetallic compounds containing only one dppm ligand. If the  $[(\text{OC})_4M(\text{dppm-PP})]$  coordinated to a second metal by opening of four-membered chelate ring then ( $\eta^2\text{-dppm-M}$ ) should form a metal–metal bond and other bridging ligands might also be formed.

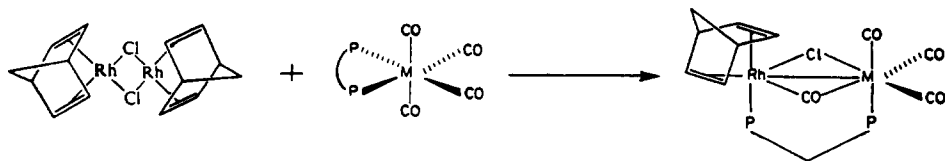
With these considerations in mind, we examined the possibility synthesizing  $\text{Rh-M}$  ( $M = \text{Mo}, \text{W}$ ) complexes containing bridged ligands such as dppm or carbonyl chloride. In our approach we employed the  $[(\text{NBD})\text{Rh-Cl}]$  fragment to coordinate to a phosphorus atom made available by ring opening of  $[(\text{OC})_4M(\text{dppm-PP})]$ . A bridged chloride and a metal–metal bond are required to complete a saturated 18-electron configuration around each metal. This approach proved successful, and we report here two new rhodium–metal bonded complexes  $[(\text{OC})_3M(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})\text{Rh}(\text{NBD})]$  [ $M = \text{Mo}$  (1),  $\text{W}$  (2)] in which the carbonyl group provides an additional bridge.

## Results and discussion

Treatment of  $[(\text{OC})_4M(\text{dppm-PP})]$  ( $M = \text{Mo}, \text{W}$ , dppm = bis(diphenylphosphine)methane) with  $[\text{RhCl}(\text{NBD})]_2$  in dichloromethane for 3 h gave the complexes  $[(\text{OC})_3M(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})\text{Rh}(\text{NBD})]$  in > 80% yield (Scheme 1); the products were characterized by elemental analysis, IR and  $^1\text{H}$ -,  $^{31}\text{P}$ - and  $^{13}\text{C}$ -NMR spectroscopy, and Table 1 summarizes some of the data. The complexes are orange solids, non-electrolytes in acetone, and stable in air in the solid state. The high stability of the tungsten derivative in the solid state and solution was somewhat unexpected.

The IR spectra of the solids exhibit four very strong  $\nu(\text{CO})$  bands, consistent with the presence of tetracarbonyl derivatives. In both cases the lowest frequencies ( $< 1800 \text{ cm}^{-1}$ ) indicate that the complexes have a semi-bridging carbonyl structure, by analogy with previously characterized species such as  $[(\text{OC})_3\text{Mo}(\mu\text{-dppm})_2\text{Rh}(\text{CO})\text{Br}]$  [8] and  $[(\text{OC})_3\text{W}(\mu\text{-dppm})_2\text{Rh}(\text{CO})\text{Cl}]$  [9].

Surprisingly the IR spectra (in  $\text{CH}_2\text{Cl}_2$  solution) showed the absence of bands at lower frequency than  $1800 \text{ cm}^{-1}$  suggesting that no bridging carbonyls are present;



Scheme 1.  $M = \text{Mo}, \text{W}$ ;  $\widehat{\text{PP}} = \text{dppm}$ .

Table 1  
 $^1\text{H}$ -,  $^3\text{P}$ ( $^1\text{H}$ )-,  $^{13}\text{C}$ ( $^1\text{H}$ )-NMR and infrared data

