New Complexes of Rhenium-(V) or -(III) with Various Diphosphines or Bis(diphenylphosphino)methane Monoxide: Crystal Structure of *mer*-[$ReCl_3$(dppm-*PP'*)(dppom-*P*)] [dppm = $Ph_2PCH_2PPh_2$, dppom = $Ph_2PCH_2P(=O)Ph_2$]†

Xavier L. R. Fontaine, Edmund H. Fowles, Timothy P. Layzell, Bernard L. Shaw* and Mark Thornton-Pett
School of Chemistry, Leeds University, Leeds LS2 9JT, UK

Treatment of [$ReOCl_3(AsPh_3)_2$] or [$ReOBr_3(AsPh_3)_2$] with the diphosphines, $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PC(=CH_2)PPh_2$ (vdpp), *cis*-$Ph_2PCH=CHPPh_2$ (dppen), or $Ph_2PCHMePPh_2$ (1,1′-dppe) gave complexes of the type [$ReOX_3$(L–L)] (L–L = chelating diphosphine, X = Cl or Br), in high yield. Treatment of [$ReOCl_3(AsPh_3)_2$] with an excess of dppm at 20 °C caused some reduction to give a mixture of two rhenium(III) complexes [$ReCl_3$(dppm-*PP'*)(dppom-*P*)] **2a** [dppom = $Ph_2PCH_2P(=O)Ph_2$] and [$ReCl_3$(dppm-*PP'*)(dppm-*P*)] **3a**, which was difficult to separate. Treatment of [$ReOCl_3(AsPh_3)_2$] with 2 mol of dppm in hot benzene gave pure **2a**, whilst treatment of [$ReCl_3(NCMe)(PPh_3)_2$] with 4–5 mol equivalents of dppm in hot benzene gave **3a** in excellent yield. The tribromide analogue [$ReBr_3$(dppm-*PP'*)(dppom-*P*)] was prepared by heating [$ReOBr_3$(dppm-*PP'*)] with dppm. On treating [$ReBr_3(NCMe)(PPh_3)_2$] with dppm, [$ReBr_3$(dppm-*PP'*)(dppm-*P*)] was formed but this was contaminated with the isomeric salt [$ReBr_2$(dppm-*PP'*)$_2$]Br from which it could not be separated; however the NMR parameters for both components were assigned. The pure salt [$ReBr_2$(dppm-*PP'*)$_2$]BPh_4 was prepared from the mixture. In their ^1H NMR spectra, these rhenium(III) complexes show large paramagnetic shifts for the methylene protons of the chelated dppm and for some of the *ortho*-protons. Some of these resonances were assigned using two-dimensional correlation spectroscopy and nuclear Overhauser effect experiments. Crystals of complex **2a** are monoclinic, space group $P2_1/n$, with a = 1147.7(4), b = 2315.5(6), c = 2069.7(6) pm, β = 91.76(3)° and Z = 4; final R factor 0.0465 for 6150 observed reflections. The structure shows octahedral co-ordination with a *mer* arrangement of chlorines, a chelated dppm and a monodentate dppm monoxide, with the P=O group unco-ordinated.

We have described the synthesis and chemistry of some complexes of the type [$ReH_5\{P(C_6H_{11})_3\}_2$(L–L)] [L–L = monodentate diphosphine = $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PC(=CH_2)PPh_2$ (vdpp), $Ph_2PCH_2CH_2PPh_2$ (dppe) or *cis*-$Ph_2PCH=CHPPh_2$ (dppen)].[1] In the course of this and related work we displaced PPh_3 from the readily available [$ReOCl_3(PPh_3)_2$] with PR_3 [$P(C_6H_{11})_3$, PPr^i_3, PBu^t_2Me or $Bu^t_2P(CH_2)_5PBu^t_2$]. However, a preliminary NMR study suggested that with $Bu^t_2P(CH_2)_5PBu^t_2$ the displacement of $AsPh_3$ from the known [$ReOCl_3(AsPh_3)_2$][2] gave better yields. The compound [$ReOCl_3(AsPh_3)_2$] is more soluble than [$ReOCl_3(PPh_3)_2$], which is very insoluble and since $AsPh_3$ would be expected to bond to Re^V less strongly than PPh_3 it should be more readily and rapidly displaced by other ligands. This suggested that it might be used as a convenient starting material for the synthesis of new rhenium(V) and other rhenium complexes. We have found this to be so and in this paper describe the synthesis of several new rhenium(V) trihalide oxide complexes and some rhenium(III) trichloro complexes containing diphosphine and diphosphine monoxide ligands. We anticipate that these could be used as intermediates to other rhenium complexes.

