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Isolation and characterization of hydroformylation 'intermediates' from stoichiometric reactions between phosphinoalkenes and some heterobinuclear complexes†

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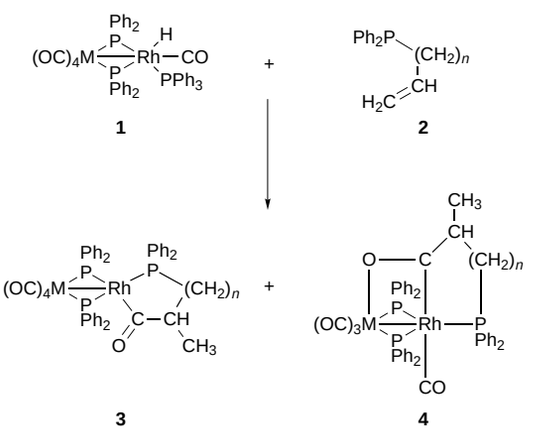
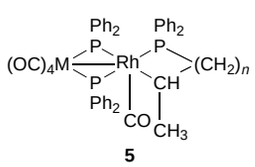
Some heterobimetallic acyl and μ-acyl-rhodium complexes have been isolated from reactions of the phosphido-bridged complexes $(OC)_4M(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$ with the phosphinoalkenes $Ph_2P(CH_2)_nCH{=}CH_2$ where M = Cr, Mo or W and n = 1–3. Several of the complexes have been fully characterized and their potential role as intermediates in the catalytic hydroformylation of the parent phosphines investigated and discussed.

The introduction of rhodium-based catalysts for olefin hydroformylation by Wilkinson and co-workers[1] led to an enormous surge of interest in alkene hydroformylation which still continues. Commercial processes using rhodium catalysts have been developed including the Rhone-Poulenc/Ruhrchemie aqueous-based system.[2] Interest continues in the assessment of ligands which lead to greater regioselectivity,[3] enantioselectivity[4] and ease of catalyst recovery.[5] A recent *ab initio* molecular orbital (MO) study of the full cycle of rhodium-catalysed alkene hydroformylation[6] includes the comment 'the mechanism of the catalytic cycle is still poorly established'.[6] The potential of both homo- and hetero-bimetallic compounds as hydroformylation catalysts is currently being investigated by several groups.[7,8] We have recently demonstrated that the phosphido-bridged compounds **1** are efficient catalysts, displaying good regioselectivity.[9] We decided to investigate the stoichiometric reactions of these compounds with the phosphinoalkenes **2** in the hope of isolating organometallic species which could either represent or mimic the intermediates in the catalytic cycle. It was felt that the stability of such intermediates may be enhanced by the combination of the bimetallic system and the potentially chelating phosphine ligand.



Scheme 1



Results and Discussion

Stoichiometric reactions of bimetallic rhodium compounds 1 with phosphinoalkenes 2

The tungsten–rhodium bimetallic complex **1** (M = W) was prepared as described previously,[10] and the chromium and molybdenum analogues (M = Cr or Mo) by an adaptation of this procedure. Each of these compounds was treated with a two-fold excess of the phosphinoalkenes **2** (n = 1 and 2) in benzene solution under mild conditions (Scheme 1). Chromatography of the products led to isolation of the acyl **3** and μ-acyl **4** complexes and yields of isolated materials are summarized in Table 1.

The acyl complexes **3** were characterized by an acyl C=O infrared stretch at 1635 cm^{-1} and multinuclear NMR data (see Experimental section). The molecular structure of **3** (M = W, n = 2) was determined from single-crystal X-ray diffraction data. The structure of the μ-acyl complexes **4** could not be determined unambiguously from spectroscopic data. The absence of a normal acyl C=O stretching absorption in the infrared spectra at first led us to suspect that an alkyl intermediate **5** had been isolated and the ^{31}P NMR data were in agreement with such a structure. However, determination of crystal structures from X-ray diffraction data for the compounds **4** (M = Cr, n = 1) and (M = Mo, n = 2) established that a μ-acyl bond was present.

The isolated yields of compounds **3** and **4** (see Table 1) showed variations with both the metal M in **1** and the chain length of the phosphinoalkene **2**. Under comparable conditions, reactions of the phosphinobutene **2** (n = 2) with **1** (M = Cr, Mo or W) showed dramatic differences in product formation. The chromium compound gave a mixture of acyl and μ-acyl complexes [reaction (3)] but the molybdenum compound gave exclusively the μ-acyl complex **4** [reaction (5)] and the tungsten compound exclusively the acyl complex **3** [reaction (8)]. The isolated yields from each of the latter two reactions were *ca.* 80%. Monitoring of reaction (5) by ^1H NMR spectroscopy showed that the acyl complex **3** (M = Mo, n = 2) was the sole product in the early stages and that conversion into the μ-acyl

† Dedicated to the memory of Geoffrey Wilkinson, a friend and inspirational chemist.

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Table 1 Reactions of rhodium bimetallics with phosphinoalkenes (1:2 mole ratio) in benzene. Yields of acyl **3** and μ-acyl **4** complexes

Reaction	M in **1**	Chain length *n* in **2**	*t*/h	*T*/°C	Yield (%) **3**	**4**
(1)	Cr	1	48	22	30	46
(2)	Cr	1	3	80	—	51
(3)	Cr	2	22	22	34	11
(4)	Mo	1	3	80	26	26
(5)	Mo	2	22	22	—	81
(6)	W	1	1	80	27	13
(7)	W	1	3	80	—	—
(8)	W	2	22	22	78	—

compound **4** only became significant after several hours. In contrast, no evidence for rearrangement of the tungsten acyl compound **3** (M = W, *n* = 2) was obtained after 22 h at ambient temperature. An attempt to promote the rearrangement by heating a solution of the compound **3** in benzene under reflux led to decomposition and no μ-acyl compound **4** was observed. We have no explanation for this interesting difference in behaviour.

Reactions of the phosphinopropenes **2** (*n* = 1) with the bimetallic complexes were somewhat slower than those of the butenyl homologues. Significant conversion was achieved after a long reaction time only for the chromium complex **1** (M = Cr) [reaction (1)] at ambient temperature. The molybdenum and tungsten systems both required elevated temperatures to achieve significant product formation [reactions (4), (6) and (7)]. All of the reactions resulted in the formation of mixtures of acyl and μ-acyl compounds with the exception of that of the chromium compound at 80 °C, which gave only the μ-acyl compound **4** [reaction (2)]. Again, it was shown by infrared spectroscopic monitoring that the acyl compound **3** (M = Cr, *n* = 1) converts into the μ-acyl complex **4**. This reaction was significantly slower than the isomerization of the corresponding butyl complex **3** (M = Mo, *n* = 2). Comparison of reactions (1) and (2) indicates that the sole isolation of the μ-acyl compound **4** at higher temperatures could be due to the above rearrangement coupled with possible decomposition of the acyl compound **3**.

Reactions of the phosphinopentene homologue **2** (*n* = 3) with the bimetallic species **1** in all cases gave evidence (^{31}P NMR) for the formation of acyl compounds **3**. However, attempts to isolate pure samples of material were unsuccessful, presumably due to instability resulting from ring-size effects.