IR	$\nu(\text{CO})$ ( $\text{cm}^{-1}$ )	$[(\text{OC})_3\text{W}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})\text{Rh}(\text{NBD})]$	$[(\text{OC})_3\text{Mo}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})\text{Rh}(\text{NBD})]$
CO		2000vs 1925vs 1870vs 1780vs <sup>a</sup> 1985vs 1900vs 1855vs 1800vs <sup>b</sup> 1310m	2005vs 1930vs 1875vs 1790vs <sup>a</sup> 1990vs 1910vs 1865vs 1810vs <sup>b</sup> 1310m
NBD	$\beta(\text{CH})$ ( $\text{cm}^{-1}$ )		
NBD	$\delta$ (ppm)	3.82 (m, $\geq$ C-H), 3.65 (m, $\geq$ C-H), 1.28 (m, $\gt$ CH <sub>2</sub> ) <sup>c</sup>	3.81 (m, $\geq$ C-H), 3.63 (m, $\geq$ C-H), 1.40 (m, $\gt$ CH <sub>2</sub> ) <sup>d</sup>
dppm	$\delta$ (ppm)	2.87 (t, CH <sub>2</sub> ), 7.00–7.42 (m, C <sub>4</sub> H <sub>5</sub> )	2.82 (t, CH <sub>2</sub> ), 7.19–7.44 (m, C <sub>6</sub> H <sub>5</sub> )
	$J$ (Hz)	<sup>2</sup> $J(\text{HP}) = 10.6$	<sup>2</sup> $J(\text{HP}) = 10.5$
dppm	$\delta$ (ppm)	11.9 (d, P <sub>A</sub> ), 35.9 (dd, P <sub>B</sub> ) <sup>c</sup>	22.1 (d, P <sub>A</sub> ), 33.6 (dd, P <sub>B</sub> ) <sup>c</sup>
	$J$ (Hz)	<sup>2</sup> $J(\text{P}_A\text{P}_B) = 75.1$ , <sup>1</sup> $J(\text{P}_B\text{Rh}) = 160.0$ , <sup>1</sup> $J(\text{P}_A\text{W}) = 233.0$	<sup>2</sup> $J(\text{P}_A\text{P}_B) = 76.9$ , <sup>1</sup> $J(\text{P}_B\text{Rh}) = 157.5$
NBD	$\delta$ (ppm)	61.8(d, C5, C6, C7, C8), 61.1 (m, C9, C10), 47.6 (s, C11) <sup>c</sup>	
	$J$ (Hz)	<sup>1</sup> $J(\text{CRh}) = 5.4$	
dppm	$\delta$ (ppm)	21.7 (dd, CH <sub>2</sub> )	
	$J$ (Hz)	<sup>1</sup> $J(\text{CP}_B) = 22.5$ , <sup>1</sup> $J(\text{CP}_A) = 12.6$	
CO	$\delta$ (ppm)	206.1 (d, C4), 207.4 (d, C1, C3), 211.9 (s, C2)	
	$J$ (Hz)	<sup>2</sup> $J(\text{C}_{trans}\text{P}_A) = 44.2$ , <sup>2</sup> $J(\text{C}_{cis}\text{P}_A) = 3.9$	

<sup>a</sup> Measured as KBr discs. <sup>b</sup> In dichloromethane solution. <sup>c</sup> In CDCl<sub>3</sub> at room temperature. <sup>d</sup> In CD<sub>2</sub>Cl<sub>2</sub> at room temperature. <sup>e</sup> In CD<sub>2</sub>Cl<sub>2</sub> at  $-20^\circ\text{C}$ .