Results and Discussion

The compound [$ReOCl_3(AsPh_3)_2$] was prepared using a modification of the literature procedure, see the Experimental section; the literature method uses insufficient hydrochloric acid.[2] We also describe a method, which is a modification of a literature procedure,[2] for the preparation of the corresponding tribromide [$ReOBr_3(AsPh_3)_2$]. When we stirred [$ReOCl_3(AsPh_3)_2$] with dppm in dichloromethane for 40 min at room temperature the previously described,[3] pale blue complex [$ReOCl_3$(dppm-*PP'*)] **1a** was readily isolated in 81% yield. Complex **1a** was characterised by elemental analysis (Table 1) and by the similarity of the Re=O stretching frequency (990 cm^{-1}) to that reported previously;[3] it was prepared previously by heating [$ReCl_4$(dppm-*PP'*)] in acetone for 48 h. Although [$ReOCl_3$(dppm-*PP'*)] was too insoluble for NMR studies, we assign a *fac* configuration **1a** by analogy with the analogous compounds in Table 2. The corresponding tribromide *fac*-[$ReOBr_3$(dppm-*PP'*)] **1b** was similarly made by treating [$ReOBr_3(AsPh_3)_2$] with dppm (see Experimental section and Table 1 for preparative details and characterisation). We similarly made and characterised several other rhenium(V) trihalide oxide complexes **1c**–**1g** using vdpp, dppen or $Ph_2PCHMePPh_2$ (1,1′-dppe); preparative details are in the Experimental section and characterising microanalytical, infrared and NMR data in Tables 1 and 2. Recently, [$ReOCl_3$(dppen-*PP'*)] has been prepared by treating [$ReOCl_3(AsPh_3)_2$] with dppen.[4]

In the synthesis of [$ReOCl_3$(dppm-*PP'*)], by treating

---

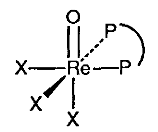
† *mer*-[Bis(diphenylphosphino)methane-κ^2*P*,*P'*][(diphenylphosphino-κ*P*)(diphenylphosphoryl)methane]trichlororhenium(III).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

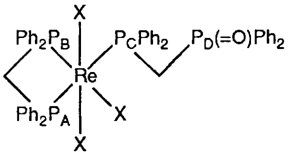
Table 1 Microanalytical[a] and infrared[b] data for rhenium(v) diphosphine complexes

	Analysis (%)			
Complex	C	H	X[c]	ν(Re=O)/cm^{-1}
1a	43.15 (43.3)	2.95 (3.2)	15.6 (15.35)	990
1b	36.15 (36.35)	2.6 (2.7)	29.05 (29.0)	980
1c	44.05 (44.3)	2.95 (3.15)	15.35 (15.1)	988
1d	37.55 (37.25)	2.55 (2.65)	28.35 (28.6)	982
1e	44.35 (44.3)	3.1 (3.15)	15.25 (15.1)	992
1f	37.2 (37.25)	2.6 (2.65)	28.35 (28.6)	984
1g	43.75 (44.2)	3.4 (3.4)	14.9 (15.05)	985
2a	56.3 (55.75)	4.15 (4.1)	10.2 (9.9)	
2b	50.4 (49.6)	3.75 (3.65)	20.1 (19.8)	
3a$\cdot$0.5C_6H_6	57.55 (57.85)	4.3 (4.3)	9.65 (9.65)	
3b/**4a**$\cdot C_6H_6$	52.55 (52.85)	3.95 (3.95)	19.3 (18.85)	
4b$\cdot$0.5CH_2Cl_2	60.15 (60.6)	4.4 (4.45)	*d*	

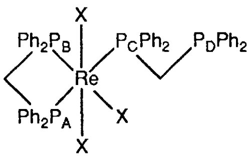
[a] Calculated values in parentheses. [b] Recorded as KBr discs. [c] X = Cl or Br, as appropriate. [d] 12.553 mg equivalent to 2.56 cm^3 of 0.005 041 mol dm^{-3} mercury(II) nitrate solution. Calculated 2.53 cm^3.



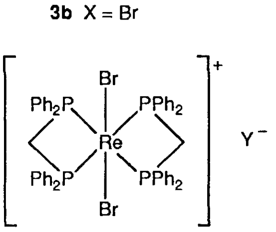
	X	P P
1a	Cl	dppm
1b	Br	dppm
1c	Cl	vdpp
1d	Br	vdpp
1e	Cl	dppen
1f	Br	dppen
1g	Cl	1,1′-dppe