Molecular structures

The molecular structures of the complexes **3** (M = W, *n* = 2), **4** (M = Cr, *n* = 1) and **4** (M = Mo, *n* = 2) are shown in Figs. 1–3. Bond lengths and angles are collected in Tables 2 and 3. There is the expected small increase in M–Rh bond distances from M = Cr to W. The W–Rh distance in **3** (M = W, *n* = 2) [2.817(1) Å] is similar to that [2.855(1) Å] in complex **1** (M = W)[10] and is consistent with a single bond. In **3** the geometry around W is reasonably described as [M(unidentate ligand)$_4$(bidentate ligand)] octahedral[11] if the W–Rh bond is ignored. The attachments of C(1), C(2), C(3), C(4) and P(1) to W show little deviation from regular geometry with all angles near 90°. The face defined by P(1), P(2) and C(4) is capped by rhodium and this distorts the angles involving these atoms. For example, the angle P(1)–W–P(2) is about 102°. The geometry around rhodium in **3** is distorted square pyramidal with P(2) in the apical position. One segment [defined by C(9), P(2), P(3)] of the coordination sphere is fairly regular with distortions in the other part enforced by the combination of bridge and metal–metal bonding. The acyl C=O distance in the metallacyclic ring is 1.19(1) Å. There are no unusual features in the bond distances or angles.

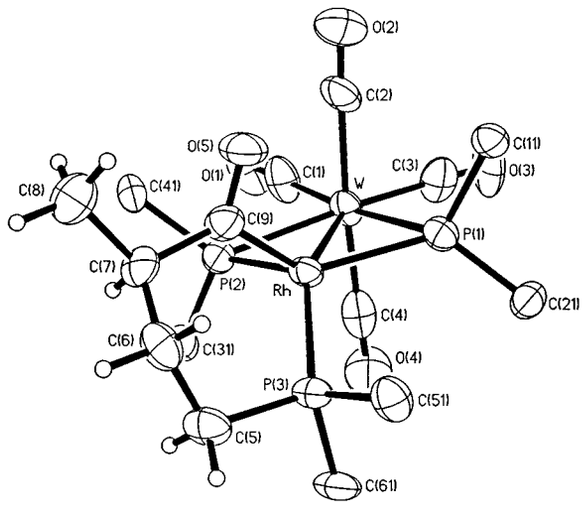


Fig. 1 Molecular projection showing the atom arrangement for compound **3** (M = W, *n* = 2); the non-hydrogen atoms are shown as 20% thermal ellipsoids and phenyl groups are removed for clarity

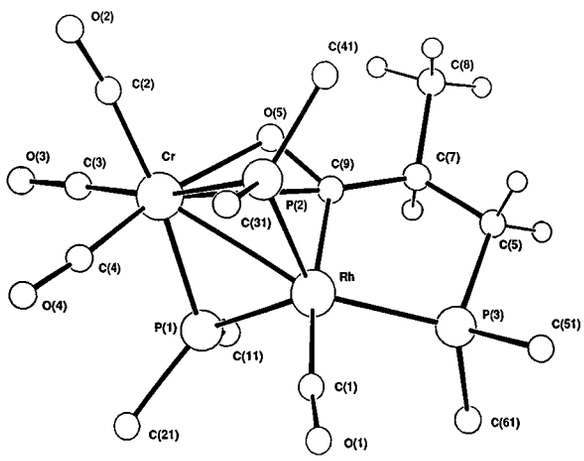


Fig. 2 Molecular projection showing the atom arrangement for compound **4** (M = Cr, *n* = 1); phenyl groups are removed for clarity

The molecular structures of compounds **4** (M = Cr, *n* = 1) and **4** (M = Mo, *n* = 2) are similar but not isomorphous. The most interesting feature is the bridging of the acyl group along the M–Rh bond; oxygen is attached to M and C to Rh. As a consequence, the C(9)–O(5) bond is lengthened from 1.19(1) in **3** to 1.24 Å (average) in **4**. We are aware of only one other report of this type of attachment of an acyl carbonyl to a metal–metal bond. In the complexes $MoMn(cp)\{\mu\text{-}C(O)R\}(\mu\text{-}PPh_2)(CO)_5$ (cp = η-C_5H_5, R = C_6H_{11} or C_3H_7)[12] the corresponding CO distance is 1.25 Å. Again, the geometry around M in **4** is reasonably regarded as capped octahedral with the three carbonyls adopting regular geometry and some distortions in the central part of the molecule. The carbonyl attached through C(4), which is *trans* to the acyl oxygen O(5), is significantly closer to the metal than the other carbonyl carbons in these complexes. If the M–Rh bond is ignored, the geometry around rhodium is reasonably described as trigonal bipyramidal with the three phosphorus atoms in the equatorial positions. The P–Rh–P′ angles range from 109 to 130°. The M–Rh bond projects through the face defined by P(1), P(2) and C(9).

Hydroformylation reactions of the phosphinoalkenes 2 using the bimetallics 1 and compounds 3 and 4 as catalysts

It has been reported previously[9] that the tungsten compound **1** (M = W) is an effective hydroformylation catalyst and that its use in reactions of the potentially chelating phosphinoalkenes **2** (*n* = 2 and 3) leads predominantly to branch-chain products. Related reactions have now been carried out using

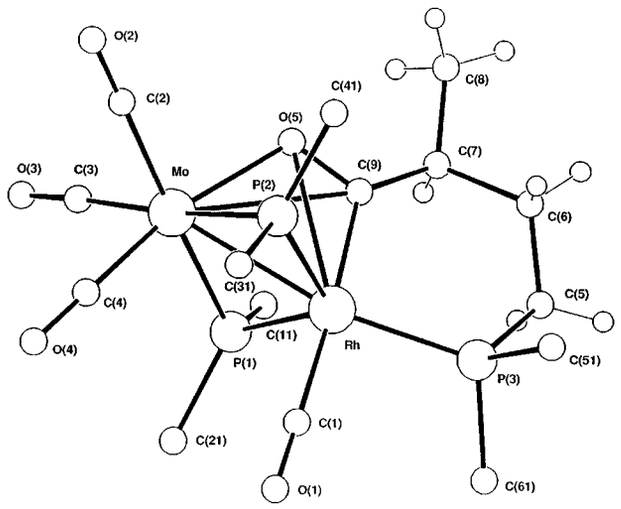
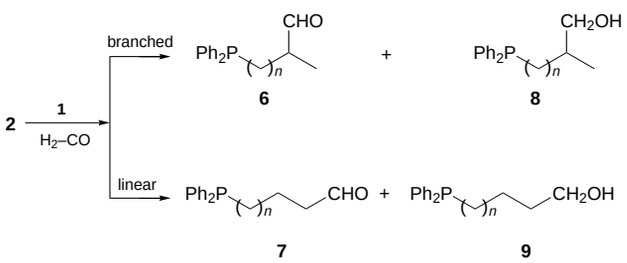


Fig. 3 Molecular projection showing the atom arrangement for **4** (M = Mo, $n = 2$); phenyl groups are removed for clarity



Scheme 2 Catalytic hydroformylation reaction of phosphinoalkenes

Table 2 Selected bond distances (Å) for compounds **3** (M = W, $n = 2$), **4** (M = Cr, $n = 1$) and **4** (M = Mo, $n = 2$)

