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Syntheses and characterisation of rhenium-(III) and -(V) complexes containing aminophosphine ligands. Crystal structures of [Re^{V}OCl$_2$(OMe)L] and [Re^{III}Cl$_3$L(PPh$_3$)], L = *o*-(diphenylphosphino)-*N*,*N*′-dimethylaniline

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Substitution reactions of labile rhenium(V) precursors with *o*-(diphenylphosphino)-*N*,*N*′-dimethylaniline, L, gave a series of monooxorhenium(V) complexes of general formula [ReOX$_2$Y(L)] (X = Y = Cl **1**; X = Cl, Y = OMe **2**) and [ReOX$_2$(OEt)L] (X = Cl **3**, Br **4** or I **5**). These complexes, which contain only one aminophosphine chelate, have a distorted-octahedral geometry, as evidenced by a crystal structure determination of **2**. Reactions conducted in basic media, or treatment of **2** in the presence of the weakly co-ordinating trifluoromethanesulfonic acid, gave the bis(chelate) cationic complexes [ReO$_2$L$_2$]$^+$ **6** and [ReCl$_2$L$_2$]$^+$ **7**, respectively. Similar ligand-exchange reactions between the lower-oxidation-state precursor [Re^{III}Cl$_3$(MeCN)(PPh$_3$)$_2$] and L or L′ [*o*-(diphenylphosphino)aniline] still produced mono-substituted aminophosphine complexes, *i.e.* [Re^{III}Cl$_3$L(PPh$_3$)] **8** or [Re^{III}Cl$_3$L′(PPh$_3$)] **9** in which there is a meridional arrangement of chloride ligands along with a *cis*-phosphorus co-ordination. The crystal structure of **8** was determined. On the contrary, treatment of [Re^{III}X$_3$(MeCN)(PPh$_3$)$_2$] (X = Cl or Br) with L′ in the presence of co-ordinating hydrohalogenic acid gave bis-substituted cationic complexes [ReX$_2$L′$_2$]$^+$ (X = Cl **10** or Br **11**). In spite of the paramagnetism of the low-spin d^4 ion, all of the rhenium(III) complexes can be conveniently characterised in solution by proton NMR spectroscopy.

Bidentate chelates comprising a ‘soft’ tertiary phosphine and a ‘hard’ anchoring donor such as an amine nitrogen or a carboxylate oxygen are of interest for the synthesis of metal complexes utilised for various purposes, *e.g.* in catalysis[1,2] and pharmaceutical development.[3] In both cases the application of this class of compounds is based on the hemilability of this chelate entity, which may open reversibly to accommodate suitable incoming groups. Chelating anionic P,O ligands are successfully applied, for example, in the nickel-catalysed oligomerisation of ethylene in the Shell higher olefin process (SHOP).[4]

The reactivity of *o*-(diphenylphosphino)-*N*,*N*′-dimethylaniline, abbreviated L, toward Group VIII metals has been investigated since 1965.[5] Complexes of Ni^{II}, Co^{II}, Pd^{II} and Pt^{II} have both the diphenylphosphino and dimethylamino arms of the chelate co-ordinated and are of general formula [MX$_2$L].[5–7] On this basis, it has been proposed that L is a useful ligand in homogeneous catalysis being able (*i*) to stabilise low-oxidation-state complexes through phosphorus co-ordination, (*ii*) to confer a high nucleophilicity upon the complex through nitrogen co-ordination and (*iii*) to generate co-ordinatively unsaturated complexes.[8] The co-ordination of other Group VIII metals such as Rh^I,[8] Ir^I[9] and Ru^{II}[10] with L has also been investigated and a number of crystal structures determined.[9–11] In addition, the five-co-ordinate precursor [RuCl$_2$(PPh$_3$)L] binds H$_2$S reversibly to generate the co-ordinatively saturated complex [RuCl$_2$(PPh$_3$)L(SH$_2$)].[12]

Very recently, chelate ring opening in bis(aminophosphine) complexes of Pt^{II} has been achieved by appropriate choice of the substituents on N and P *via* a selective and reversible binding to the DNA base guanine under biologically relevant conditions of pH and chloride concentration.[3] Thus, while the complex containing the primary amino–tertiary phosphine ligand H$_2$N(CH$_2$)$_2$PPh$_2$ has a bis(chelate) structure in solution and in the solid state, the related complex containing the tertiary amino–tertiary phosphine Me$_2$N(CH$_2$)$_2$PPh$_2$, based on solution-state ^{31}P and ^{195}Pt NMR signals, exhibits a pattern consistent with an equilibrium between the bis(chelate) and *cis*-[PtCl{Me$_2$N(CH$_2$)$_2$PPh$_2$-*N*,*P*}{Me$_2$N(CH$_2$)$_2$PPh$_2$-*P*}]Cl species. Preliminary cytotoxicity tests on these bis-chelated and ring-opened complexes provide interesting results when compared to those of [PtCl$_2$(NH$_3$)$_2$] (cisplatin).[3,13]