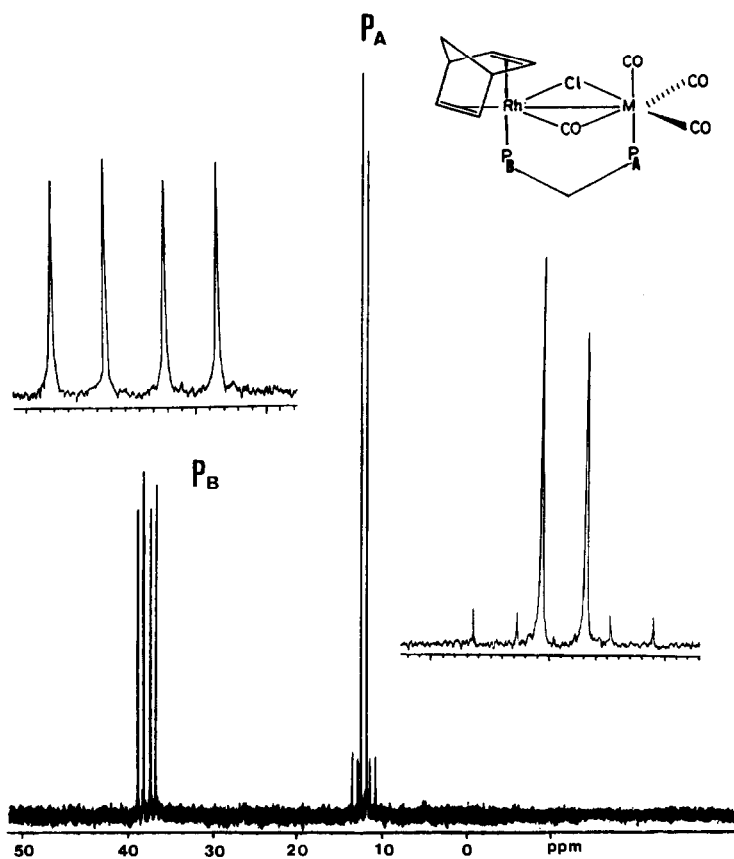


Fig. 1.  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum (121.42 MHz) of  $[(\text{OC})_3\text{W}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})\text{Rh}(\text{NBD})]$  (1) in  $\text{CDCl}_3$  at room temperature.

however, the other three carbonyl bands appear at slightly lower frequencies than in the solid state. This indicates that the semi-bridging carbonyl structure disappears in solution. No  $\nu(\text{RhCl})$  bands are observed in the far-IR region, presumably because of their low intensity; metal-halogen stretching vibrations are commonly of low intensity in heterobimetallic systems containing dppm [9].

The  $^{31}\text{P}$ -NMR spectrum of a  $\text{CD}_2\text{Cl}_2$  solution of **1** at  $-20^\circ\text{C}$  shows resonances at  $\delta$  33.6 ppm as a doublet of doublets for the phosphorus atom bonded to the rhodium atom P<sub>B</sub> ( $^1J(\text{P}_B\text{Rh}) = 157.5$  Hz) and a doublet at  $\delta$  22.1 ppm for the other phosphorus atom bonded to the molybdenum metal P<sub>A</sub>, confirming the bridging nature of the dppm ligand. The same conclusions are reached for the tungsten derivative **2** in which the same splitting pattern was observed (35.9 ppm dd, 11.9 ppm.d;  $^1J(\text{P}_A\text{Rh}) = 160.0$  Hz). In this case the satellites due to the phosphorus A-tungsten coupling ( $^1J(\text{P}_A\text{W}) = 233.0$  Hz) are also observed (Fig. 1). The relative coordination shifts are consistent with the nature of the metals, i.e. Mo (43.8) > W (33.6).

The  $^1\text{H}$ -NMR spectra show a triplet for the  $\text{PCH}_2\text{P}$  protons at 2.82 ppm ( $M = \text{Mo}$ ) and 2.87 ppm ( $M = \text{W}$ ). This is attributed to the coupling of the two

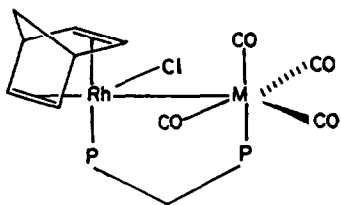


Fig. 2. Proposed molecular rearrangement for the complexes 1 and 2 in solution.

equivalent methylene protons with the phosphorus atoms. The equivalence of the methylene protons of the dppm ligand was previously observed for many complexes containing  $M(\text{dppm})_xM'$  moieties, and Shaw and his colleagues suggest a rapid "flipping" of the MPCM' ring to explain this effect [9–11]. We suggest that the  $\text{PCH}_2\text{P}$  protons in our complexes are rendered equivalent in this way. Presence of a bridging chloride is thought to be unlikely because this would be expected to render the  $\text{PCH}_2\text{P}$  protons inequivalent at room or moderately low temperature, and we take this to show that  $M \cdots \text{Cl}$  interaction is at best weak.

The signals corresponding to the norbornadiene ligand and the phenyl groups of the dppm ligand are also present (Table 1).