	3 (W)	**4** (Cr)	**4** (Mo)
M–Rh	2.817(1)	2.7311(9)	2.7788(9)
M–P(1)	2.499(3)	2.361(1)	2.469(2)
M–P(2)	2.488(3)	2.364(1)	2.494(2)
Rh–P(1)	2.347(3)	2.330(1)	2.320(2)
Rh–P(2)	2.258(3)	2.324(1)	2.342(2)
Rh–C(1)	—	1.934(4)	1.949(6)
M–C(1)	2.008(16)	—	—
M–C(2)	2.036(11)	1.858(5)	2.005(7)
M–C(3)	2.010(13)	1.873(5)	2.003(7)
M–C(4)	2.008(13)	1.815(3)	1.944(7)
C(1)–O(1)	1.14(2)	1.140(5)	1.123(7)
C(2)–O(2)	1.14(1)	1.150(7)	1.138(9)
C(3)–O(3)	1.15(2)	1.139(6)	1.151(9)
C(4)–O(4)	1.16(2)	1.156(4)	1.157(8)
Rh–P(3)	2.242(3)	2.281(1)	2.290(2)
P(3)–C(5)	1.839(10)	1.834(4)	1.815(7)
C(5)–C(6)	1.52(1)	—	1.51(2), 1.41(2)
C(5)–C(7)	—	1.493(7)	—
C(6)–C(7)	1.53(2)	—	1.62(2), 1.35(2)
C(7)–C(9)	1.52(1)	1.542(5)	1.51(1), 1.51(1)
C(9)–Rh	1.985(10)	2.015(3)	2.052(6)
C(9)–O(5)	1.19(1)	1.230(5)	1.249(7)
O(5)–M	—	2.142(2)	2.248(4)

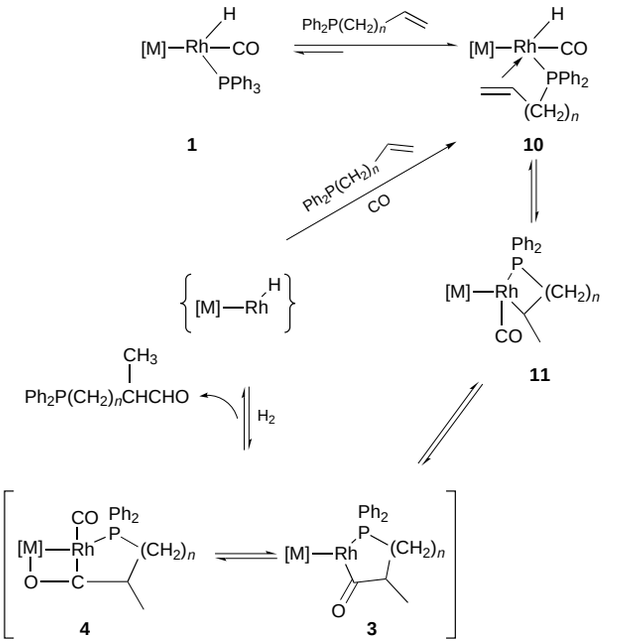
Table 3 Selected bond angles (°) for compounds **3** (M = W, $n = 2$), **4** (M = Cr, $n = 1$) and **4** (M = Mo, $n = 2$)

	3 (W)	**4** (Cr)	**4** (Mo)
Rh–M–P(1)	51.92(6)	53.87(3)	52.06(4)
Rh–M–P(2)	49.92(8)	53.69(3)	52.39(4)
Rh–M–O(5)	—	69.46(8)	66.4(1)
Rh–M–C(1)	131.4(3)	—	—
Rh–M–C(2)	91.5(4)	137.9(1)	134.3(2)
Rh–M–C(3)	137.9(4)	135.6(2)	135.3(2)
Rh–M–C(4)	90.4(4)	103.4(2)	102.4(2)
P(1)–M–P(2)	101.8(1)	106.53(5)	103.88(6)
P(1)–M–O(5)	—	84.18(8)	78.7(1)
P(1)–M–C(1)	174.5(4)	—	—
P(1)–M–C(2)	86.0(4)	168.2(2)	169.2(2)
P(1)–M–C(3)	86.1(4)	83.8(2)	83.7(2)
P(1)–M–C(4)	92.4(5)	90.0(1)	94.2(2)
P(2)–M–O(5)	—	81.97(7)	80.5(1)
P(2)–M–C(1)	82.0(5)	—	—
P(2)–M–C(2)	98.6(4)	85.1(1)	84.3(2)
P(2)–M–C(3)	169.4(4)	169.1(2)	172.3(2)
P(2)–M–C(4)	85.3(4)	95.4(1)	93.1(2)
O(5)–M–C(2)	—	99.5(1)	96.0(2)
O(5)–M–C(3)	—	96.0(1)	102.6(2)
O(5)–M–C(4)	—	172.6(2)	168.8(2)
C(1)–M–C(2)	89.5(5)	—	—
C(1)–M–C(3)	90.6(5)	—	—
C(1)–M–C(4)	91.8(6)	—	—
C(2)–M–C(3)	88.8(5)	84.6(2)	88.4(3)
C(2)–M–C(4)	176.1(5)	87.1(2)	92.4(3)
C(3)–M–C(4)	87.5(5)	87.9(2)	85.0(3)
M–Rh–P(1)		54.93(3)	57.07(4)
M–Rh–P(2)		55.05(3)	57.54(5)
M–Rh–P(3)		149.93(3)	164.70(5)
M–Rh–C(1)	—	117.8(1)	104.3(2)
M–Rh–C(9)		67.9(1)	71.9(2)
P(1)–Rh–P(2)	114.3(1)	108.90(4)	113.91(6)
P(1)–Rh–P(3)	108.1(1)	117.01(3)	120.04(6)
P(1)–Rh–C(1)	—	105.8(1)	92.6(2)
P(1)–Rh–C(9)	131.0(4)	82.2(1)	82.6(2)
P(2)–Rh–P(3)	123.2(1)	129.12(4)	125.47(6)
P(2)–Rh–C(1)	—	95.6(1)	94.5(2)
P(2)–Rh–C(9)	92.2(4)	83.0(1)	86.3(2)
P(3)–Rh–C(1)	—	92.2(1)	90.6(2)
P(3)–Rh–C(9)	86.9(3)	82.6(1)	92.9(2)
C(1)–Rh–C(9)	—	171.9(2)	175.0(2)
M–P(1)–Rh	71.0(1)	71.21(3)	70.86(5)
M–P(2)–Rh	72.6(1)	71.26(3)	70.07(5)
Rh–P(3)–C(5)	114.7(4)	103.1(2)	113.9(2)
M–O(5)–C(9)	—	104.0(2)	108.5(3)
Rh–C(1)–O(1)	—	173.2(4)	177.2(5)
M–C(*n*)–O(*n*) range	176.5–179.4	174.3–177.2	176.8–178.9(6)
P(3)–C(5)–C(6/7)	111.7(7)	110.7(3)	107.6(7), 119.0(9)
C(5)–C(6)–C(7)	115.5(9)	—	113(1), 121(1), 132(2)
C(5)–C(7)–C(9)	—	110.3(3)	—
C(6)–C(7)–C(9)	109.1(10)		110.3(9), 120(1)
Rh–C(9)–O(5)	112.0(8)	118.5(2)	113.1(4)
Rh–C(9)–C(7)	126.8(8)	123.1(3)	131.7(6), 127.3(6)
O(5)–C(9)–C(7)	121.1(9)	118.2(3)	113.3(6), 119.6(7)

the chromium and molybdenum analogues, and all three compounds have been evaluated as catalysts in hydroformylation reactions of diphenylphosphinopropene **2** ($n = 1$) (Scheme 2). The results are summarized in Table 4.

