Synthesis and Reactions of $[(OC)_2Re(\mu\text{-dppm})_2(\mu\text{-Cl})_2Rh(\eta^2\text{-}C_2H_4)]$ (dppm = $Ph_2PCH_2PPh_2$): Crystal Structure of the 1 : 2 Chlorobenzene Solvate†

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Treatment of $[ReCl(CO)_5]$ with $Ph_2PCH_2PPh_2$ (dppm) gives *mer,cis*-$[ReCl(CO)_2$(dppm-*PP'*)(dppm-*P*)] (**1**). The uncomplexed phosphorus of (**1**) is readily quaternized by $[OMe_3][BF_4]$ to give *mer,cis*-$[ReCl(CO)_2$(dppm-*PP'*)$(Ph_2PCH_2PPh_2Me)]BF_4$ (**2**). Treatment of complex (**1**) with $[Rh_2Cl_2(C_2H_4)_4]$ gives $[(OC)_2Re(\mu\text{-dppm})_2(\mu\text{-Cl})_2Rh(\eta^2\text{-}C_2H_4)]$ (**3**). The ethylene ligand in (**3**) is readily displaced by allene to give $[(OC)_2Re(\mu\text{-dppm})_2(\mu\text{-Cl})_2Rh(\eta^2\text{-}C_3H_4)]$ (**4**). When complex (**3**) is treated with dihydrogen $[(OC)_2Re(\mu\text{-dppm})_2(\mu\text{-Cl})(\mu\text{-H})RhH(Cl)]$ (**5**) is formed; with CO $[Cl(OC)Re(\mu\text{-dppm})_2(\mu\text{-Cl})(\mu\text{-CO})Rh(CO)]$ (**6**) is initially formed but this reacts further to give $[(OC)_3Re(\mu\text{-dppm})_2(\mu\text{-Cl})Rh(CO)]Cl$ (**7a**). The complexes (**6**) and (**7a**) were more readily prepared by treating (**1**) with $[Rh_2Cl_2(CO)_4]$. The chloride salt (**7a**) was converted into the corresponding PF_6 (**7b**) and BPh_4 (**7c**) salts. We also report the corresponding iridium salt $[(OC)_3Re(\mu\text{-dppm})_2(\mu\text{-Cl})Ir(CO)]PF_6$ (**8**). N.m.r. and i.r. data are given. Crystals of (**3**) are monoclinic, space group $P2_1/n$ (= $P2_1/c$, no.14) with a = 1 027.5(8), b = 2 996.5(9), c = 2 142.2(5) pm, and β = 92.50(2)°; final R and R' values 0.0485 and 0.0518, respectively for 6 816 unique reflections with $I > 2.0\sigma(I)$. The crystal structure shows an η^2-ethylene, terminally bound to the rhodium atom, with an unusually long carbon–carbon distance [150(2) pm].

There is considerable interest in the synthesis and reactions of complexes containing the framework $M(\mu\text{-dppm})_2M'$, where M and M′ are different metals and dppm = $Ph_2PCH_2PPh_2$. However, no examples of complexes of this type containing rhenium have been reported. Previously, we have described the preparation and reactions of bis(dppm) complexes containing manganese with other metals such as platinum, rhodium, or iridium.[1–3] These were prepared using *mer,cis*-$[MnCl(CO)_2$(dppm-*PP'*)(dppm-*P*)] as precursor. We now report the synthesis of the corresponding rhenium complex and its use in the synthesis of some heterobimetallic complexes with rhodium or iridium, particularly a rhenium–rhodium–ethylene complex. The chemistry of rhenium–dppm complexes has thus far been restricted to dirhenium carbonyls,[4] to complexes containing rhenium–rhenium multiple bonds,[5] and also *fac*-$[ReH(CO)_3$(dppm-*PP'*)] and its carbon disulphide adduct.[6]

Results and Discussion

Displacement of the carbon monoxides from $[ReCl(CO)_5]$, by other ligands, is quite slow but we find that when heated with dppm in boiling mesitylene the required complex *mer,cis*-$[ReCl(CO)_2$(dppm-*PP'*)(dppm-*P*)] (**1**) is formed and was isolated in 87% yield. Preparative details are in the Experimental section and the Scheme and characterizing microanalytical and i.r. and n.m.r. data are given in Tables 1 and 2. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed four non-equivalent phosphorus nuclei with chemical shifts at $\delta(P_a) = -27.0$, $\delta(P_b) = 10.3$, $\delta(P_c) = -20.2$, and $\delta(P_d) = -43.7$ p.p.m., each showing phosphorus–phosphorus coupling. Of note is $^2J(P_bP_c)$ of 181 Hz which is typical of *trans*-phosphines co-ordinated to a metal such as rhenium(I). The $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum, in the PCH_2P region, shows two AB quartets; the one at higher frequency is typical of a chelating ligand and the other is typical of a monodentate dppm ligand. The i.r. spectrum in the carbonyl region shows two very strong bands, at 1 936 and 1 837 cm^{-1}. On treatment with $[OMe_3][BF_4]$ complex (**1**) was readily quaternized to give (**2**) (see Scheme).