2a X = Cl
2b X = Br



3a X = Cl
3b X = Br



4a Y = Br
4b Y = BPh$_4$

[ReOCl$_3$(AsPh$_3$)$_2$] with dppm, an excess (10%) of dppm was used. From the dichloromethane–diethyl ether mother-liquor yellow crystals slowly deposited. Proton and phosphorus-31 NMR spectroscopy established that this was a two-component mixture of closely related species; the major component was eventually shown to be the rhenium(III)–dppm/dppm monoxide species [ReCl$_3$(dppm-*PP*′)(dppom-*P*)] **2a** [dppom = Ph$_2$PCH$_2$P(=O)Ph$_2$] and the minor species [ReCl$_3$(dppm-*PP*′)(dppm-*P*)] **3a** (see below). We were unable to separate this mixture by fractional crystallisation but subsequently prepared both components in a pure state. The phosphine monoxide complex **2a** was prepared in about 30% yield by heating [ReOCl$_3$(AsPh$_3$)$_2$] with dppm (2 equivalents) in benzene for 40 min (see Experimental section). This phosphine monoxide complex was characterised by elemental analysis (Table 1) and shown to be [ReCl$_3$(dppm-*PP*′)(dppom-*P*)] **2a** by an X-ray crystal structure determination (see below). We were unable to separate the other component of the mixture, the bis(dppm) complex **3a** from the above-mentioned mixture in spite of many attempts. We therefore looked for a better synthesis and found that by heating the known rhenium(III) complex [ReCl$_3$(NCMe)(PPh$_3$)$_2$][5] with 4 equivalents of dppm in benzene for 20 min the required complex **3a**, free from the dppm monoxide complex, was obtained in 95% yield. It was characterised by elemental analysis (Table 1) and particularly by NMR spectroscopy. Rhenium(III)–tertiary phosphine complexes of the type [ReCl$_3$(PR$_3$)$_3$] show second-order paramagnetism with some of the proton resonances in the NMR spectra at unusually large chemical shifts and the phosphorus-31 resonances are too broad to observe, because of rapid relaxation.[6] The rhenium(III) complex **3a** has four chemically distinct P nuclei, three of which P$_A$, P$_B$ and P$_C$ are bonded to rhenium and are not observed in the ^{31}P-{^{1}H} NMR spectrum, which only consists of a broad singlet at 162 MHz, $w_{\frac{1}{2}}$ = *ca.* 10 Hz, due to P$_D$ whilst at 40.3 MHz the resonance is a doublet with coupling to P$_C$ just resolved (J = 24 Hz). In the ^{1}H NMR spectrum (400 MHz) (data in Table 3) the resonances at δ 20.01 and 2.60 are singlets and are assigned to the methylene protons of the chelating and the monodentate dppm, respectively. These resonances show no resolvable coupling to the unco-ordinated phosphorus of the monodentate dppm. The three resonances at δ 16.84, 15.19 and 12.02 are doublets and assigned to the *ortho*-phenyl protons attached to P$_A$, P$_C$ and P$_B$. It is well known that such protons of phenylphosphines directly co-ordinated to rhenium(III) show large chemical shifts.[6] By using two-dimensional ^{1}H NMR correlation spectroscopy (COSY) we have shown which *meta*- and *para*-protons these three kinds of *ortho*-protons are coupled to. The doublet at δ 16.84 was shown to be associated with a triplet at δ 9.25 (*meta*-protons) and a triplet at δ 8.13 (*para*-protons). Similarly, the resonance at δ 15.19 (*ortho*) was associated with triplet resonances at δ 7.85 (*meta*-protons) and 7.62 (*para*-proton) and the doublet at δ 12.02 (*ortho*) was associated with a multiplet resonance at *ca.* δ 8.57 (*meta*- and *para*-protons). The three remaining aromatic resonances, which are multiplets at δ 8.42, 7.38 and 7.32, are assigned to the *ortho*-, *meta*- and *para*-protons

Table 2 $^{31}P-\{^1H\}$ and ^1H NMR data[a] for some new rhenium(V) diphosphine complexes

Complex	δ(P)	δ(H)	Coupling constants
1c $[ReOCl_3(vdpp)]$	−30.4	6.96 (=CH_2)	55.7 [*cis*- + *trans*-$^3J(PC{=}CH_2)$]
1d $[ReOBr_3(vdpp)]$	−40.0	7.04 (=CH_2)	55.6 [*cis*- + *trans*-$^3J(PC{=}CH_2)$]
1e $[ReOCl_3(dppen)]$	17.8	*b*	
1f $[ReOBr_3(dppen)]$	10.0	*b*	
1g $[ReOCl_3(1,1'\text{-dppe})]$	−39.4	1.41 [δ(CH_3)]	7.6 [$^3J(CH_3CH)$][c] 17.1 [$^3J(PCHCH_3)$]

[a] $^{31}P-\{^1H\}$ recorded at 40.3 MHz and ^1H at 100 MHz in dichlorodeuteriomethane; chemical shifts in ppm and coupling constants in Hz. Spectra not recorded for $[ReOCl_3(dppm)]$ **1a** and $[ReOBr_3(dppm)]$ **1b** since they were too insoluble in common NMR solvents. [b] Olefinic protons obscured by aromatic multiplet. [c] The resonance pattern of PC*H* was obscured by an impurity peak (probably water) and was not analysed.

Table 3 Proton and $^{31}P-\{^1H\}$ NMR data[a] for the complexes $[ReX_3(dppm\text{-}PP')(dppom\text{-}P)]$ **2a** (X = Cl) and **2b** (X = Br) and $[ReX_3(dppm\text{-}PP')(dppm\text{-}P)]$ **3a** (X = Cl) and **3b** (X = Br)