Reactions of the phosphinobutene **2** ($n = 2$) and phosphinopentene **2** ($n = 3$) showed virtually complete regioselectivity for branch-chain products. The butenyl compounds were mainly isolated as the alcohol **8** ($n = 2$) whereas the product of reaction of the pentenyl compound was mainly the aldehyde **6** ($n = 3$). Reactions of the phosphinopropene **2** ($n = 1$) were not highly regioselective and gave mixtures of alcohols arising from both linear and branched hydroformylation. We interpret these results as reflecting a preference for six- *versus* seven-membered chelate rings when $n = 2$, seven- *versus* eight-membered rings when $n = 3$, and little discrimination between five- and six-membered rings when $n = 1$. The stability of the five- and six-membered ring chelates leads to further reduction resulting in alcohol formation. This does not occur with the seven-membered ring. The relative lack of stability of this larger ring system was reflected in our inability to isolate products arising from stoichiometric reactions of the phosphinopentene **2** ($n = 3$).

Two of the products arising from stoichiometric reactions, the acyltungsten compound **3** (M = W, $n = 2$) and the μ-



Scheme 3 Simplified catalytic cycle for hydroformylation involving heterobimetallic catalysts and intermediates {[M] = $(OC)_nM(\mu\text{-}PPh_2)_2$}

Table 4 Catalytic hydroformylation of phosphinoalkenes[a]

Catalyst **1**, M	Alkene **2**, *n*	Ratio of products **6**	**8**	**7**	**9**	Branched : linear ratio	Yield (%)
W	1	—	36	—	18	67 : 33	54[b]
Mo	1	—	35	—	21	62 : 38	56[b]
Cr	1	—	24	—	10	71 : 29	34[b]
W	2	—	100	—	—	100 : 0	77
Mo	2	—	100	—	—	100 : 0	98
Cr	2	17	83	—	—	100 : 0	100
W	3	77	17	6	—	83 : 17	100
Mo	3	92	8			100 : 0	
Cr	3	90	10	—	—	100 : 0	100

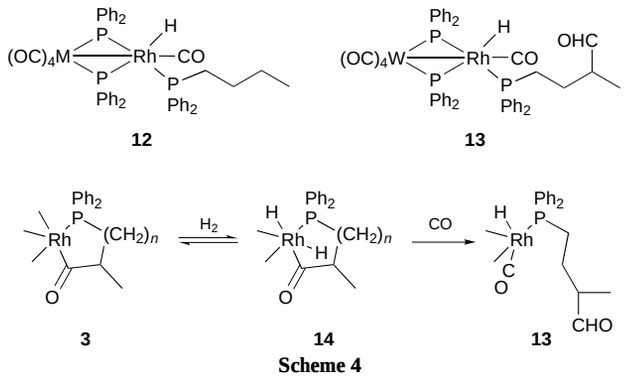
[a] Reactions at 80 °C, 400 psi H_2–CO with catalyst : substrate ratio of 1 : 120 in benzene. [b] Starting alkene recovered.

acylmolybdenum compound **4** (M = Mo, *n* = 2), were evaluated as catalysts for hydroformylation of the phosphinobutene **2** (*n* = 2) in a catalyst to substrate ratio of 1 : 120. In each case the branched alcohol **8** (*n* = 2) was obtained in quantitative yield.

Investigations using these two compounds were also conducted using a catalyst to substrate ratio of 1 : 4 and with a short reaction time (30 min). Each of these reactions gave the branched aldehyde **6** (*n* = 2) as the sole product from the phosphinobutene **2** (*n* = 2). Chromatographic separation of the organometallic compounds led to partial recovery of the acyltungsten compound **3** (M = W, *n* = 2) together with some μ-acyl compound **4** (M = W, *n* = 2) in ratio *ca.* 60 : 40. The μ-acyl compound was fully characterized and its formation contrasts with the stoichiometric reactions described above where only the acyl compound **3** (M = W, *n* = 2) was isolated. Chromatographic separation of the organometallic compounds from the reaction involving the μ-acylmolybdenum compound **4** (M = Mo, *n* = 2) led to recovery of the μ-acyl compound in good yield (66%); no evidence for formation of any acyl compound **3** (M = Mo, *n* = 2) was obtained. The implications of these results in terms of the mechanism of hydroformylation are discussed below.

Mechanistic considerations

Wilkinson proposed[1] two catalytic cycles for rhodium-catalysed hydroformylation designated associative and dissociative which



Scheme 4

have been extensively analysed in a recent theoretical paper.[6] Although not all of the details of these mechanisms are fully understood, it is generally accepted that π-alkene (**10**), σ-alkyl (**11**) and σ-acyl (**3**) rhodium intermediates are involved. The isolation of an acyl complex in our work allowed us to investigate the acyl to aldehyde step in the catalytic cycle. A simplified catalytic cycle but involving the μ-acyl compounds is shown in Scheme 3.

An acyl intermediate $Rh(COEt)(CO)_2(PPh_3)_2$ was obtained in solution by Wilkinson and co-workers[13] and shown to react with hydrogen losing CO and forming aldehyde. To our surprise, attempted reaction of the acyltungsten compound **3** (M = W, *n* = 2) with hydrogen (400 psi; 1 psi = 6894.76 Pa) at 80 °C led to recovery of the unchanged acyl compound together with a small amount of a new compound which was tentatively identified from spectroscopic data as the phosphinobutane rhodium hydride **12** (M = W). It is possible that this compound is formed by reaction with hydrogen of the σ-alkyl compound **11** which itself arises from **3** by microscopic reversibility. Reaction of the μ-acylmolybdenum compound **4** (M = Mo, *n* = 2) with hydrogen under similar conditions again led to recovery of unchanged μ-acyl compound together with a small amount of a new compound which again appeared to contain the Rh(H)-$PPh_2CH_2CH_2CH_2CH_3$ moiety.

These observations prompted us to study similar reactions of the acyl compounds **3** (M = W, *n* = 2) with synthesis gas rather than with hydrogen. Heating this compound for 0.5 h at 80 °C with 400 psi H_2–CO (1 : 1) gave mainly recovered acyl compound **3** (M = W, *n* = 2) (*ca.* 50%) with some μ-acyl compound **4** (M = W, *n* = 2) (*ca.* 35%). A small amount (*ca.* 15%) of a further compound was tentatively identified as the co-ordinated phosphinobutanal complex **13** on the basis of spectroscopic data.

These results suggest that conversion of the acyl complexes **3** into phosphinoaldehyde complexes, *e.g.* **13**, must involve CO as well as H_2. It can be argued that the conversion requires a slow, reversible oxidative addition of hydrogen to the acyl compound **3** forming a dihydrido species **14** which only proceeds to the co-ordinated aldehyde **13** in the presence of CO (Scheme 4). The acyl ⇌ μ-acyl interconversion appears to be an equilibrium as both species are catalytically active even though it has only proven possible to see the acyl to μ-acyl conversion and not the reverse.

Experimental

General

All reactions involving phosphines and rhodium catalysts were carried out under an atmosphere of nitrogen in oven-dried Schlenk flasks where appropriate. Purification was achieved by thin-layer chromatography on silica (Merck). Melting points were determined on an Electrothermal apparatus and are uncorrected. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago, New Zealand.