We have used complex (**1**) for the synthesis of mixed rhenium–rhodium complexes and the most interesting of these is the one generated from $[Rh_2Cl_2(C_2H_4)_4]$, which we describe first. Treatment of (**1**) with $[Rh_2Cl_2(C_2H_4)_4]$ in benzene gave a hoped for rhenium–rhodium–ethylene complex, as a pale yellow powder. In order to prepare crystals of this complex suitable for *X*-ray diffraction we performed a similar synthesis using chlorobenzene as solvent and obtained the same heterobimetallic complex as air-stable yellow prisms of the chlorobenzene solvate. The crystal structure determination (see below) shows this complex to be $[(OC)_2Re(\mu\text{-dppm})_2(\mu\text{-Cl})_2Rh(\eta^2\text{-}C_2H_4)]$ (**3**) (see Scheme and below). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**3**) was deceptively very simple, showing a singlet at 6.9 p.p.m. and a doublet at 28.0 p.p.m. [$^1J(RhP)$ = 117 Hz, width at half height = 0.2 Hz] of equal total relative intensity. Usually bis(dppm) complexes of this type give rise to AA′XX′ or AA′BB′ type $^{31}P\text{-}\{^1H\}$ n.m.r. spectra and the very unusual pattern for complex (**3**) presumably arises because $K \gg L$ and $M \gg L$ and 'N' = 0.[7]‡ Treatment of (**3**) with other ligands gave complexes showing typical AA′MXX′ spin systems (see below). The $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum of (**3**) showed a singlet of relative intensity two at 4.27 p.p.m. (typical of bridging PCH_2P) and a doublet of relative intensity four at 0.98 p.p.m. [$^2J(RhH)$ = 2.7 Hz], which is assigned to the η^2-ethylene ligand. This chemical shift is at the lower end of the range reported for co-ordinated ethylene ligands.[8] In the ^1H n.m.r. spectrum the ethylene hydrogens are coupled to the P nuclei bound to rhodium, giving a 1 : 2 : 1 triplet with an apparent coupling constant of 4.6 Hz. There is no evidence for ethylene rotation in the complex, the n.m.r. spectrum being temperature invariant from +30 to −50 °C, below which temperature the complex starts to crystallize: thus

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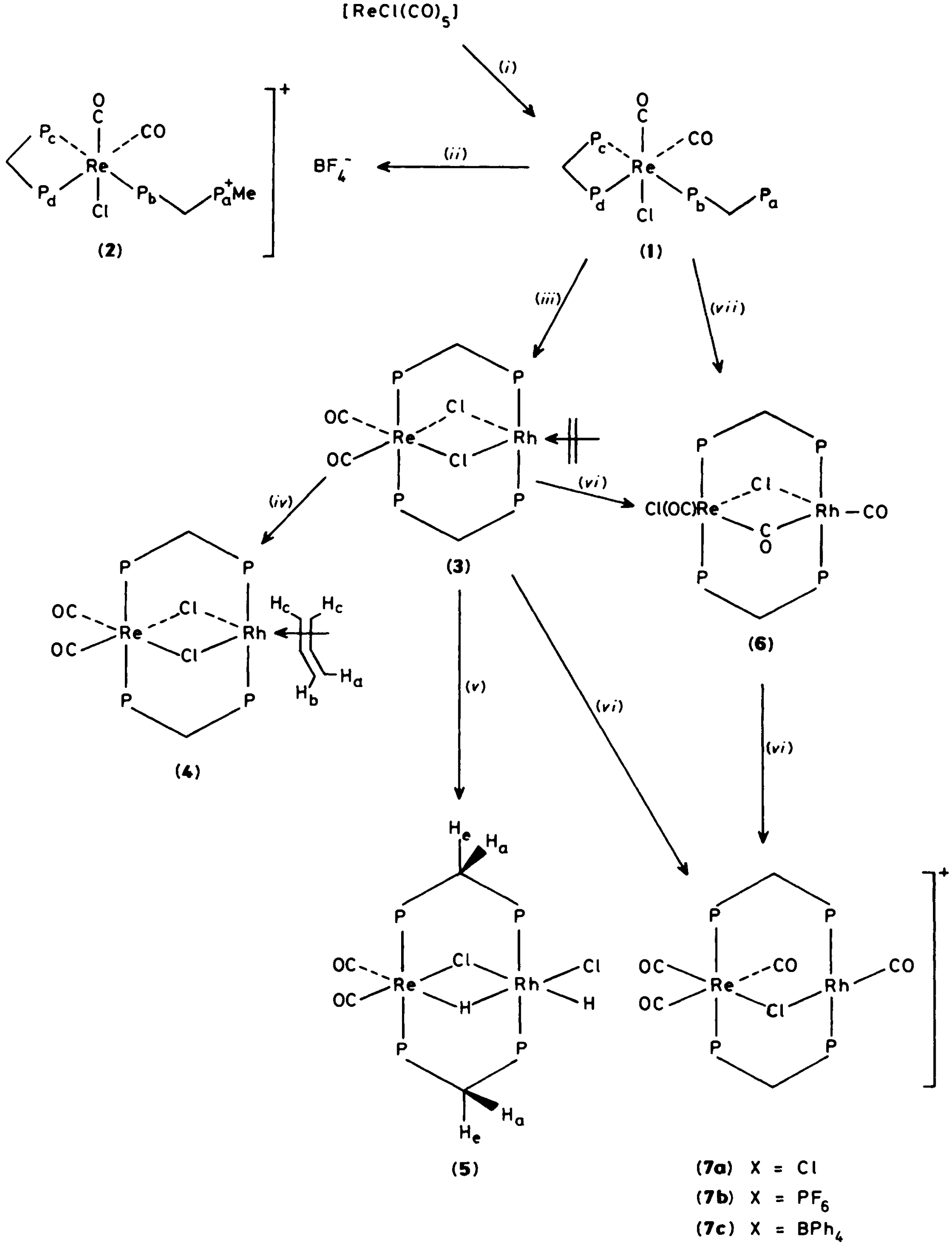
† Bis[μ-bis(diphenylphosphino)methane]-2,2-dicarbonyl-di-μ-chloro-1-η-ethylenerhodiumrhenium–chlorobenzene (1/2).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

‡ AA′XX′ spectra are defined in terms of four parameters K, L, M, and N, where $K = J(AA') + J(XX')$, $L = J(AX) + J(AX')$, $M = J(AA') - J(XX')$, and $N = J(AX) - J(AX')$.