	Phenyl protons[b]					CH_2[c]		P_D	
Complex	*ortho*	*meta*	*para*	$^3J(H_oH_m)$	$^3J(H_mH_p)$	δ	^2J(PH)	δ	^2J(PP)
2a P_A	16.84(d)	9.23(t)	8.19(t)	7.7	7.5	H_a 20.04(s)		−34.8	29.2
P_B	11.74(d)	7.74(t)	7.55(t)	7.8	7.3	H_b 1.66(d)	9.6		
P_C	15.49(d)	8.64(m)	8.64(m)	7.4	n.r.				
P_D	8.64(m)	7.48(m)	7.42(m)	n.r.	n.r.				
2b P_A	16.45(d)	9.12(t)	8.27(t)	7.5	7.4	H_a 16.30(s)		−32.8	29.3
P_B	12.26(d)	7.72(t)	7.58(t)	7.6	7.3	H_b 1.83(d)	9.5		
P_C	15.33(d)	8.58(m)	8.47(t)	7.5	7.1				
P_D	8.58(m)	7.47(m)	7.47(m)	n.r.	n.r.				
3a P_A	16.84(d)	9.25(t)	8.13(t)	7.6	7.4	H_a 20.01(s)		−26.6	24.4
P_B	12.02(d)	7.85(t)	7.62(t)	7.8	7.5	H_b 2.60(s)			
P_C	15.19(d)	8.57(m)	8.57(m)	6.1	n.r.				
P_D	8.42(m)	7.38(m)	7.32(m)	n.r.	n.r.				
3b P_A	16.44(d)	9.12(t)	8.21(t)	7.5	7.4	H_a 16.14(s)		−14.3	22.0
P_B	12.56(d)	7.81(t)	7.60(t)	7.7	7.4	H_b 2.47(s)			
P_C	14.97(d)	8.50(t)	8.43(t)	7.0	7.2				
P_D	8.36(m)	7.37(m)	7.37(m)	n.r.	n.r.				

n.r. = Not resolved. [a] Proton NMR data recorded at 400 MHz and $^{31}P-\{^1H\}$ at 40.3 MHz in dichlorodeuteriomethane; chemical shifts in ppm and coupling constants in Hz. [b] P_A, P_B, P_C, P_D refer to the phosphorus atoms to which the respective phenyl groups are attached. [c] H_a refers to CH_2 of chelate dppm, H_b to CH_2 of monodentate dppm.

Table 4 Results of difference NOE studies on $[ReCl_3(dppm\text{-}PP')(dppm\text{-}P)]$ **3a**. Percentage enhancements are shown, blank spaces indicate undetectable % NOE

	Irradiation at						
	δ 20.01 (H_a)	2.60 (H_b)	16.84 A	12.02 B	15.19 C	8.42 D	8.57
H_a	—		1.4	1.0			
H_b		—			1.0	0.9	
ortho A	7.0		—	0.5			
ortho B	6.1		0.7	—	1.6		
ortho C		4.7		1.3	—		0.7
ortho D		14.5			1.5	—	
meta A			14.4				
meta B				13.9			
meta/*para* C				1.0	12.6		—
meta D						13.0	

attached to the unco-ordinated phosphorus atom P_D, since they are sharper than the other aromatic resonances and also coupled to phosphorus (as established by the difference between the ^1H and the $^1H-\{^{31}P\}$ NMR spectra).

Nuclear Overhauser effect (NOE) difference spectroscopy was used to assign the sets of aromatic (*ortho*-, *meta*- and *para*-) protons attached to the four phosphorus atoms P_A, P_B, P_C and P_D. For simplicity, we will only discuss the *ortho*-protons. Irradiation of the methylene resonating at δ 20.01 caused enhancement of the signals at δ 16.84 and 12.02 by 7.0 and 6.1%, respectively. This not only allowed us to assign these to the aromatic rings attached to the phosphorus atoms of the chelate dppm (P_A and P_B) but also confirms the assignment of the resonance at δ 20.01 to the methylene of the chelated dppm. Thus the resonance at δ 15.19 should be due to the *ortho*-protons of the phenyl groups attached to the co-ordinated phosphorus (P_C) of the monodentate dppm. This was confirmed by irradiating the methylene protons of the monodentate dppm (at δ 2.60) which enhanced the resonances at δ 15.19 and 8.42 by 4.7 and 14.5%, respectively. Successive irradiation of other signals confirmed these assignments; the results are summarised in Table 4. The *mer* stereochemistry for complex **3a** follows from the singlet methylene resonance of the chelated dppm and also from the similarity of the proton NMR pattern of **3a** with that of **2a**, the structure of which was established by X-ray diffraction. The phosphorus atom P_A is probably in *trans* position to P_C since irradiation of the *ortho*-protons resonating at δ 15.19 (*ortho*-protons of phenyls attached to P_C) caused an enhancement of 1.6% in the signal at δ 12.02 (*ortho*-protons of phenyls attached to P_B) but had no effect on the *ortho*-protons of phenyls attached to P_A, suggesting that the aromatic protons of the phenyls on P_B and P_C are closer than those of P_A and P_C. Thus we could assign all the resonances as shown in Table 3.

The proton resonances of the dppm monoxide complex $[ReCl_3(dppm\text{-}PP')(dppom\text{-}P)]$ **2a** were very similar to those of the *bis*(dppm) complex **3a** and were similarly assigned using two-dimensional COSY. The results are summarised in Table 3. The methylene resonance at δ 20.04 is a singlet and assigned to the chelate ring whereas the methylene resonance at δ 1.66 is a doublet and assigned to the methylene protons of the monodentate diphosphine oxide ligand coupled to P_D, $^2J(P\text{–}H)$ = 9.6 Hz. Complex **2a** showed a ν(P=O) absorption band at 1192 cm^{-1} in its IR spectrum (Nujol mull).