Hydroformylation reactions

Hydroformylation reactions were carried out in a stainless-steel Parr autoclave (100 cm^3) equipped with a glass sleeve and magnetic stirrer. The autoclave and solvent were flushed thoroughly with nitrogen before the addition of the substrate and catalyst. The autoclave was then flushed several times with a 1:1 molar mixture of carbon monoxide and hydrogen (3 × 200 psi), pressurized to the required pressure and heated to reaction temperature. The reaction temperature was regulated by use of a thermocouple inserted between the autoclave and heating block. When reaction was complete the autoclave was cooled and the contents transferred to another flask, under nitrogen for air-sensitive products. Isomer ratios were determined immediately after reaction from ^{1}H and ^{31}P NMR spectral data.

Instrumentation

Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer, NMR spectra on Bruker AC200 or AM300 spectrometers. The ^{1}H NMR spectra were measured at 200 or 300 MHz, ^{13}C at 50 MHz and ^{31}P at 121.5 MHz; $CDCl_3$ was used as internal lock. Chemical shifts are in parts per million from internal $SiMe_4$ for ^{1}H and ^{13}C, and from external 85% H_3PO_4 for ^{31}P; in all cases a positive chemical shift denotes a shift downfield from the reference. Electron-impact mass spectra were obtained by using a VG micromass 70/70-F or VG Trio-1 spectrometer operating at 70 eV (*ca*. 1.12×10^{-17} J) and 200 °C inlet temperature.

Materials

Solvents were of analytical grade and purified by standard procedures.[14] All solvents were purged with nitrogen prior to use. Phosphinoalkenes **2** (n = 1–3) were prepared as described previously.[9]

Preparation of the phosphido-bridged compounds 1 (M = Cr, Mo or W)

All three complexes were prepared by the literature method reported for the tungsten complex.[10] The latter had identical spectroscopic data to those reported in the literature.

$(OC)_4Mo(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$: yield 71%, m.p. 121–123 °C (Found: C, 57.8; H, 3.9. $C_{47}H_{36}MoO_5P_3Rh$ requires C, 58.0; H, 3.7%). NMR ($CDCl_3$): ^{1}H (200 MHz), δ −13.1 (t, 1 H, RhH, J_{RhH} = 16) and 6.80–7.85 (m, 35 H, C_6H_5); ^{31}P-{^{1}H} (121.5 MHz), δ 56.7 (dt, 1P, RhP, J_{RhP} = 164, $^2J_{PP}$ = 42) and 191.9 (dd, 2P, μ-PPh_2, J_{RhP} = 111, $^2J_{PP}$ = 42 Hz). IR: (CH_2Cl_2) ν(CO) 2032vs, 1944vs and 1927vs; (Nujol) ν(Rh−H) 2059m, ν(CO) 2029vs, 1962s, 1944s and 1920vs cm^{-1}. EI mass spectrum: *m*/*z* 262 (98), 183 (100), 152 (20), 108 (56) and 78 (64%).

$(OC)_4Cr(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$: yield 74%, m.p. 135–138 °C (Found: C, 60.0; H, 4.0; P, 10.1. $C_{47}H_{36}CrO_5P_3Rh$ requires C, 60.8; H, 3.9; P, 10.0%). NMR ($CDCl_3$): ^{1}H (200 MHz), δ −13.0 (t, 1 H, RhH, $^1J_{RhH}$ = 14.5) and 6.9–7.65 (m, 35 H, C_6H_5); ^{31}P-{^{1}H} (121.5 MHz), δ 57.5 (dt, 1P, RhP, $^1J_{RhP}$ = 163, $^2J_{PP}$ = 44) and 215.8 (dd, 2P, μ-PPh_2, $^1J_{RhP}$ = 118, $^2J_{PP}$ = 44 Hz). IR: (CH_2Cl_2) ν(CO) 2018s, 1978m (sh) and 1924vs; (NaCl plates, Nujol) ν(Rh−H) 2054m, ν(CO) 2016s, 1968m, 1942s and 1910vs cm^{-1}. EI mass spectrum: *m*/*z* 342 (5), 314 (93), 152 (25), 108 (75), 78 (90) and 52 (50%).

Reactions of phosphido-bridged compounds 1 with phosphinoalkenes 2

1(M = Cr) with 2 (n = 1). The phosphine **2** (n = 1) (33 μl, 20.15 mmol) was added to a solution of compound **1** (M = Cr) (70 mg, 0.075 mmol) in benzene (25 cm^3) and the resultant mixture was refluxed for 3 h. The colour changed from a bright red to a dark red-brown. Removal of solvent *in vacuo* gave a dark red-brown oily residue. Preparative TLC (eluent hexane–dichloromethane, 1:2) gave **4** (M = Cr, n = 1) (34 mg, 51%) as a brown-red solid (Found: C, 58.9; H, 3.90; P, 10.1. $C_{44}H_{36}CrO_5P_3Rh$ requires C, 59.2; H, 4.07; P, 10.4%). NMR ($CDCl_3$): ^{1}H (200 MHz), δ −0.22 (d, 3 H, CH_3, $^3J_{HH}$ = 6.4), 0.7–1.0 (m, 2 H, CH_2), 1.9–2.15 (m, 1 H, CH) and 6.9–7.9 (m, 30 H, C_6H_5); ^{31}P-{^{1}H} (121.5 MHz), δ 68.9 (ddd, 1P, RhP, $^1J_{RhP}$ = 171, $^2J_{PP}$ = 45, 41), 217.0 (ddd, 1P, μ-PPh_2, $^1J_{RhP}$ = 111, $^2J_{PP}$ = 108, 45) and 227.2 (ddd, 1P, μ-PPh_2, $^1J_{RhP}$ = 111, $^2J_{PP}$ = 108, 41 Hz); ^{13}C (50 MHz), δ 12.9 (d, CH_3, $^3J_{PC}$ = 21.0), 35.2 (d, CH_2, $^1J_{PC}$ = 27.8), 58.75 (d, CH, $^2J_{PC}$ = 29.5 Hz) and 127.7–141.5 (C_6H_5). IR (CH_2Cl_2): ν(CO) 2015m, 1959vs, 1907s and 1851s cm^{-1}. EI mass spectrum: *m*/*z* 277 (12), 262 (41), 183 (47), 152 (12), 108 (25), 107 (14), 78 (100) and 77 (38%).

A reaction on a similar scale but for 48 h at ambient temperature gave the μ-acyl complex **4** (M = Cr, n = 1) (35 mg, 46%) together with a compound tentatively identified as the acyl compound **3** (M = Cr, n = 1) (24 mg, 31%). IR (CH_2Cl_2): ν(CO) 2018vs, 1932vs and 1637s cm^{-1}. This slowly converted into the μ-acyl compound **4** (M = Cr, n = 1) on standing in dichloromethane solution.