Scheme. (*i*) dppm in boiling xylene; (*ii*) $[OMe_3][BF_4]$; (*iii*) $[Rh_2Cl_2(C_2H_4)_4]$; (*iv*) allene; (*v*) H_2; (*vi*) CO; (*vii*) $[Rh_2Cl_2(CO)_4]$

the four ethylene hydrogens and the two rhodium-bound P nuclei form a second-order spin system and the triplet ^1H n.m.r. pattern is a virtual triplet. The i.r. spectrum of (**3**) (Table 1) shows two strong carbonyl bands, at 1 849 and 1 952 cm^{-1}. The crystal structure is described below.

Treatment of complex (**3**) with allene caused displacement of ethylene and gave the allene complex $[(OC)_2Re(\mu\text{-dppm})_2(\mu\text{-}Cl)_2Rh(\eta^2\text{-}C_3H_4)]$ (**4**). Analytical and i.r. data are given in Table 1. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed a deceptively simple AA'MXX' spin pattern with $N = 2$ Hz. The $^1H\text{-}\{^{31}P\}$ n.m.r. pattern of the PCH_2P protons appears as an AB quartet, presumably because of the asymmetry introduced by the allene ligand. The allene proton resonances occur at δ 4.37, 4.43, and 0.46 p.p.m. with relative intensities of 1 : 1 : 2. Selective $^1H\text{-}\{^{31}P\}\text{-}\{^1H\}$ decoupling experiments gave the proton–proton and rhodium–proton coupling constants shown in Table 2. In the ^1H n.m.r. spectrum both the PCH_2P and allene protons gave complex multiplets due to phosphorus coupling. The i.r. spectrum (Nujol mull) in the carbonyl region gave two bands with similar frequencies to those of the ethylene complex (**3**), see Table 1.

The ethylene complex (**3**), when treated with dihydrogen (1

Table 1. Analytical and i.r. data

Complex	Analysis (%)^{a} C	H	Cl	$\nu(C{\equiv}O)^{b}$/cm^{-1}
(1)	59.4 (59.7)	4.2 (4.2)	3.5 (3.4)	1 837s, 1 936s
(2)	55.6 (55.4)	4.2 (4.1)	2.7 (3.1)	1 858s, 1 933s
(3)·2C_6H_5Cl	54.85 (55.1)	4.05 (4.05)	9.2 (9.8)	1 849s, 1 952s
(4)	53.8 (53.95)	3.7 (3.95)	5.7 (5.8)	1 849s, 1 955s
(5)	52.35 (52.6)	3.6 (3.9)	6.1 (5.95)	1 857s, 1 936s
(6)·0.5C_6H_6	53.7 (53.7)	3.7 (3.8)	5.75 (5.75)	1 817s, 1 925s, 1 983s
(7b)·0.33CH_2Cl_2	46.9 (47.3)	3.2 (3.3)	4.25 (4.25)	1 895 (sh), 1 910m, 1 943s, 1 998s, 2 028m [1 906 (sh), 1 932s, 1 997s, 2 042w]^{c}
(7c)	61.65 (61.45)	4.2 (4.25)	2.75 (2.35)	1 880m, 1 912s, 1 933m, 1 978s, 1 995s, 2 040m [1 912 (sh), 1 938s, 2 001s, 2 047w]^{c}
(8)	45.3 (45.1)	3.3 (3.1)	2.7 (2.5)	1 892s,br, 2 007s

^{a} Calculated values in parentheses. The presence of solvent of crystallization was confirmed by ^{1}H n.m.r. spectroscopy. ^{b} As Nujol mulls, unless stated otherwise; s = strong, m = medium, w = weak, br = broad, and sh = shoulder. ^{c} In CH_2Cl_2 solution.

Table 2. ^{31}P-$\{^{1}$H$\}$,^{a,b} ^{1}H,^{b,c} and ^{1}H-$\{^{31}$P$\}^{b,c}$ n.m.r. data