The  $^{13}\text{C}$ -NMR spectrum of 2 shows three  $\delta_{\text{C}}$  signals (211.9, s; 207.4, d; 206.1, d), consistent with the presence of three types of carbonyl ligands. The signal at highest field is attributed to the carbon atom of carbonyl group *trans* to the W-bonded  $\text{P}_A$  ( $^2J(\text{CP}_A) = 44.2$  Hz), and the two *cis* carbonyl groups show a signal at 207.4 ppm ( $^2J(\text{CP}_A) = 3.9$  Hz). The signal which appears as a singlet at lowest field is attributed to the carbonyl group directed towards the rhodium atom, which has a semi-bridged nature in the solid state as shown by the crystal structure determination. The low stability of the related molybdenum complex prevented recording of a good  $^{13}\text{C}$ -NMR spectrum.

In the light of the above data, considered together with the assumption that the presence of bridging ligands such as CO or Cl between Mo and Rh atoms would involve non-equivalence of the methylene protons, we propose for the complex in solution the structure depicted in Fig. 2. In this structure the 34-electron configuration could be attained if the basic 16-electron rhodium(I) complex donates a pair of electrons to the 16-electron molybdenum complex to produce an 18-electron configuration through a donor–acceptor metal–metal bond. The ability of  $\text{Rh}^{\text{I}}$  complexes to act as Lewis bases is well documented [12], and single dative interactions between metals have been proposed for a number of bimetallic complexes [13–15]. However the situation may be different in the solid state, and so we determined the crystal structure of complex  $[(\text{OC})_3\text{Mo}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})\text{Rh}(\text{NBD})]$  (1). The complex was crystallized from dichloromethane–hexane (1 : 3). Its structure is shown in Fig. 3 [16], and selected interatomic distances and angles are listed in Table 2. The molybdenum and rhodium moieties are linked by the dppm, carbonyl, and chloride bridges. The  $\text{Mo}\text{-Cl}\text{-CO}\text{-Rh}$  ring has an almost planar structure. Related complexes containing group 6 metals, specifically  $[(\text{OC})_4\text{Mo}(\mu\text{-PEt}_2)_2]_2$ , have planar  $\text{Mo}\text{-P}\text{-P}\text{-Mo}$  rings [18]. The  $\text{Mo}\text{-Rh}$  length (2.945(4) Å) is less than the average  $\text{Mo}\text{-Rh}$  bond length in the complex  $[(\text{C}_5\text{Me}_5)(\text{CH}_3)\text{Rh}(\mu\text{-PMe}_2)_2\text{Mo}(\text{CO})_3\text{I}]$  (2.957(1) Å) [18], and is in the range proposed for a single  $\text{Mo}\text{-Rh}$  bond (2.59–2.96 Å) [8]. Another interesting feature of the structure is that one of the carbonyl