1 (M = Mo) with 2 (n = 1). The phosphinoalkene **2** (n = 1) (35 μl, 0.16 mmol) was added by syringe to a solution of compound **1** (M = Mo) (80 mg, 0.082 mmol) in benzene (30 cm^3) and the resultant red solution was refluxed for 3 h. The reaction was monitored by TLC (eluent hexane–dichloromethane, 1:2) which showed the formation of two bands. The solvent was removed *in vacuo* and the red-brown residue chromatographed. Elution with hexane–dichloromethane (1:2) gave two bands. One compound (20 mg) was not identified. The other red band was identified as the μ-acyl compound **4** (M = Mo, n = 1) (20 mg, 26%), m.p. 232–234 °C (Found: C, 56.3; H, 3.80. $C_{44}H_{36}MoO_5P_3Rh$ requires C, 56.4; H, 3.85%). NMR ($CDCl_3$): ^{1}H (300 MHz), δ −0.05 (d, 3 H, CH_3, $^3J_{HH}$ = 6.3), 0.75–1.0 (m, 2 H, CH_2), 2.1–2.3 (m, 1 H, CH) and 6.95–7.85 (m, 30 H, C_6H_5); ^{31}P-{^{1}H} (121.5 MHz), δ 69.2 (ddd, 1P, RhP, $^1J_{RhP}$ = 169, $^2J_{PP}$ = 43, 39) and 203.1 (ddd, 1P, μ-PPh_2, $^1J_{RhP}$ = 104, $^2J_{PP}$ = 104, 39 Hz); ^{13}C-{^{1}H} (50 MHz), δ 13.1 (d, CH_3, $^3J_{PC}$ = 21.2), 34.8 (d, CH_2, $^1J_{PC}$ = 28.2), 59.5 (d, CH, $^2J_{PC}$ = 26.2 Hz) and 127.7–141.6 (m, C_6H_5). IR (CH_2Cl_2): ν(CO) 2024m, 1976vs, 1924s and 1849s cm^{-1}. EI mass spectrum: *m*/*z* 262 (11), 183 (15), 108 (15), 96 (100), 78 (31) and 35 (17%).

1 (M = W) with 2 (n = 1). The phosphinoalkene **2** (n = 1) (4l μl, 0.19 mmol) was added by syringe to a solution of compound **1** (M = W) (0.10 g, 0.09 mmol) in benzene (30 cm^3) and the resultant red mixture was refluxed for 1 h. The reaction was monitored by TLC for the disappearance of **3** (M = W). Preparative TLC (eluent hexane–dichloromethane, 1:2) first eluted **4** (M = W, n = 1) as a red-brown film (13 mg, 13%) followed by the acyl complex **3** (M = W, n = 1) (27 mg, 28%). The μ-acyl complex **4** (M = W, n = 1) had m.p. 230–232 °C (Found: C, 51.3; H, 3.5; P, 9.25. $C_{44}H_{36}O_5P_3RhW$ requires C, 51.6; H, 3.5; P, 9.1%). NMR ($CDCl_3$): ^{1}H (300 MHz), δ −0.04 (d, 3 H, CH_3, $^3J_{HH}$ = 6.4), 0.8–1.2 (m, 2 H, CH_2), 1.95–2.10 (m, 1 H, CH) and 6.95–7.90 (m, 30 H, C_6H_5); ^{31}P-{^{1}H} (121.5 MHz), δ 66.9 (ddd, 1P, RhP, $^1J_{RhP}$ = 169, $^2J_{PP}$ = 34, 32), 175.9 (ddd, 1P, μ-PPh_2, $^1J_{PP}$ = 118, $^2J_{PP}$ = 101, 34) and 185.7 (ddd, 1P, μ-PPh_2, $^1J_{RhP}$ = 118, $^2J_{PP}$ = 101, 32 Hz); ^{13}C-{^{1}H} (50 MHz), δ 12.9 (d, CH_3, $^3J_{PC}$ = 20.4), 35.1 (d, CH_2 $^1J_{PC}$ = 28.3), 60.3 (d, CH, $^2J_{PC}$ = 21.1 Hz) and 127.8–141.0 (C_6H_5). IR (CH_2Cl_2): ν(CO) 2072s, 1970vs, 1909vs and 1844s cm^{-1}. Electrospray mass spectrum: *m*/*z* 1024 (62, P^+), 996 (100), 968 (38) and 944 (12%).

The acyl compound **3** (M = W, n = 1) had m.p. 125–128 °C. NMR ($CDCl_3$): ^{1}H (300 MHz), δ 1.0 (d, 3 H, CH_3, $^3J_{HH}$ = 7.0), 2.10–2.28 (m, 1 H, CH), 2.55–2.80 (m, 1 H, CH_2), 2.8–2.0 (m, 1 H, CH_2) and 6.70–7.85 (m, 30 H, C_6H_5); ^{31}P-{^{1}H} (121.5 MHz), δ 80.2 (dt, 1P, RhP, $^1J_{RhP}$ = 213, $^2J_{PP}$ = 32 Hz) and 174–190 (br m, 2P, μ-PPh_2). IR (CH_2Cl_2): ν(CO) 2031vs, 1946vs (br), 1638s cm^{-1}.

A reaction on a similar scale but which was heated under reflux for 3 h gave the complexes **4** and **3** (M = W, $n = 1$) in 26 and 16% yields respectively.

1 (M = Mo) with 2 ($n = 2$). The phosphinoalkene **2** ($n = 2$) (37 mg, 0.154 mmol) was added to a solution of compound **1** (M = Mo) (75 mg, 0.077 mmol) in benzene (20 cm^3) and the resultant mixture stirred at ambient temperature for 22 h. Removal of the solvent *in vacuo* resulted in a dark red-orange oil which on preparative TLC (eluent hexane–dichloromethane, 1:2) gave the complex **4** (M = Mo, $n = 2$) as a red-orange solid (60 mg, 81%) with m.p. 195–197 °C (Found: C, 57.0; H, 4.3. $C_{45}H_{38}MoO_5P_3Rh$ requires C, 56.9; H, 4.0%). NMR ($CDCl_3$): ^{1}H (200 MHz), δ −0.20 (d, 3 H, CH_3, $^3J_{HH} = 6.8$), 0.35–0.55 (m, 1 H, CH), 1.9–2.2 (m, 1 H, CH_2), 2.6–2.85 (m, 1 H, CH_2) and 7.0–7.95 (m, 30 H, C_6H_5); ^{31}P-{^{1}H} (121.5 MHz), δ 31.2 (ddd, 1P, RhP, $^1J_{RhP} = 161$, $^2J_{PP} = 46$, 40), 192.0 (ddd, 1P, μ-PPh_2, $^1J_{RhP} = 118$, $^2J_{PP} = 104$, 46) and 198.7 (ddd, 1P, μ-PPh_2, $^1J_{RhP} = 118$, $^2J_{PP} = 104$, 40 Hz); ^{13}C (50 MHz), δ 15.75 (s, CH_3), 26.2 (d, CH_2, $^1J_{PC} = 28.1$), 27.3 (d, CH_2, $J_{PC} = 27.4$), 51.5 (d, CH, $^3J_{PC} = 12.1$ Hz) and 127.65–141.6 (C_6H_5). IR (CH_2Cl_2): ν(CO) 2034s, 1973vs, 1922s and 1846s cm^{-1}. EI mass spectrum: *m*/*z* 262 (85), 183 (100), 152 (18), 108 (58), 78 (97), 77 (48) and 51 (42%).