Complex	$\delta(P_A)^{d}$	$\delta(P_B)^{d}$	$^{1}J(RhP)$	N^{e}	Methylene	Other hydrogens
(3)	6.9	28.0	117	0	4.27	C_2H_4 0.98 [$^{2}J(RhH) = 2.7$, $^{3}J(PH) = 4.6$]
(4)^{f}	7.2	23.9	118	2	4.67, 3.97 [$^{2}J(HH) = 13.1$]	H_a 4.43, H_b 4.37, H_c 0.46 [$J(RhH_a) = 2.1$, $J(RhH_b) = 1.8$, $J(RhH_c) = 2.5$, $J(H_aH_b) = 2.2$, $J(H_aH_c) = 2.5$, $J(H_bH_c) = 2.5$]
(5)^{f}	9.4	15.4	101	83	H_e 4.42, H_a 3.36 [$^{2}J(H_eH_a) = 13.0$, $J(RhH_e) = 2.1$, $J(H_eH_d) = 2.2$]	Hydrides H_c −16.04, H_d −17.50 [$J(RhH_c) = 19.0$, $J(RhH_d)$ 31.0, $J(H_cH_d) = 2.5$]
(6)	4.1	19.2	120	33	4.40, 3.70 [$^{2}J(HH) = 12.8$]	
(7b)	−0.4	21.4	110	49	3.84 (s at 21 °C) 4.16, 3.42 [$^{2}J(HH) = 12.8$ (−60 °C)]	
(7c)	−0.3	21.5	108	47	3.79 (br s at 21 °C) 4.11, 3.37 [$^{2}J(HH) = 12.7$ (−50 °C)]	
(8)	2.1	7.0		59	4.40, 3.70 [$^{2}J(HH) = 12.8$]	

^{a} Chemical shifts ($\delta \pm 0.1$ p.p.m.) relative to 85% H_3PO_4 (positive to high frequency); coupling constants, $J \pm 2$ Hz. Spectra were recorded at +21 °C, unless stated otherwise. ^{b} In CD_2Cl_2 solution. ^{c} Chemical shifts ($\delta \pm 0.01$ p.p.m.) relative to tetramethylsilane; coupling constants, $J \pm 0.2$ Hz. Spectra recorded at 21 °C, unless stated otherwise. ^{d} P_A and P_B refer to the phosphorus atoms co-ordinated to rhenium and rhodium, respectively. ^{e} $N = |^{2}J(P_AP_B) + {}^{4}J(P_AP_B)|$. ^{f} The hydrogens for compounds (4) and (5) are labelled as in the Scheme.

Table 3. Selected interatomic distances (pm) and angles (°) for $[(OC)_2Re(\mu\text{-dppm})_2(\mu\text{-Cl})_2Rh(\eta^2\text{-}C_2H_4)]$ (3) with estimated standard deviations (e.s.d.s) in parentheses

Re···Rh	364.4(5)		
Re–Cl(1)	251.9(5)	Rh–Cl(1)	252.3(5)
Re–Cl(2)	251.7(5)	Rh–Cl(2)	254.4(5)
Re–P(2)	263.4(5)	Rh–P(1)	250.1(5)
Re–P(4)	262.8(5)	Rh–P(3)	250.2(5)
Re–C(1)	189(1)	Rh–C(3)	211(1)
Re–C(2)	188(1)	Rh–C(4)	207(1)
C(1)–O(1)	115(1)	C(3)–C(4)	150(2)
C(2)–O(2)	114(1)		
Re–Cl(1)–Rh	92.6(2)	Re–Cl(2)–Rh	92.1(2)
P(2)–Re–P(4)	168.0(1)	P(1)–Rh–P(3)	172.0(1)
Cl(1)–Re–Cl(2)	88.0(2)	Cl(1)–Rh–Cl(2)	87.3(2)
C(1)–Re–C(2)	86.0(5)	C(3)–Rh–C(4)	41.9(4)
Re–C(1)–O(1)	178.3(8)	Rh–C(3)–C(4)	67.8(6)
Re–C(2)–O(2)	175.8(8)		

atm, *ca.* 10^5 Pa) for 16 h in dichloromethane solution, gave the dihydride $[(OC)_2Re(\mu\text{-dppm})_2(\mu\text{-Cl})(\mu\text{-H})RhH(Cl)]$ (5), as yellow crystals: analytical and i.r. data are in Table 1. The ^{31}P-$\{^{1}$H$\}$ n.m.r. spectrum showed the expected AA′MXX′ pattern (Table 2). In the ^{1}H-$\{^{31}$P$\}$ n.m.r. spectrum, one hydride resonates at −16.04 and the other at −17.5 p.p.m.; both are coupled to rhodium, $^{1}J(RhH) = 19.0$ and 31.0 Hz, respectively, and mutually coupled, $^{2}J(HH) = 2.5$ Hz. Selective decoupling experiments on the ^{1}H spectral resonances established that the hydride resonating at −17.5 p.p.m. is coupled to all four P nuclei whilst the other is coupled only to the P nuclei bonded to rhodium [$^{3}J(PH) = 15.7$ Hz]. These data indicate that the hydride resonating at −17.5 p.p.m. is bridging or semi-bridging and the other, resonating at −16.04 p.p.m., is terminal on rhodium. Moreover, the ^{1}H-$\{^{31}$P$\}$ n.m.r. pattern of the PCH_2P protons shows non-equivalent hydrogens, one of which (the pseudo-equatorial hydrogen, H_e) is coupled to both rhodium (2.1 Hz) and to the bridging hydride [$^{4}J(HH) = 2.2$ Hz], whilst the pseudo-axial hydrogen, H_a, is not coupled to either but is of course coupled to H_e [$^{2}J(H_eH_a) = 13.0$ Hz]. We have observed coupling of pseudo-equatorial dppm (CH_2) hydrogens to metals and to bridging hydrides, previously,[9] whereas pseudo-axial methylene hydrogens do not show these couplings: the coupling is dependent on the dihedral angle H–C–P–M (M = metal), which will be approximately 180° for the pseudo-equatorial hydrogen but only about 60° for the pseudo-axial hydrogen.[10,11] The i.r. spectrum shows two $\nu(C{=}O)$ bands with similar frequencies to those of complexes (3) and (4), indicating that both carbonyls are terminal: no metal–hydrogen stretching frequencies were observed; presumably the band due to $\nu(Rh–H)$ was too low in intensity to observe or was obscured by a more intense band due to $\nu(C{=}O)$. We assign structure (5) to this dihydride complex.