Table 5 Proton NMR data* for the complexes [$ReBr_2$(dppm-*PP′*)$_2$]Br **4a** and [$ReBr_2$(dppm-*PP′*)$_2$]BPh_4 **4b**

Complex	CH_2	*ortho*	*meta/para*	$^3J(H_oH_m)$
4a	14.51(s)	14.88(d)	8.36(m)	7.0
4b	14.33(s)	14.83(d)	8.34(m)	7.5

* Recorded at 100 MHz in dichlorodeuteriomethane; chemical shifts in ppm and coupling constants in Hz.

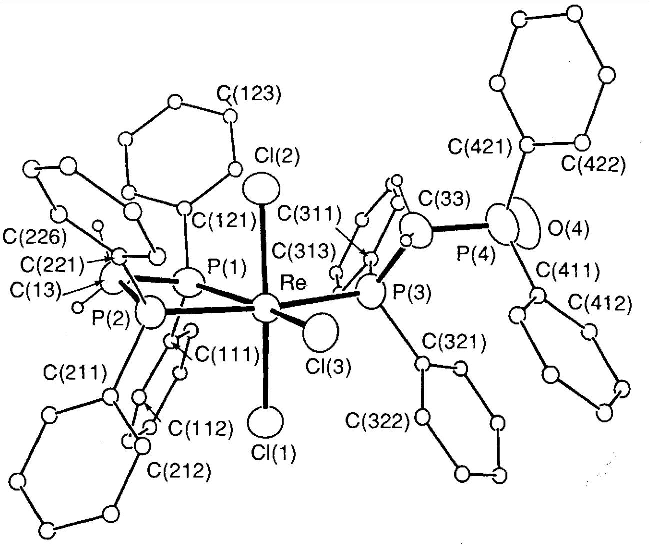


Fig. 1 ORTEP diagram of the crystallographically determined structure of *mer*-[$ReCl_3$(dppm-*PP′*)(dppom-*P*)] **2a**

Similar experiments were carried out with [$ReOBr_3(AsPh_3)_2$] which when treated with an excess of dppm gave [$ReOBr_3$(dppm)] **1b** (see Experimental section and Table 1 for characterising data). From the mother-liquor in this preparation a very small amount of another product was precipitated which was characterised by its ^1H NMR spectrum and subsequently synthesised in good yield (see below) and identified as [$ReBr_3$(dppm-*PP′*)(dppom-*P*)] **2b**. As described above, the corresponding chloride complex **2a** was made in good yield by heating [$ReOCl_3(AsPh_3)_2$] with dppm. However, when we heated [$ReOBr_3(AsPh_3)_2$] with 4 equivalents of dppm in benzene for 10 min a mixture of three complexes was produced. The ^{31}P-{^1H} NMR spectrum of this mixture consisted of doublets at δ −32.8 and −14.3 consistent with a mixture of **2b** and *mer*-[$ReBr_3$(dppm-*PP′*)(dppm-*P*)] **3b**. The ^1H and ^1H-{^{31}P} NMR spectra were consistent with the presence of these two species and also showed that a third paramagnetic species was present, which we tentatively formulated as *trans*-[$ReBr_2$(dppm-*PP′*)$_2$]Br **4a**. We therefore set out to devise specific syntheses of these three complexes. Complex **2b** was made in 77% yield by heating [$ReOBr_3$(dppm-*PP′*)] with equivalents of dppm in benzene for 15 min, see Experimental section and Tables 1 and 3 for characterising data. However, when we treated [$Re(NCMe)Br_3(PPh_3)_2$] with an excess of dppm in an attempt to make **3b** we obtained an excellent yield of an orange crystalline precipitate, the elemental analytical (Table 1) and NMR (Tables 3 and 5) data for which indicated that **3b** was mixed with an approximately equal amount of the isomeric salt *trans*-[$ReBr_2$(dppm-*PP′*)$_2$]Br **4a**. It is possible that these two isomers are interconverting in solution and we were unable to separate their mixture by fractional crystallisation. However, when we treated the **3b**/**4a** mixture with $NaBPh_4$ the pure tetraphenylborate salt *trans*-[$ReBr_2$(dppm-*PP′*)$_2$]BPh_4 **4b** was obtained which was characterised by elemental analysis (Table 1) and by its ^1H NMR spectrum (Table 5). The correspondence between these data for **4b** and the data for **4a** in the mixture is excellent (Table 5), confirming the presence of the cation *trans*-[$ReBr_2$(dppm-*PP′*)$_2$]$^+$ in the three- and the two-component mixtures described above. A two-dimensional COSY NMR experiment was used to assign the ^1H NMR resonances of **3b**/**4a** in the mixture. Analogous complexes, *trans*-[ReX_2(dppen-*PP′*)$_2$]X (X = Cl or Br) have been prepared by treating [NBu_4]$_2$[Re_2X_8] with dppen.[7]