1 (M = Cr) with 2 ($n = 2$). To a solution of compound **1** (M = Cr) (90 mg, 0.097 mmol) in benzene (30 cm^3) was added $Ph_2P(CH_2)_2CH{=}CH_2$ (47 mg, 0.196 mmol) and the reaction stirred at ambient temperature for 22 h. Solvent removal *in vacuo* and subsequent preparative TLC (eluent hexane–diethyl ether, 1:1) separated **3** (30 mg, 34%) and **4** (10 mg, 11%). The products were identified spectroscopically.

Compound **3** (M = Cr, $n = 2$): m.p. 200–202 °C. NMR ($CDCl_3$): ^{1}H (200 MHz), δ 0.5 (d, 3 H, CH_3, $^3J_{HH} = 6.5$), 1.55–1.85 (m, 1 H, CH), 1.9–2.9 (m, 4 H, CH_2) and 6.5–7.6 (m, 30 H, C_6H_5); ^{31}P-{^{1}H} (121.5 MHz), δ 32.0 (dt, 1P, RhP, $^1J_{RhP} = 208$, $^2J_{PP} = 41$) and 162.6 (dd, 2P, μ-PPh_2, $^1J_{RhP} = 142$, $^2J_{PP} = 41$ Hz); ^{13}C-{^{1}H} (50 MHz), δ 17.7 (s, CH_3), 28.6 (d, CH_2, $^1J_{PC} = 31$), 29.4 (d, CH_2, $^2J_{PC} = 4$), 56.9 (d, CH, $^3J_{PC} = 14$ Hz) and 127.6–141.6 (C_6H_5). IR (CH_2Cl_2): ν(CO) 2017vs, 1930vs and 1625s cm^{-1}. EI mass spectrum: *m*/*z* 183 (91), 152 (15), 108 (50), 78 (100), 52 (30) and 51 (38). Electrospray mass spectrum: *m*/*z* 906 (16, P^+).

Compound **4** (M = Cr, $n = 2$): NMR ($CDCl_3$), ^{1}H (200 MHz), δ −0.34 (d, 3 H, CH_3, $^3J_{HH} = 6.8$), 1.5–3.0 (br m) and 7.0–7.95 (m, 30 H, C_6H_5); ^{31}P-{^{1}H} (121.5 MHz), δ 31.4 (ddd, 1P, RhP, $^1J_{RhP} = 162$, $^2J_{PP} = 49$, 42), 215.6 (ddd, 1P, μ-PPh_2, $^1J_{RhP} = 122$, $^2J_{PP} = 113$, 49) and 223.0 (ddd, 1P, μ-PPh_2, $^1J_{RhP} = 122$, $^2J_{PP} = 113$, 42 Hz). IR (CH_2Cl_2): ν(CO) 2029m, 1957vs, 1904s and 1849s cm^{-1}.

1 (M = W) with 2 ($n = 2$). To a solution of compound **1** (M = W) (40 mg, 0.038 mmol) in benzene (30 cm^3) was added $Ph_2P(CH_2)_2CH{=}CH_2$, **2** ($n = 2$) (18 mg, 0.076 mmol). The solution was stirred at room temperature. It turned from bright red to a dark red-orange within 5 min and IR spectroscopy and TLC analysis indicated complete conversion. The solvent was removed *in vacuo*, and the residue chromatographed. Elution with hexane–dichloromethane (1:2) gave the complex **3** (M = W, $n = 2$) (31 mg, 80%) as an orange film, m.p. 161 °C (Found: C, 52.3; H, 3.4. $C_{45}H_{38}O_5P_3RhW$ requires C, 52.1; H, 3.7%). NMR ($CDCl_3$): ^{1}H (300 MHz), δ 0.5 (d, 3 H, CH_3, $^3J_{HH} = 6.7$), 2.1 (m, 1 H, CH), 2.5–2.9 (m, 4 H, CH_2) and 6.6–7.8 (m, 30 H, C_6H_5); ^{31}P-{^{1}H} (121.5 MHz), δ 29.3 (dt, 1P, RhP, $^1J_{RhP} = 206$, $^2J_{PP} = 34$) and 177 (poorly resolved dd, 2P, μ-PPh_2, $^1J_{RhP} \approx 133$, $^2J_{PP} \approx 34$ Hz); ^{13}C-{^{1}H} (50 MHz), δ 18.1 (CH_3), 28.8, 29.2 (CH_2), 57.1 (CH), 127.5–141.3 (C_6H_5), 195.7 (WCO) and 208.0 (d, RhCO, $^1J_{RhC} = 94.5$ Hz). IR (CH_2Cl_2): ν(CO) 2031vs, 1934vs and 1628s cm^{-1}. Electrospray mass spectrum: *m*/*z* 1038 (100, P^+), 1010 (22) and 954 (14%).

A similar reaction which was stirred for 22 h at ambient temperature gave compound **3** (M = W, $n = 2$) in 78% yield.

1 (M = Cr, Mo or W) with 2 ($n = 3$). The compound $Ph_2P(CH_2)_3CH{=}CH_2$ **2** ($n = 3$) (21 mg, 0.082 mmol) was added to a solution of complex **1** (M = Cr, Mo or W) (0.04 mmol) in C_6D_6 (2 cm^3) in an NMR tube. The reactions were monitored by NMR spectroscopy which provided evidence for the formation of acyl complexes **3** in all cases: M = Mo, ^{31}P-{^{1}H} NMR (C_6D_6, 121.5 MHz), δ 47.0 (dt, 1P, RhP, $^1J_{RhP} = 160$, $^2J_{PP} = 42$) and 195.5 (dd, 2P, μ-PPh_2, $^1J_{RhP} = 111$, $^2J_{PP} = 42$); M = W, ^{31}P-{^{1}H} NMR (C_6D_6, 121.5 MHz), δ 43.7 (dt, 1P, RhP, $^1J_{RhP} = 159$, $^2J_{PP} = 34$) and 169.8 (dd, 2P, μ-PPh_2, $^1J_{RhP} = 107$, $^2J_{PP} = 34$); M = Cr, ^{31}P-{^{1}H} NMR (C_6D_6, 121.5 MHz), δ 32.8 (dt, 1P, RhP, $^1J_{RhP} = 209$, $^2J_{PP} = 41$) and 209.9 (dd, 2P, μ-PPh_2, $^1J_{RhP} = 142$, $^2J_{PP} = 41$ Hz).

Reactions of the acyl (3) and μ-acyl (4) compounds with H_2, CO and H_2–CO

4 (M = Mo, $n = 2$) with CO. A solution of compound **4** (M = Mo, $n = 2$) (54 mg, 0.057 mmol) in benzene (15 cm^3) was treated with CO (400 psi) at 80 °C for 30 min. Solvent removal *in vacuo* and subsequent preparative TLC (eluent hexane–dichloromethane, 1:2), yielded unchanged **4** (45 mg).

3 (M = W, $n = 2$) with H_2–CO. A solution of compound **3** (M = W, $n = 2$) (55 mg, 0.053 mmol) in benzene (15 cm^3) was treated with H_2 and CO (1:1, 400 psi) at 80 °C for 30 min. Removal of the solvent *in vacuo* gave the crude product as a red residue (60 mg). Spectroscopic analysis showed the presence of **3** (M = W, $n = 2$) (48%), **4** (M = W, $n = 2$) (36%) and **13** (16%).