When a dichloromethane solution of complex (3) was treated with CO there was an immediate colour change to bright yellow

Table 4. Rhodium–carbon and carbon–carbon bond lengths (pm) for the rhodium–ethylene unit of some crystallographically characterized rhodium–ethylene complexes

Complex[a]	C–C	Rh–C^1	Rh–C^2	Ref.
(3)	150(2)	211(1)	207(1)	Present work
[Rh(acac)(C_2F_4)(C_2H_4)]	142(2)	219(1)	219(1)	*b*
[Rh(acac)(C_2H_4)$_2$]	141(3)	213(2)	214(2)	*b*
[Rh(C_5Me_5)(PPh_3)(C_2H_4)]	140.8(16)	209.6(9)	208.9(11)	*c*
[Rh(MeCN)(C_2H_4)$_3$]BF_4	136(3)	224(2)	225(2)	*d*
[RhCl(PPr^i_3)$_2$(C_2H_4)]	131.9(4)	211.6(2)	212.8(2)	*e*

[a] acac = Acetylacetonate. [b] J. A. Evans and D. R. Russell, *Chem. Commun.*, 1971, 197. [c] W. Porzio and M. Zocchi, *J. Am. Chem. Soc.*, 1978, **100**, 2048. [d] G. Del Piero, G. Perego, and M. Cesari, *Cryst. Struct. Commun.*, 1974, 3, 15. [e] C. Busetto, A. D'Alfonso, F. Maspero, G. Perego, and A. Zaggettta, *J. Chem. Soc., Dalton Trans.*, 1977, 1828.

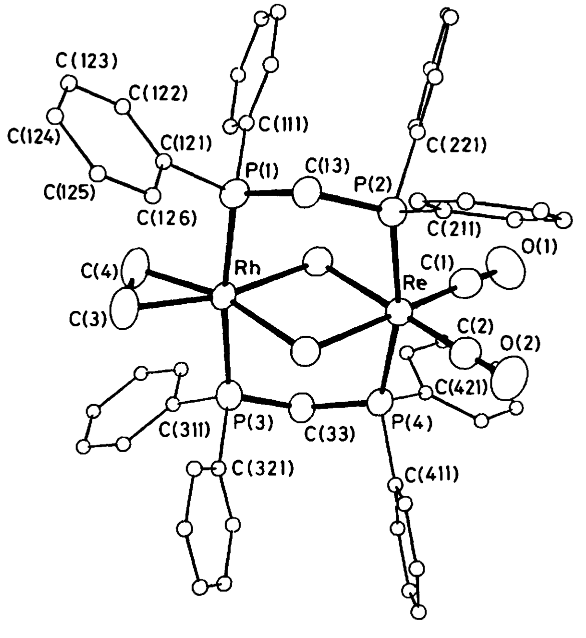


Figure. Molecular structure of [$(OC)_2Re(\mu\text{-dppm})_2(\mu\text{-Cl})_2Rh(\eta^2\text{-}C_2H_4)$] (3) showing the principal atomic numbering

and a $^{31}P\text{-}\{^1H\}$ n.m.r. study showed that the tricarbonyl complex (**6**) was formed (see below for characterization), but that further treatment with CO gave the tetracarbonyl salt (**7a**). This salt was not obtained analytically pure and was only characterized by its $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum which showed virtually identical parameters to those of the PF_6 (**7b**) and BPh_4 (**7c**) salts (below). A better method of preparing (**6**) was to treat (**1**) with [$Rh_2Cl_2(CO)_4$], when it was obtained as yellow prisms. A similar treatment of (**1**) with [$Rh_2Cl_2(CO)_4$] in the presence of ammonium hexafluorophosphate gave the tetracarbonyl hexafluorophosphate salt (**7b**), which was in turn converted into the BPh_4 salt on treatment with $NaBPh_4$; preparative details are in the Experimental section and microanalytical data are given in Table 1. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of complex (**6**) showed the expected AA'MM'X pattern. The $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum in the PCH_2P region showed an AB quartet (Table 2). The i.r. spectrum showed three strong C=O bands, at 1 983, 1 925, and 1 817 cm^{-1}, the lowest-frequency band suggesting a bridging or semi-bridging carbonyl ligand. We think it likely that one of the bridging chlorines remains and therefore we formulate the complex as shown. The tetracarbonyl salts (**7b**) and (**7c**) each show four carbonyl bands with frequencies $>1\ 900$ cm^{-1} and clearly there are no bridging or semi-bridging carbonyls: it also seems very likely that the bridging chloride ligand is retained, indeed the crystal structure of (**7c**) has been determined.* The BPh_4^- salt (**7c**) gives an AA'MM'X $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum whilst the $^1H\text{-}\{^{31}P\}$ spectrum shows a singlet at +21 °C but an AB quartet at −60 °C, as would be expected from the assigned structure. We do not know what this fluxional process is: a similar equivalence of CH_2 protons was observed for complexes of type *trans,trans*-[$(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2IrCl(CO)$] for which we tentatively suggested the involvement of an intermediate *cis*-planar $P_2IrCl(CO)$ moiety.[9] Alternatively, in our compound (**7c**), the CO groups and the Cl might be scrambling around both metals at room temperature: because of the complex spin–spin coupling by the P_4 spin system it was not possible to record ^{13}C n.m.r. spectra to try to confirm this. The i.r. spectrum, both in dichloromethane solution and as a Nujol mull (see Table 1), showed that all the carbonyls are terminal. The PF_6 salt (**7b**) shows similar behaviour and clearly has an analogous structure.