Table 6 Selected bond lengths (pm) and angles (°) for complex **2a**

Re–Cl(1)	232.7(4)	Re–Cl(2)	235.7(4)
Re–Cl(3)	243.9(4)	Re–P(1)	245.6(4)
Re–P(2)	245.0(4)	Re–P(3)	248.0(4)
C(13)–P(1)	186.2(9)	C(13)–P(2)	184.0(9)
C(33)–P(3)	183.8(10)	C(33)–P(4)	181.4(9)
O(4)–P(4)	148.5(7)		
Cl(2)–Re–Cl(1)	175.5(1)	Cl(3)–Re–Cl(1)	93.4(2)
P(1)–Re–Cl(1)	90.6(2)	P(2)–Re–Cl(1)	93.1(2)
P(3)–Re–Cl(1)	92.4(2)	Cl(3)–Re–Cl(2)	91.1(2)
P(1)–Re–Cl(2)	85.0(2)	P(2)–Re–Cl(2)	86.2(2)
P(3)–Re–Cl(2)	88.1(2)	P(1)–Re–Cl(3)	164.5(1)
P(2)–Re–Cl(3)	95.4(2)	P(3)–Re–Cl(3)	86.7(2)
P(2)–Re–P(1)	69.4(2)	P(3)–Re–P(1)	108.2(2)
P(3)–Re–P(2)	174.0(1)		
P(2)–C(13)–P(1)	97.9(4)	P(4)–C(33)–P(3)	121.4(5)
C(13)–P(1)–Re	121.3(3)	C(13)–P(2)–Re	95.9(3)
C(33)–P(3)–Re	107.9(3)	C(33)–P(4)–O(4)	114.1(5)

Crystal Structure of mer-[$ReCl_3$(dppm-*PP′*)(dppom-*P*)] **2a**.—The crystal structure is shown in Fig. 1 and selected bond lengths and angles are given in Table 6. The structure shows that the arrangement of the chlorines is *mer*, that the dppm ligand is chelated and that the dppm oxide ligand is monodentate through phosphorus and that the P=O moiety is not co-ordinated.

Experimental

Microanalyses were carried out by Mr. A. Hedley and his assistants in the Microanalytical Laboratory of the School of Chemistry, University of Leeds. In the NMR spectra, ^1H and ^1H-{^{31}P}, chemical shifts are to high frequency of tetramethylsilane and ^{31}P-{^1H} chemical shifts are to high frequency of 85% H_3PO_4. NMR spectra were recorded on a JEOL JNM-FX100 spectrometer at +22 °C with deuteriated solvent used to provide a field/frequency lock, *i.e.* ^1H spectra were measured at 100 MHz and ^{31}P-{^1H} at 40.3 MHz, unless otherwise stated. All two-dimensional NOE spectra, as well as some one-dimensional spectra, where indicated, were measured on a Bruker AM-400 spectrometer at 400 (^1H and ^1H-{^{31}P}) or 162 MHz (^{31}P-{^1H}). Infrared spectra were recorded on a Perkin-Elmer 257 (4000–600 cm^{-1}) or a Philips Analytical SP2000 (4000–400 cm^{-1}) spectrophotometer as Nujol mulls on potassium bromide plates, or as potassium bromide discs.

Reactions were carried out in an atmosphere of argon or dinitrogen using degassed solvents. All solid products were dried *in vacuo* over P_2O_5 and labile compounds were stored at −20 °C. Benzene was dried by refluxing over sodium–benzophenone in argon, followed by distillation.

Preparations.—[$ReOCl_3(AsPh_3)_2$]. This was prepared using a modified literature procedure (see Discussion). A rhenium pellet (2.65 g, 14.2 mmol) was dissolved in 30% hydrogen peroxide (100 cm^3) and the resultant solution evaporated to an oil on a bath of hot water. The oil was dissolved in concentrated HCl (5.3 cm^3) and the resultant solution added to a degassed solution of $AsPh_3$ (13.3 g, 43.3 mmol) in glacial acetic acid (250 cm^3). The resultant mixture was stirred for 30 min giving the required product as yellow-green microcrystals. This was filtered off, washed with diethyl ether and dried. Yield 9.58 g, 74%.