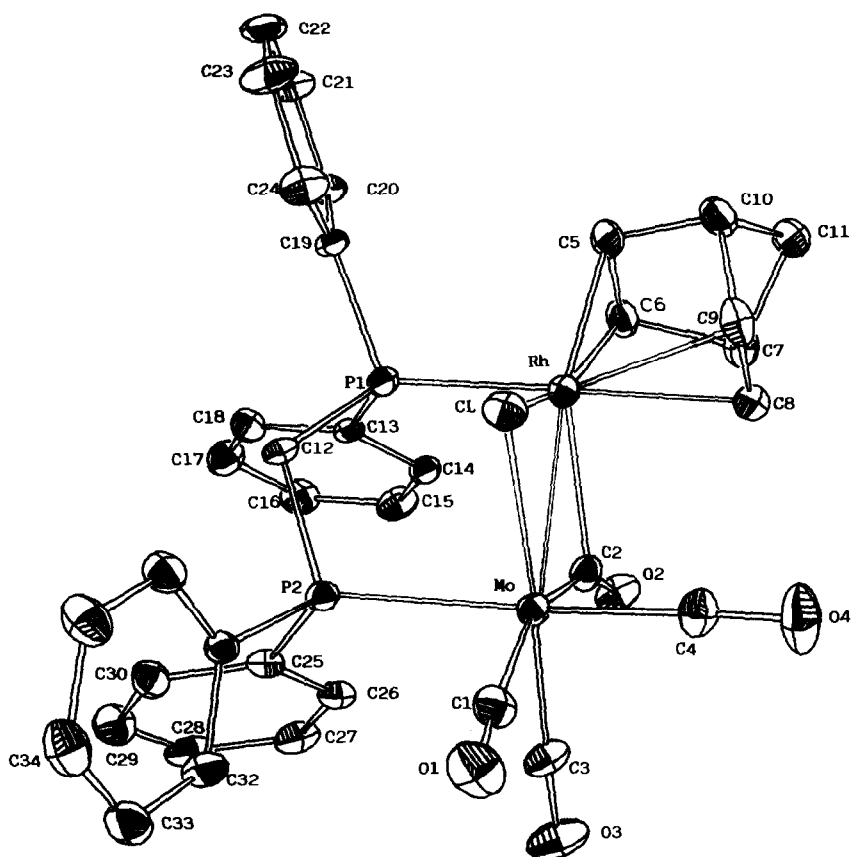


Fig. 3. Molecular structure of  $[(OC)_3Mo(\mu-Cl)(\mu-CO)(\mu-dppm)Rh(NBD)]$  (1) showing the principal atomic numbering.

ligands, C(2)-O(2), of the Mo atom is directed towards the Rh atom along the Rh-Mo bond. The bond length Rh-C(2) (2.343(10) Å) is larger than that in the homonuclear dirhodium complexes (1.956–2.054 Å) and slightly larger than that assigned to semibridging CO groups (2.200(7) Å) in some CrRh and MnRh species [13,14]. The Mo-C(2) bond length (2.070(10) Å) is close to those for CO bridging systems involving Mo atoms [19,20]. The values of the angles Mo-C(2)-O(2) (155.1(9)°) and Rh-C(2)-O(2) (121.2(8)°) indicate that the C(2)-O(2) ligand is bent with respect to the molybdenum and rhodium atoms.

In the complex both metal centres show some distortion from idealized geometries. The  $(OC)_4MoClP$  unit has a distorted octahedral geometry, sharing an edge with the trigonal-bipyramidal geometry observed in the  $RhCl(CO)(NBD)$  unit. The Mo-Rh bond is directed towards the middle of this shared edge.

## Experimental

The NMR spectra were recorded on Varian XL-300 and Bruker 300 spectrometers with  $(CH_3)_4Si$  as internal standard for  $^1H$  and 85% phosphoric acid as external

Table 2

Bond distances (Å) and angles (°), with e.s.d.'s in parentheses, for [(OC)<sub>3</sub>Mo(μ-Cl)(μ-CO)(μ-dppm)Rh(NBD)] (1)