We also report the synthesis of the iridium complex [$(OC)_3Re(\mu\text{-dppm})_2(\mu\text{-Cl})Ir(CO)$]$PF_6$ (**8**), formed by treating (**1**) with [$IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)$]. We suggest it has an analogous structure to (**7b**). Its $^1H\text{-}\{^{31}P\}$ spectrum, however, shows an AB pattern in the PCH_2P region, *i.e.* it is not fluxional on the n.m.r. time-scale at ambient temperature.

Crystal Structure of [$(OC)_2Re(\mu\text{-dppm})_2(\mu\text{-Cl})_2Rh(\eta^2\text{-}C_2H_4)$]$\cdot 2C_6H_5Cl$ (**3**).—The structure is shown in the Figure and selected intramolecular distances and angles are given in Table 3. The structure shows an essentially planar $(OC)_2Re(\mu\text{-Cl})_2Rh(C_2)$ moiety which is approximately perpendicular to the plane of the four phosphorus atoms. The two carbonyl ligands are terminally bound to the rhenium and the two chloride ligands symmetrically bridge the rhenium and rhodium atoms. The ethylene is η^2-terminally bound to the rhodium with a carbon–carbon distance [150(2) pm] which is significantly longer than any previously reported for η^2-bound ethylene. Table 4 summarizes the data for η^2-ethylene complexes of rhodium. The unusually long carbon–carbon distance in (**3**) and also the unusually short Rh–C(3) and Rh–C(4) distances (see Table 4) suggest that the ethylene ligand is unusually strongly bonded to the rhodium. This strong bonding may in part be due to the strongly donating phosphine ligands promoting back co-ordination, d_π(rhodium)→π^*(ethylene). The remarkably low δ value for the ethylene hydrogens (0.98 p.p.m., Table 2) also suggests an unusually bonded ethylene ligand, *viz.* a rhodacyclopropane type structure.

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* The crystal structure of (**7c**) was determined as its dichloromethane solvate, in a sealed capillary, in the presence of solvent and gave a rather poor data set. However, the structure could be solved and shows three terminal carbonyls on rhenium and one on rhodium and a bridging chlorine. It was not of sufficient accuracy to publish in this paper but further details may be obtained from the Authors.

Experimental

The general procedures and apparatus used were the same as in other recent publications from this Laboratory.[1]

mer,cis-$[ReCl(CO)_2(dppm\text{-}PP')(dppm\text{-}P)]$ (**1**).—A solution of $[ReCl(CO)_5]$ (0.50 g, 1.38 mmol) and dppm (1.12 g, 2.91 mmol) in mesitylene (30 cm^3) was refluxed until the $\nu(C\equiv O)$ band at 2 036 cm^{-1}, corresponding to $[ReCl(CO)_3(dppm\text{-}PP')]$, had disappeared, typically 9 h. The solution was then allowed to cool, giving the required product (**1**) as white microcrystals. Yield 1.27 g, 87%. N.m.r. (CD_2Cl_2): $^{31}P\text{-}\{^1H\}$, $\delta(P_a)$ −27.0, $\delta(P_b)$ 10.3, $\delta(P_c)$ −20.2, $\delta(P_d)$ −43.7 p.p.m.; $^2J(P_aP_b) = 47$, $^4J(P_aP_c) = 5$, $^2J(P_bP_c) = 181$, $^2J(P_bP_d) = 27$, $^2J(P_cP_d) = 6$ Hz; $^1H\text{-}\{^{31}P\}$, δ(H) 5.35, 4.81 [$^2J(HH) = 14.7$]; 3.77, 2.47 p.p.m. [$^2J(HH) = 15.4$ Hz].

mer,cis-$[ReCl(CO)_2(dppm\text{-}PP')(Ph_2PCH_2PPh_2Me)]BF_4$ (**2**).—The salt $[OMe_3][BF_4]$ (0.042 g, 0.29 mmol) was added to a solution of complex (**1**) (0.20 g, 0.19 mmol) in dichloromethane (8 cm^3) and the mixture was stirred for 3 h. It was then filtered and the filtrate evaporated to dryness. The residue was triturated with diethyl ether, giving the required product as white microcrystals. Yield 0.20 g, 92%. N.m.r. (CD_2Cl_2): $^{31}P\text{-}\{^1H\}$, $\delta(P_a)$ 19.9, $\delta(P_b)$ 11.7, $\delta(P_c)$ −20.5, $\delta(P_d)$ −46.4 p.p.m.; $^2J(P_aP_b) = 12$, $^4J(P_aP_c) = 2$, $^2J(P_bP_c) = 190$, $^2J(P_bP_d) = 27$, $^2J(P_cP_d)$ *ca.* 0 Hz. $^1H\text{-}\{^{31}P\}$, $\delta(PCH_2P)$ 5.39, 4.74 [$^2J(HH) = 14.9$], 4.85, 3.47 [$^2J(HH) = 14.4$]; $\delta(PCH_3)$ 2.61 p.p.m. [$^2J(PH) = 14.1$ Hz].