Table 7 Non-hydrogen atomic coordinates (× 10^4) for complex **2a**

Atom	*x*	*y*	*z*
Re	1 872.3(2)	879.9(1)	8 166.3(1)
Cl(1)	2 508(2)	813(1)	9 242(1)
Cl(2)	1 379(2)	928(1)	7 054(1)
Cl(3)	−139(2)	1 079(1)	8 443(1)
P(1)	3 678(2)	422(1)	7 818(1)
P(2)	1 611(2)	−166(1)	8 060(1)
P(3)	2 155(2)	1 942(1)	8 149(1)
P(4)	596(2)	3 012(1)	7 692(1)
O(4)	1 606(5)	3 414(2)	7 695(3)
C(111)	4 906(4)	307(2)	8 380(2)
C(112)	4 811(4)	−78(2)	8 894(2)
C(113)	5 741(4)	−149(2)	9 337(2)
C(114)	6 767(4)	164(2)	9 265(2)
C(115)	6 863(4)	549(2)	8 751(2)
C(116)	5 932(4)	621(2)	8 308(2)
C(121)	4 401(4)	560(2)	7 063(2)
C(122)	4 274(4)	1 084(2)	6 737(2)
C(123)	4 846(4)	1 175(2)	6 161(2)
C(124)	5 546(4)	741(2)	5 911(2)
C(125)	5 673(4)	217(2)	6 237(2)
C(126)	5 100(4)	126(2)	6 813(2)
C(13)	3 012(6)	−303(3)	7 678(4)
C(211)	1 513(4)	−617(2)	8 770(2)
C(212)	672(4)	−474(2)	9 215(2)
C(213)	520(4)	−822(2)	9 757(2)
C(214)	1 209(4)	−1 312(2)	9 853(2)
C(215)	2 050(4)	−1 456(2)	9 407(2)
C(216)	2 202(4)	−1 108(2)	8 865(2)
C(221)	483(4)	−466(2)	7 529(2)
C(222)	−653(4)	−263(2)	7 591(2)
C(223)	−1 558(4)	−494(2)	7 208(2)
C(224)	−1 328(4)	−928(2)	6 762(2)
C(225)	−192(4)	−1 131(2)	6 699(2)
C(226)	713(4)	−900(2)	7 083(2)
C(311)	3 514(4)	2 205(3)	7 830(3)
C(312)	4 526(4)	1 997(3)	8 139(3)
C(313)	5 616(4)	2 154(3)	7 915(3)
C(314)	5 692(4)	2 519(3)	7 381(3)
C(315)	4 680(4)	2 728(3)	7 073(3)
C(316)	3 591(4)	2 571(3)	7 297(3)
C(321)	2 086(5)	2 328(2)	8 918(2)
C(322)	1 329(5)	2 129(2)	9 384(2)
C(323)	1 254(5)	2 420(2)	9 972(2)
C(324)	1 935(5)	2 909(2)	10 094(2)
C(325)	2 692(5)	3 108(2)	9 628(2)
C(326)	2 768(5)	2 817(2)	9 041(2)
C(33)	991(7)	2 256(3)	7 631(4)
C(411)	−277(5)	3 070(3)	8 397(3)
C(412)	−77(5)	3 544(3)	8 802(3)
C(413)	−754(5)	3 623(3)	9 343(3)
C(414)	−1 631(5)	3 228(3)	9 480(3)
C(415)	−1 831(5)	2 755(3)	9 075(3)
C(416)	−1 155(5)	2 676(3)	8 534(3)
C(421)	−372(6)	3 151(3)	7 010(3)
C(422)	−1 450(6)	3 416(3)	7 086(3)
C(423)	−2 140(6)	3 563(3)	6 544(3)
C(424)	−1 752(6)	3 444(3)	5 926(3)
C(425)	−674(6)	3 178(3)	5 850(3)
C(426)	16(6)	3 032(3)	6 392(3)

[$ReOBr_3(AsPh_3)_2$]. This was similarly prepared using concentrated HBr. Yield 81%.

[$ReOCl_3$(dppm-*PP′*)] **1a**. A mixture of [$ReOCl_3(AsPh_3)_2$] (0.460 g, 0.500 mmol), dppm (0.209 g, 0.544 mmol) and dichloromethane (10 cm^3) was stirred under dinitrogen for 40 min. The volume of the solvent was then reduced to 4 cm^3 under reduced pressure and the mixture was set aside at −20 °C for 4 h to give the required product as blue-green microcrystals. These were washed with dichloromethane until the washings were colourless. Yield 0.280 g, 81%.

[$ReOBr_3$(dppm-*PP′*)] **1b**. This was prepared similarly as a green powder. Yield 84%.

[$ReOCl_3$(vdpp-*PP′*)] **1c**. This was prepared in an analogous manner to [$ReOCl_3$(dppm-*PP′*)] except that the volume of the dichloromethane solution was reduced to 2 cm^3 before leaving to crystallise. Yield 82%.

[$ReOBr_3$(vdpp-*PP′*)] **1d**. This was prepared in an analogous manner to [$ReOCl_3$(vdpp-*PP′*)], as a pale green powder. Yield 78%.

The following three complexes were prepared in an analogous fashion to [$ReOCl_3$(dppm-*PP′*)]: [$ReOCl_3$(dppen-*PP′*)] **1e**, as a pale blue powder, yield 55%; [$ReOBr_3$(dppen-*PP′*)] **1f**, as a green powder, yield 44%; [$ReOCl_3$(1,1′-dppe-*PP′*)] **1g**, as a blue-green powder, yield 82%.

mer-[$ReCl_3$(dppm-*PP′*)(dppom-*P*)] **2a**. A mixture of [$ReOCl_3(AsPh_3)_2$] (0.303 g, 0.329 mmol), dppm (0.254 g, 0.659 mmol), and benzene (12 cm^3) was heated at 80 °C under dinitrogen for 40 min, during which the initial, pale green suspension turned to a dark blue-green solution {due presumably to [$ReOCl_3$(dppm-*PP′*)]} then finally to a dark orange solution. The solution was filtered, evaporated to a small volume and diethyl ether added until precipitation started. This gave the required product as a yellow powder which was recrystallised from dichloromethane–diethyl ether as yellow microcrystals. Yield 0.112 g, 32%.

mer-[$ReBr_3$(dppm-*PP′*)(dppom-*P*)] **2b**. A mixture of [$ReOBr_3$(dppm)] (0.221 g, 0.267 mmol), dppm (0.103 g, 0.268 mmol) and benzene (10 cm^3) was heated at 80 °C under nitrogen for 15 min during which time the initial green suspension became a red solution. Diethyl ether was added to the cooled solution and the mixture was set aside for 3 h. This gave the required compound as orange crystals. Yield 0.249 g, 77%.