Rh-Mo	2.945(4)	C(7)-C(11)	1.53(2)
Rh-P(1)	2.989(3)	C(8)-C(9)	1.37(2)
Rh-Cl	2.529(3)	C(9)-C(10)	1.52(2)
Rh-C(2)	2.34(1)	C(10)-C(11)	1.55(2)
Rh-C(5)	2.10(1)	C(13)-C(14)	1.40(1)
Rh-C(6)	2.09(1)	C(13)-C(18)	1.37(1)
Rh-C(8)	2.30(1)	C(14)-C(15)	1.38(1)
Rh-C(9)	2.31(1)	C(15)-C(16)	1.39(2)
Mo-P(2)	2.517(2)	C(16)-C(17)	1.38(2)
Mo-Cl	2.578(5)	C(17)-C(18)	1.37(2)
Mo-C(1)	2.04(1)	C(19)-C(20)	1.39(2)
Mo-C(2)	2.07(1)	C(19)-C(24)	1.39(1)
Mo-C(3)	1.95(1)	C(20)-C(21)	1.38(2)
Mo-C(4)	1.96(1)	C(21)-C(22)	1.37(2)
P(1)-C(12)	1.84(1)	C(22)-C(23)	1.37(2)
P(1)-C(13)	1.84(1)	C(23)-C(24)	1.39(2)
P(1)-C(19)	1.82(1)	C(25)-C(26)	1.38(1)
P(2)-C(12)	1.83(1)	C(25)-C(30)	1.39(1)
P(2)-C(25)	1.82(1)	C(26)-C(27)	1.39(1)
P(2)-C(31)	1.82(1)	C(27)-C(28)	1.37(2)
C(1)-O(2)	1.14(2)	C(27)-C(28)	1.37(2)
C(2)-O(2)	1.14(1)	C(29)-C(30)	1.38(1)
C(3)-O(3)	1.15(1)	C(31)-C(32)	1.38(1)
C(4)-O(4)	1.16(1)	C(31)-C(36)	1.38(1)
C(5)-C(6)	1.39(1)	C(32)-C(33)	1.39(2)
C(5)-C(10)	1.51(2)	C(33)-C(34)	1.38(2)
C(6)-C(7)	1.54(1)	C(34)-C(35)	1.35(2)
C(6)-C(8)	1.51(2)	C(35)-C(36)	1.38(2)
C(8)-Rh-C(9)	34.5(4)	C(3)-Mo-C(4)	91.1(5)
C(6)-Rh-C(9)	76.7(4)	C(2)-Mo-C(4)	87.6(4)
C(6)-Rh-C(8)	65.1(4)	C(2)-Mo-C(3)	77.7(4)
C(5)-Rh-C(9)	63.6(4)	C(1)-Mo-C(4)	87.9(5)
C(5)-Rh-C(8)	76.0(4)	C(1)-Mo-C(3)	83.4(5)
C(5)-Rh-C(6)	38.8(5)	C(1)-Mo-C(2)	160.5(5)
C(2)-Rh-C(9)	108.1(4)	Cl-Mo-C(4)	90.4(4)
C(2)-Rh-C(8)	78.5(4)	Cl-Mo-C(3)	175.9(3)
C(2)-Rh-C(6)	101.2(4)	Cl-Mo-C(2)	106.2(4)
C(2)-Rh-C(5)	139.3(4)	Cl-Mo-C(1)	92.9(4)
Cl-Rh-C(9)	88.9(3)	P(2)-Mo-C(4)	174.3(4)
Cl-Rh-C(8)	111.5(3)	P(2)-Mo-C(3)	93.5(4)
Cl-Rh-C(6)	157.4(4)	P(2)-Mo-C(2)	96.6(3)
Cl-Rh-C(5)	118.9(3)	P(2)-Mo-C(1)	89.4(3)
Cl-Rh-C(2)	99.8(3)	P(2)-Mo-Cl	84.9(1)
P(1)-Rh-C(9)	155.9(4)	Rh-P(1)-C(19)	112.1(3)
P(1)-Rh-C(8)	158.6(3)	Rh-P(1)-C(13)	119.7(3)
P(1)-Rh-C(6)	96.4(3)	C(13)-P(1)-C(19)	103.2(5)
P(1)-Rh-C(5)	96.4(3)	C(12)-P(1)-C(19)	102.0(4)
P(1)-Rh-C(2)	95.9(3)	C(12)-P(1)-C(13)	103.6(4)
P(1)-Rh-Cl	89.8(1)	Mo-P(2)-C(3)	111.9(3)
Mo-Rh-C(9)	106.1(3)	Mo-P(2)-C(25)	122.7(3)
Mo-Rh-C(8)	97.1(3)	Mo-P(2)-C(12)	111.2(3)
Mo-Rh-C(6)	145.1(3)	C(25)-P(2)-C(31)	102.2(5)

Table 2 (continued)

Mo–Rh–C(5)	169.3(3)	C(12)–P(2)–C(31)	104.0(5)
Mo–Rh–C(2)	44.3(3)	C(12)–P(2)–C(25)	102.9(5)
Mo–Rh–Cl	55.6(1)	Rh–Cl–Mo	74.0(1)
Mo–Rh–P(1)	92.8(1)	Mo–C(1)–O(1)	176.8(9)
Rh–Mo–C(4)	90.4(4)	Rh–C(2)–Mo	83.5(4)
Rh–Mo–C(3)	129.8(3)	Mo–C(2)–O(2)	155.1(9)
Rh–Mo–C(2)	52.2(3)	Rh–C(2)–O(2)	121.2(8)
Rh–Mo–C(1)	146.8(4)	Mo–C(3)–O(3)	175.7(9)
Rh–Mo–Cl	54.0(1)	Mo–C(4)–O(4)	177(2)
Rh–Mo–P(2)	89.2(1)		

standard for  $^{31}\text{P}$ . IR spectra were recorded on a Perkin Elmer 1300 spectrophotometer. Analyses (C,H,N) were performed by Elemental Micro-Analysis Ltd. Laboratories, Devon, England. All reactions were carried out under oxygen-free dry nitrogen. Analytical grade solvents were used. Previously described methods were used to prepare  $[(\text{OC})_4\text{M}(\text{dppm-PP})]$  [21] and  $[\text{RhCl}(\text{NBD})]$  [22].