$[(OC)_2Re(\mu\text{-}dppm)_2(\mu\text{-}Cl)_2Rh(\eta^2\text{-}C_2H_4)]$ (**3**).—The complex $[Rh_2Cl_2(C_2H_4)_4]$ (0.093 g, 0.24 mmol) was added to a solution of (**1**) (0.50 g, 0.48 mmol) in benzene (15 cm^3) and the resultant mixture stirred for 2 h. This gave the required product as yellow microcrystals which were collected, *etc.* Yield 0.40 g, 69%. When chlorobenzene was used instead of benzene, (**3**) was obtained, as a chlorobenzene solvate, in 40% yield.

$[(OC)_2Re(\mu\text{-}dppm)_2(\mu\text{-}Cl)_2Rh(\eta^2\text{-}C_3H_4)]$ (**4**).—A solution of complex (**3**) (0.15 g, 0.12 mmol) in dichloromethane (10 cm^3) was saturated with allene, stoppered, and the solution put aside for 16 h. Benzene was then added and the volume of the solution reduced under vacuum to *ca.* 3 cm^3. This gave the required product as pale yellow prisms. Yield 0.091 g, 61%.

$[(OC)_2Re(\mu\text{-}dppm)_2(\mu\text{-}Cl)(\mu\text{-}H)RhH(Cl)]$ (**5**).—A solution of complex (**3**) (0.15 g, 0.12 mmol) in dichloromethane (10 cm^3) was stirred under 1 atm of dihydrogen for 16 h. The resultant solution was concentrated to *ca.* 5 cm^3, under reduced pressure, and n-hexane (10 cm^3) added. This gave the required complex as yellow prisms. Yield 0.042 g, 29%. Evaporation of the filtrate to dryness under reduced pressure and trituration of the residue with n-hexane gave a further quantity (0.075 g) of less pure product.

$[Cl(OC)Re(\mu\text{-}dppm)_2(\mu\text{-}Cl)(\mu\text{-}CO)Rh(CO)]$ (**6**).—(*i*) From complex (**1**). A solution containing $[Rh_2Cl_2(CO)_4]$ (0.019 g, 0.047 mmol) and complex (**1**) (0.10 g, 0.096 mmol) in benzene (10 cm^3) was stirred for 5 min, filtered, and ethanol (10 cm^3) was added to the filtrate. The volume of the filtrate was reduced to 3 cm^3 under vacuum to give the required product, as yellow prisms. Yield 0.056 g, 48%.

(*ii*) From complex (**7b**) (*see below*). A solution of

Table 5. Fractional atomic co-ordinates for complex (**3**) (× 10^4) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Re	7 061.0(3)	1 304.1(1)	3 790.2(1)
Rh	8 160.8(6)	1 446.8(2)	2 208.3(3)
Cl(1)	6 114(2)	1 612(1)	2 775(1)
Cl(2)	9 095(2)	1 120(1)	3 228(1)
P(1)	9 043(2)	2 190(1)	2 548(1)
P(2)	7 835(2)	2 139(1)	3 901(1)
P(3)	7 155(2)	696(1)	2 016(1)
P(4)	6 495(2)	482(1)	3 449(1)
C(1)	7 777(9)	1 079(3)	4 554(4)
O(1)	8 185(7)	937(3)	5 022(3)
C(2)	5 547(9)	1 416(3)	4 228(4)
O(2)	4 661(7)	1 467(3)	4 522(3)
C(3)	8 085(10)	1 625(4)	1 256(4)
C(4)	9 378(10)	1 433(4)	1 462(4)
C(111)	10 690(4)	2 193(2)	2 867(3)
C(112)	11 162(4)	2 555(2)	3 221(3)
C(113)	12 449(4)	2 556(2)	3 456(3)
C(114)	13 265(4)	2 196(2)	3 339(3)
C(115)	12 793(4)	1 835(2)	2 986(3)
C(116)	11 506(4)	1 834(2)	2 750(3)
C(121)	9 058(5)	2 718(2)	1 974(2)
C(122)	10 231(5)	2 874(2)	1 752(2)
C(123)	10 232(5)	3 232(2)	1 337(2)
C(124)	9 060(5)	3 434(2)	1 142(2)
C(125)	7 887(5)	3 278(2)	1 364(2)
C(126)	7 887(5)	2 920(2)	1 779(2)
C(13)	8 104(8)	2 463(3)	3 156(4)
C(211)	6 681(5)	2 591(2)	4 248(2)
C(212)	6 229(5)	2 986(2)	3 969(2)
C(213)	5 412(5)	3 269(2)	4 290(2)
C(214)	5 047(5)	3 157(2)	4 890(2)
C(215)	5 500(5)	2 763(2)	5 169(2)
C(216)	6 317(5)	2 480(2)	4 848(2)
C(221)	9 335(4)	2 259(2)	4 370(3)
C(222)	10 230(4)	1 913(2)	4 459(3)
C(223)	11 412(4)	1 990(2)	4 786(3)
C(224)	11 699(4)	2 414(2)	5 024(3)
C(225)	10 803(4)	2 760(2)	4 953(3)
C(226)	9 621(4)	2 683(2)	4 608(3)
C(311)	7 980(6)	290(2)	1 459(3)
C(312)	9 162(6)	90(2)	1 642(3)
C(313)	9 801(6)	−182(2)	1 225(3)
C(314)	9 258(6)	−254(2)	625(3)
C(315)	8 076(6)	−54(2)	443(3)
C(316)	7 437(6)	218(2)	860(3)
C(321)	5 484(5)	716(2)	1 708(3)
C(322)	4 952(5)	1 115(2)	1 479(3)
C(323)	3 670(5)	1 126(2)	1 238(3)
C(324)	2 920(5)	738(2)	1 225(3)
C(325)	3 452(5)	339(2)	1 454(3)
C(326)	4 734(5)	328(2)	1 695(3)
C(33)	7 169(8)	275(3)	2 702(4)
C(411)	4 821(4)	270(2)	3 354(3)
C(412)	3 849(4)	596(2)	3 335(3)
C(413)	2 544(4)	472(2)	3 257(3)
C(414)	2 210(4)	22(2)	3 198(3)
C(415)	3 181(4)	−303(2)	3 216(3)
C(416)	4 486(4)	−179(2)	3 294(3)
C(421)	7 224(5)	25(2)	3 997(2)
C(422)	6 473(5)	−137(2)	4 474(2)
C(423)	7 032(5)	−418(2)	4 932(2)
C(424)	8 343(5)	−536(5)	4 911(2)
C(425)	9 093(5)	−373(2)	4 433(2)
C(426)	8 534(5)	−94(2)	3 976(2)