Compound **4** (M = W, $n = 2$): m.p. 195–198 °C (Found: C, 51.3; H, 3.8; P, 8.3. $C_{45}H_{38}O_5P_3RhW$ requires C, 52.1; H, 3.7; P, 8.9%). NMR ($CDCl_3$): ^{1}H (200 MHz), δ −0.20 (d, 3 H, CH_3, $^3J_{HH} = 6.8$), 0.4–0.65 (m, 1 H, CH), 1.9–2.2 (m, 2 H, CH_2), 2.6–2.9 (m, 2 H, CH_2) and 7.0–7.95 (m, 30 H, C_6H_5); ^{31}P-{^{1}H} (121.5 MHz), δ 27.5 (ddd, 1P, RhP, $^1J_{RhP} = 159$, $^2J_{PP} = 39$, 32), 173.9 (ddd, 1P, μ-PPh_2, $^1J_{RhP} = 132$, $^2J_{PP} = 101$, 39) and 181.1 (ddd, 1P, μ-PPh_2, $^1J_{RhP} = 132$, $^2J_{PP} = 101$, 32); ^{13}C-{^{1}H} (50 MHz), δ 13.7 (s, CH_3), 23.9 (d, CH_2, $^1J_{PC} = 16$), 26.6 (s, CH_2), 34.8 (d, CH_2, $^1J_{PC} = 30$ Hz), 127.5–143 (C_6H_5) and 194.7 (s, WCO). IR (CH_2Cl_2): ν(CO) 2029s, 1933vs, 1918vs and 1840vs cm^{-1}.

Compound **13** (M = W): NMR ($CDCl_3$), ^{1}H (200 MHz), δ −13.1 (t, 1 H, RhH, $^1J_{RhH} = 13.6$), 0.85 (d, 3 H, CH_3, $^3J_{HH} = 6.6$), 9.3 (s br, 1 H, CHO), other peaks hidden by resonances due to **3** and **4**; ^{31}P-{^{1}H} (121.5 MHz), δ 44.0 (dt, 1P, RhP, $^1J_{RhP} = 159$, $^2J_{PP} = 34$) and 169.5 (dd, 2P, μ-PPh_2, $^1J_{RhP} = 107$, $^2J_{PP} = 34$ Hz).

4 (M = Mo, $n = 2$) with H_2. A solution of compound **4** (M = Mo, $n = 2$) (0.11 g, 0.12 mmol) in benzene (15 cm^3) was treated with H_2 (400 psi) at 80 °C for 30 min. Solvent removal *in vacuo* gave the crude product as a dark red residue (0.11 g). Spectroscopic analysis showed the presence of **4** and a small amount of another compound. Purification of the crude product by preparative TLC (eluent hexane–dichloromethane, 1:1) resulted in isolation of a minor red band (12 mg) tentatively characterized as **12**, followed by a major red-orange band identified as **4** (60 mg).

Complex **12** (M = Mo): NMR ($CDCl_3$), ^{1}H (200 MHz), δ −13.8 (t, 1 H, RhH, $^1J_{RhH} = 14$), methylene and methyl region could not be assigned due to impurities, 6.5–8.2 (m, 30 H, C_6H_5); ^{31}P-{^{1}H} (121.5 MHz), δ 46.6 (dt, 1P, RhP, $^1J_{RhP} = 160$, $^2J_{PP} = 42$) and 195.2 (dd, 2P, μ-PPh_2, $^1J_{RhP} = 110$, $^2J_{PP} = 42$ Hz).

3 (M = W, $n = 2$) with H_2. A solution of compound **3** (M = W, $n = 2$) (55 mg, 0.053 mmol) in benzene (15 cm^3) was treated with H_2 (400 psi) at 80 °C for 30 min. Solvent removal *in vacuo*

Table 5 Crystal and refinement data for compounds **3** (M = W, *n* = 2), **4** (M = Cr, *n* = 1) and **4** (M = Mo, *n* = 2)

	3 (M = W, *n* = 2)	**4** (M = Cr, *n* = 1)	**4** (M = Mo, *n* = 2)*
Formula	$C_{45}H_{38}O_5P_3RhW$	$C_{44}H_{36}CrO_5P_3Rh$	$C_{45}H_{38}MoO_5P_3Rh$
M_r	1038.5	892.6	950.6
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	20.377(2)	18.180(5)	11.867(3)
b/Å	16.449(3)	11.070(2)	19.203(5)
c/Å	12.931(1)	22.327(5)	18.344(6)
β/°	102.66(1)	115.54(2)	98.57(2)
U/Å^3	4229(1)	4054(2)	4134(2)
D_c/g cm^{-3}	1.63	1.46	1.53
Z	4	4	4
F(000)	2048	1816	1920
μ(Mo-Kα)/cm^{-1}	33.1	8.2	8.4
Crystal size/mm	0.27 × 0.20 × 0.10 (dark red, tabular)	0.20 × 0.40 × 0.70 (dark red, prism)	0.65 × 0.30 × 0.65 (dark red, prism)
$\bar{T}_{min,\ max}$	0.52, 0.72	0.75, 0.85	0.75, 0.88
$2\theta_{max}$/°	60	55	50
N	12 305	11 800	7234
N_o	4062	7950	5937
R	0.048	0.043	0.054
R'	0.041	0.044	0.065

* The phenyl (4*n*) ring was disordered over two sites each with population = 0.5. Atoms C(6) and C(7) were also refined in two positions also with population = 0.5.

resulted in a red residue (50 mg), which was tentatively characterized as **12** from spectroscopic data: NMR ($CDCl_3$), ^{1}H (200 MHz), δ −13.1 (t, 1 H, RhH, $^1J_{RhH}$ = 14 Hz), 0.69 (t, 3 H, CH_3, $^3J_{HH}$ = 7.0), 0.8–0.95 (m, 2 H, CH_2), 1.1–1.7 (m br, 2 H, CH_2), 2.3–2.6 (m, 2 H, CH_2) and 6.8–7.95 (m, 30 H, C_6H_5); ^{31}P-{^{1}H} (121.5 MHz), δ 43.4 (dt, 1P, RhP, $^1J_{RhP}$ = 159, $^2J_{PP}$ = 35 Hz) and 169.8 (dd, 2P, μ-PPh_2, $^1J_{RhP}$ = 108, $^2J_{PP}$ = 35 Hz); IR (CH_2Cl_2) ν(CO) 2029m, 1933vs and 1918s cm^{-1}; EI mass spectrum: *m*/*z* 262 (65), 242 (16), 199 (90), 183 (98), 152 (20), 108 (55), 107 (35), 91 (19), 78 (100), 77 (45) and 51 (34%).

Crystallography

Unique room-temperature four-circle diffractometer data sets were measured (2θ–θ scan mode, $2\theta_{max}$ as specified; monochromatic Mo-Kα radiation, λ = 0.7107$_3$ Å; $T \approx 295$ K) yielding N independent reflections, N_o of these being used in the full-matrix least-squares refinement after analytical, **3** (M = W), or Gaussian, **4** (M = Cr or Mo), absorption corrections and solution of the structures by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values [exception: **4** (M = Cr) in which they were refined]. Conventional residuals R, R' on $|F_o|$ are quoted at convergence, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$, **4** (M = Cr or Mo), or $\sigma^2(I) = \sigma^2(I_{diff})$, **3** (M = W), being employed. Computation used TEXSAN, **3** (M = W),[15] or XTAL 3.2, **4** (M = Cr or Mo),[16] program systems, neutral atom complex scattering factors being employed. Pertinent crystal data are given in Table 5.

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