#### Preparation of $[(\text{OC})_3\text{Mo}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})\text{Rh}(\text{NBD})]$ (1)

A dichloromethane solution (5 cm<sup>3</sup>) of  $[(\text{OC})_4\text{M}(\text{dppm-PP})]$  (154.1 mg, 0.260 mmol) was added to one of  $[\text{RhCl}(\text{NBD})]_2$  (60 mg, 0.130 mmol) in the same solvent (5 cm<sup>3</sup>), at  $-20^\circ\text{C}$ . The colour of the solution turned from yellow to orange after 15 min of reaction. After 3 h at  $-20^\circ\text{C}$  the mixture was concentrated (5 cm<sup>3</sup>) under reduced pressure. Hexane (20 cm<sup>3</sup>) was then added to precipitate an orange solid, which was filtered off and dried *in vacuo* to give a yield of 82%. The product was recrystallized from dichloromethane–hexane as orange crystals. (Found: C, 52.21; H, 3.76%.  $\text{C}_{36}\text{ClH}_{30}\text{MoO}_4\text{P}_2\text{Rh}$  calc.: C, 52.51; H, 3.64%.)

The Rh–W complex **2** was prepared by a similar procedure at room temperature in 85% yield. (Found: C, 47.02; H, 3.35%.  $\text{C}_{36}\text{ClH}_{30}\text{O}_4\text{P}_2\text{RhW}$  calc.: C, 47.43; H, 3.29%.)

#### Crystallographic studies

An orange prismatic crystal of  $0.2 \times 0.2 \times 0.3$  nm was mounted in a Nonius CAD4 diffractometer. The cell dimensions were refined by least-squares fitting of the  $\theta$  values of 25 reflections.

*Crystal data.*  $\text{C}_{36}\text{ClH}_{30}\text{MoO}_4\text{P}_2\text{Rh}$ ,  $M = 822.56$ , monoclinic,  $a$  14.11(1),  $b$  9.805(3),  $c$  24.29(4) Å,  $\beta$  100.6(3)°,  $U$  3297(6) Å<sup>3</sup>,  $Z = 4$ ,  $D_c$  1.66 g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha)$  10.79 cm<sup>-1</sup>,  $F(000) = 1648$ , space group  $P2_1/c$ ,  $T$  295 K,  $R = 0.041$  for 2959 observed reflections.

*Data collection.* Intensities of 6183 unique reflections with  $1^\circ < \theta < 25^\circ$ ,  $h, k, l - 16, 0, 0$  to 16, 11, 28 were measured at 295 K with monochromatic Mo- $K_\alpha$  radiation ( $\lambda$  0.71069 Å) and a  $\omega/2\theta$  scan technique; three reflexions monitored periodically during data collection showed no decays; the intensities were corrected for Lorentz and polarization effects, and 2959 of these with  $I \leq 2\sigma(I)$ , were considered as observed.

*Structure determination.* The heavy atoms and Cl atom were located from a three-dimensional Patterson map. The positions of the remaining atoms were obtained from Fourier synthesis. An empirical absorption correction [24] was



applied at the end of the isotropic refinement. Final mixed refinement, with fixed isotropic factors and calculated positions for the H-atoms and unit weights, led to  $R = 0.041$  and  $R_w = 0.044$ . No trends in  $\Delta f/\text{vs } F_o$  or  $\sin \theta/\lambda$  were observed. Average shift-to-error ratios were  $0.02 \text{ \AA}^{-1}$ . Final difference synthesis showed no