tetraethylammonium chloride (0.024 g, 0.15 mmol) in methanol (10 cm^3) was added to a solution of complex (**7b**) (0.10 g, 0.074 mmol) in dichloromethane (10 cm^3). The volume of the solution was then reduced to *ca.* 5 cm^3 to give the required product. Yield 0.068 g, 76%.

$[(OC)_3Re(\mu\text{-dppm})_2(\mu\text{-Cl})Rh(CO)]PF_6$ (**7b**).—The complex $[Rh_2Cl_2(CO)_4]$ (0.019 g, 0.043 mmol) was added to a solution of (**1**) (0.10 g, 0.096 mmol) in dichloromethane (15 cm^3) and the resultant solution was then treated with a solution of ammonium hexafluorophosphate (0.080 g, 0.48 mmol) in methanol (20 cm^3). The mixture was then stirred for 1 h under an atmosphere of CO, after which it was evaporated to dryness under reduced pressure. The required product was isolated with dichloromethane and formed yellow needles from dichloromethane–n-hexane. Yield 0.091 g, 71%.

$[(OC)_3Re(\mu\text{-dppm})_2(\mu\text{-Cl})Rh(CO)]BPh_4$ (**7c**).—A solution of sodium tetraphenylborate (0.061 g, 0.18 mmol) in methanol (20 cm^3) was added to a solution of complex (**7b**) (0.12 g, 0.089 mmol) in acetone (10 cm^3). The solution was then evaporated to *ca.* 5 cm^3 under reduced pressure and set aside. This gave the required complex as yellow needles. Yield 0.081 g, 62%.

$[(OC)_3Re(\mu\text{-dppm})_2(\mu\text{-Cl})Ir(CO)]PF_6$ (**8**).—The complex $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$ (0.037 g, 0.096 mmol) was added to a mixed solution, saturated with CO, and prepared from (**1**) (0.10 g, 0.096 mmol) in dichloromethane (15 cm^3) and ammonium hexafluorophosphate (0.080 g, 0.48 mmol) in methanol (20 cm^3). The resultant mixture was stirred for 1 h and then evaporated to dryness under reduced pressure. The required product was isolated with dichloromethane and formed yellow needles from dichloromethane–n-hexane. Yield 0.056 g, 41%.

Single-crystal X-Ray Diffraction Analysis.—A suitable crystal of complex (**3**) obtained from chlorobenzene was coated with epoxy resin to prevent decomposition.

Crystal data. $C_{66}H_{58}Cl_4O_2P_4Rh$, M = 1 251.80, monoclinic, a = 1 027.5(8), b = 2 996.5(9), c = 2 142.2(5) pm, β = 92.50(2)°, U = 2.872 nm^3, Z = 4, D_c = 1.40 g cm^{-3}, space group $P2_1/n$ ($= P2_1/c$, no. 14), $\mu(Mo\text{-}K_\alpha)$ = 22.51 cm^{-1}, $F(000)$ = 2 872.

Data collection and structure solution. The unit cell and intensity data for the compound were recorded on a Nicolet P3/F diffractometer operating in the ω—2θ scan mode using graphite-monochromated Mo-K_α radiation (λ = 71.069 pm) following a procedure outlined in detail elsewhere.[12] The data set was corrected for absorption empirically.[13] Scans running from 0.9° below $K_{\alpha1}$ to 0.9° above $K_{\alpha2}$, scan speeds 2.0—29.3° min^{-1}, $4.0 < 2\theta < 45.0°$. 8 170 Data were collected, of which 6 816 were regarded as observed [$I > 2.0\sigma(I)$], T = 290 K.

The structure was determined *via* standard heavy-atom methods and refined by blocked full-matrix least squares, using the SHELX program system.[14] All non-hydrogen atoms were refined anisotropically except for the two chlorobenzene molecules of crystallization. These chlorobenzene molecules were each refined with overall isotropic thermal parameters. All phenyl groups were treated as rigid bodies with idealized hexagonal symmetry (C–C 139.5 pm); all hydrogen atoms (except those on the ethylene ligand, which were not located) were included in calculated positions (C–H 108 pm) and were assigned overall isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used in which the parameter g was included in refinement so as to give acceptable agreement analyses (number of parameters 518, g = 0.000 35, R = 0.0485, R' = 0.0518). Atomic co-ordinates are given in Table 5.

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