[$ReCl_3$(dppm-*PP′*)(dppm-*P*)] **3a**. A mixture of [$ReCl_3$(NCMe)$(PPh_3)_2$] (3.28 g, 3.82 mmol), dppm (6.50 g, 16.9 mmol) and benzene (50 cm^3) was heated at 80 °C under nitrogen for 20 min, during which time the yellow-orange suspension became a yellow-orange solution. The solution was cooled, diethyl ether added until precipitation started and nitrogen was slowly bubbled through the solution for 2 h. This gave the required product as yellow microcrystals. Yield 3.84 g, 95%.

Attempted preparation of [$ReBr_3$(dppm-*PP′*)(dppm-*P*)] **3b**. A mixture of [$ReBr_3$(NCMe)$(PPh_3)_2$] (0.407 g, 0.410 mmol), dppm (0.798 g, 2.08 mmol) and benzene (10 cm^3) was heated at 80 °C under nitrogen for 15 min, during which time the orange suspension became a deep red solution. The solution was cooled, diethyl ether was added until precipitation started and nitrogen was slowly passed through the solution for 2 h; this gave an orange crystalline precipitate, which was shown to be an approximate 1:1 mixture of [$ReBr_3$(dppm-*PP′*)(dppm-*P*)] **3b** and *trans*-[$ReBr_2$(dppm-*PP′*)$_2$]Br **4a**, see Discussion. Yield 0.460 g, 94%.

trans-[$ReBr_2$(dppm-*PP′*)$_2$]BPh_4 **4b**. To a solution of the **3b**/**4a** mixture (see above) (0.060 g, 0.05 mmol) in dichloromethane (2 cm^3) was added a solution of $NaBPh_4$ (0.035 g, 0.10 mmol) in acetone (1 cm^3). Slow evaporation of the solution under reduced pressure gave the required product as an orange-red microcrystalline solid. Yield 0.035 g, 48%.

Single-crystal X-Ray Diffraction Analysis.—All crystallographic measurements were made in a Nicolet P3/F diffractometer operating in the ω–2θ scan mode using graphite-monochromated Mo-Kα radiation (λ = 71.069 pm) following a standard procedure.[8] The data set was corrected for absorption empirically once its structure had been determined.[9]

The structure of complex **2a** was determined by standard heavy-atom methods and was refined by full-matrix least squares using the SHELX program system.[10] All non-hydrogen atoms were refined with anisotropic thermal parameters except for the non-hydrogen atoms of three distinct disordered solvent molecules (one of which was of 0.5 occupancy) which were refined with isotropic thermal parameters. Phenyl rings were treated as rigid bodies with idealised hexagonal symmetry (C–C 139.5 pm). All hydrogen atoms were included in calculated positions (C–H 96 pm) and were assigned an overall isotropic thermal parameter. The weighting scheme $w = [\sigma^2(F_o) + 0.0004(F_o)^2]^{-1}$ was used. Atomic coordinates are given in Table 7.

Crystal data. $C_{50}H_{44}Cl_3OP_4Re\cdot2.5CH_2Cl_2$, $M = 1258.72$ (includes solvate molecules), monoclinic, space group $P2_1/n$, $a = 1147.7(4)$, $b = 2315.5(6)$, $c = 2069.7(6)$ pm, $\beta = 91.76(3)°$, $U = 5.497(3)$ nm^3, $Z = 4$, $D_c = 1.52$ Mg m^{-3}, $\mu = 26.07$ cm^{-1}, $F(000) = 2571.9$.

Data collection and structure refinement. Scan width 2.0° + α-doublet splitting, scan speeds 2.0–29.3° min^{-1}, $4.0 < 2\theta < 45.0°$. 7500 Data collected, 6150 with $I > 2.0\sigma(I)$ considered observed, $T = 290$ K. Number of parameters = 499, $R = 0.0465$, $R' = 0.0473$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the SERC and British Petroleum Company plc for a CASE award (to E. H. F.), for a studentship (to T. P. L.) and for other support. We also thank Dr. G. E. Morris (BP) for valuable discussions.

References

1 S. W. Carr, X. L. R. Fontaine, E. H. Fowles and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1990, 573.
2 N. P. Johnson, C. J. Lock and G. Wilkinson, *J. Chem. Soc.*, 1964, 1054.
3 R. E. Myers and R. A. Walton, *Inorg. Chem.*, 1976, **15**, 3065.
4 Xiao-Liang Luo and R. H. Crabtree, *J. Am. Chem. Soc.*, 1990, **112**, 4813.
5 G. Rouschias and G. Wilkinson, *J. Chem. Soc. A*, 1967, 993.
6 J. Chatt, G. J. Leigh, D. M. P. Mingos, E. W. Randall and D. Shaw, *Chem. Commun.*, 1968, 419.
7 M. Bakir, P. E. Fanwick and R. A. Walton, *Polyhedron*, 1987, **6**, 907.
8 A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1974, 2065.
9 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
10 G. M. Sheldrick, SHELX 76, Program System for X-Ray Structure Determinations, University of Cambridge, 1976.

Received 22*nd October* 1990; *Paper* 0/04740F