Table 3

Atomic coordinates for  $[(OC)_3Mo(\mu-Cl)(\mu-CO)(\mu-dppm)Rh(NBD)]$ 

Atom	x	y	z	$U_{eq}^a$
Rh	0.75595(6)	0.12841(7)	0.19956(3)	371(3)
Mo	0.85706(6)	0.09228(8)	0.10464(4)	365(3)
P(1)	0.71397(17)	-0.09715(25)	0.19989(10)	347(8)
P(2)	0.82351(18)	-0.15980(25)	0.10628(10)	353(8)
Cl	0.93130(18)	0.06089(27)	0.20924(11)	498(9)
C(1)	0.98416(80)	0.05109(108)	0.07951(45)	514(41)
C(2)	0.71645(75)	0.15617(99)	0.10205(43)	451(38)
C(3)	0.80849(70)	0.10788(118)	0.02443(43)	527(39)
C(4)	0.89472(75)	0.28529(112)	0.10888(52)	571(45)
C(5)	0.70295(81)	0.18304(103)	0.27182(47)	536(42)
C(6)	0.63185(79)	0.20402(101)	0.22449(47)	521(41)
C(7)	0.64025(75)	0.35680(107)	0.21076(47)	542(40)
C(8)	0.73683(80)	0.36081(106)	0.19204(45)	522(41)
C(9)	0.80525(77)	0.33735(103)	0.23904(51)	570(43)
C(10)	0.75010(84)	0.31913(108)	0.28665(46)	565(43)
C(11)	0.66433(90)	0.41772(114)	0.26957(48)	639(47)
C(12)	0.79913(64)	-0.21277(94)	0.17453(37)	373(33)
C(13)	0.59569(65)	-0.15259(89)	0.16153(35)	351(31)
C(14)	0.53155(69)	-0.05793(95)	0.13200(38)	396(34)
C(15)	0.44353(72)	-0.10179(124)	0.10248(43)	562(41)
C(16)	0.41875(84)	-0.23927(125)	0.10294(47)	615(45)
C(17)	0.48217(82)	-0.33092(112)	0.13271(47)	580(43)
C(18)	0.56982(73)	-0.28708(98)	0.16102(41)	463(37)
C(19)	0.71565(71)	-0.16078(91)	0.27053(38)	384(33)
C(20)	0.63226(73)	-0.17642(108)	0.29252(41)	476(38)
C(21)	0.63624(84)	-0.21972(124)	0.34710(44)	615(46)
C(22)	0.72379(89)	-0.24393(124)	0.38072(43)	600(46)
C(23)	0.80706(88)	-0.22496(147)	0.36043(48)	744(53)
C(24)	0.80374(72)	-0.18424(123)	0.30542(46)	573(43)
C(25)	0.72663(66)	-0.24132(104)	0.05719(38)	401(35)
C(26)	0.65239(70)	-0.16167(103)	0.02883(38)	420(34)
C(27)	0.57581(81)	-0.22314(132)	-0.00683(45)	604(46)
C(28)	0.57465(87)	-0.36118(140)	-0.01441(43)	658(48)
C(29)	0.65073(93)	-0.44253(118)	0.01304(50)	654(48)
C(30)	0.72556(78)	-0.38187(110)	0.04900(42)	547(40)
C(31)	0.92822(70)	-0.26101(91)	0.09762(38)	379(33)
C(32)	0.94628(82)	-0.27653(115)	0.04395(45)	571(44)
C(33)	1.02891(98)	-0.34377(120)	0.03508(53)	678(52)
C(34)	1.09305(78)	-0.39424(123)	0.08036(58)	656(49)
C(35)	1.07592(79)	-0.37806(127)	0.13295(51)	660(46)
C(36)	0.99351(75)	-0.3126(107)	0.14229(43)	508(39)
O(1)	1.05472(61)	0.03340(93)	0.06397(40)	817(40)
O(2)	0.64333(49)	0.19834(79)	0.08115(30)	557(28)
O(3)	0.77471(56)	0.12111(104)	-0.02225(33)	840(38)
O(4)	0.91492(70)	0.40009(88)	0.10929(50)	1038(49)

<sup>a</sup> Coordinates and thermal parameters as  $U_{eq} = \frac{1}{3} \sum (U_{ij} \cdot A_i^* \cdot A_j^* \cdot A_i \cdot A_j \cdot \cos(A_i, A_j)) \cdot 10^{-4}$ .

significant electron density. Most of the calculations were carried out by use of program X-RAY 76 [25]. Table 3 gives the atomic coordinates for 1.

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