This paper reports on the synthesis and characterisation of some complexes of Re^{III} and Re^V containing L. The co-ordination of only one chelate in a neutral compound appears to be preferred, as demonstrated by the molecular structures of two representative complexes: [Re^{V}OCl$_2$(OMe)L] and [Re^{III}Cl$_3$L(PPh$_3$)]. Nevertheless, the bis-substituted cationic complexes, [Re^{V}O$_2$L$_2$]$^+$ and [Re^{III}Cl$_2$L$_2$]$^+$, have also been obtained. Other rhenium complexes containing the primary amino–tertiary phosphine *o*-(diphenylphosphino)aniline (L′) have been prepared for comparison purposes. This study is a continuation of our investigation on the synthesis and chemistry of complexes of M^{III} and M^V (M = Tc or Re) of unsymmetrical phosphinoamine ligands[14–16] with the aim of designing prototype molecules useful for the development of radiopharmaceuticals based on the ^{99m}Tc and $^{186/188}$Re isotopes.[17] We have shown that L′ affords a series of bis-substituted complexes in which the nitrogen donor can behave as an amino, amido or imido group depending on the reaction conditions employed.[14–16] Although the versatility of this chelate is challenging from the chemical and stereochemical points of view, the possible application of this class of compounds as potential radiopharmaceuticals is precluded by the high number of species produced. A drastic reduction in the species involved has been achieved by enhancing the chelating ability of a bidentate aminophosphine ligand, *e.g.* by linking the amine nitrogens of two L′ with a

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propylene chain, giving a tetradentate P_2N_2 macrocycle,[18] or by functionalising the primary amino group of L′ to obtain a tertiary amino–tertiary phosphine chelate.

Results and Discussion

Synthesis

The bidentate phosphinoamine L reacts with $[ReOCl_4]^-$ in methanol at room temperature to give the light blue monooxorhenium(V) derivative $[ReOCl_3L]$ **1**, which is converted into violet alkoxo species $[ReOCl_2(OR)L]$ (R = Me **2** or Et **3**) in the appropriate refluxing alcohol. In addition, by treating the pentavalent rhenium precursor $[ReOX_2(OEt)(PPh_3)_2]$ (X = Cl, Br or I) with L in refluxing ethanol a series of compounds of general formula $[ReOX_2(OEt)L]$ (X = Cl **3**, Br **4** or I **5**) is produced. Conversely, basic media, *e.g.* sodium ethoxide, induce transformation to the bis-substituted dioxo species $[ReO_2L_2]^+$ **6**. Another bis-substituted yellow species, namely $[ReCl_2L_2]^+$ **7**, is produced by dissolving **2** in dichloromethane–methanol solutions in the presence of water and an excess of trifluoromethanesulfonic acid. Reaction of the substitution labile rhenium(III) complex $[ReCl_3(MeCN)(PPh_3)_2]$ with an excess of L in refluxing methanol does not lead to the expected bis-substituted rhenium(III) species just described, but to the neutral monosubstituted orange complex *mer*-$[ReCl_3L(PPh_3)]$ **8**. The isostructural rhenium(III) complex *mer*-$[ReCl_3L'(PPh_3)]$ **9** is obtained in a similar way, whereas the cations $[ReX_2L'_2]^+$ (X = Cl **10** or Br **11**) are prepared by treatment of $[ReCl_3(MeCN)(PPh_3)_2]$ with 2 equivalents of L′ in the presence of an excess of the appropriate concentrated hydrohalogenic acid.

Characterisation

Monooxorhenium(V) complexes prepared in this work have been characterised by (*i*) elemental analyses, which are in agreement with the proposed formulations, (*ii*) conductivity measurements, which show values consistent with uncharged complexes, (*iii*) spectroscopic measurements, *i.e.* IR, NMR, positive-ion FAB mass spectrometry and the crystal structure determination of a prototypical complex $[ReOCl_2(OMe)L]$ **2**. The IR spectra of complexes **1**–**5** and $[ReOCl_3L']$ **12** show a very strong absorption in the 915–992 cm^{-1} range, which is assigned to the ν(Re=O) stretching vibration. A remarkable bathochromic shift of this vibration is observed on going from the chloro (982–992 cm^{-1}) to the corresponding alkoxo compounds (915–940 cm^{-1}) (*trans* to the oxo moiety; see also NMR). In addition, a number of absorptions characteristic of the phenylphosphine moiety of L is observed. No unco-ordinated NMe_2 groups are present in the molecules, as indicated by the absence of the band at 2780 cm^{-1} which is typical of free NMe_2 groups.[19] The IR spectrum of the dioxo derivative **6** exhibits the asymmetric O=Re=O stretching vibration at 821 cm^{-1}, whereas the 1:1 electrolytic nature of this complex is established by conductivity measurement. The formulation of the rhenium(V) complexes was further assessed by the positive ion FAB mass spectra which show the molecular ion peaks together with several fragment ions corresponding to loss of chloride and/or alkoxo groups, as summarised in Table 1.

Proton NMR spectra establish that both the phosphino and the amino arms are co-ordinated also in solution. Thus, the signal due to the *N*-methyl resonance in free L is split into two singlets, upon co-ordination, the *N*-methyl groups being fixed in two magnetically inequivalent environments[8] (see below). As seen in Table 1, the *N*-methyl resonances are significantly shifted downfield upon co-ordination, whereas the aliphatic portion of the alkoxo group is shielded. This contrasting effect, which is the result of a combination of the electron density located along the Re=O axis and of the acidity of the $Re=O^{3+}$ core,[20,21] allows the assignment of stereochemistry in these complexes; thus, the alkoxo groups are ligated *trans* to the oxo moiety and receive electron density from, and the chelate co-ordinated in the equatorial plane donates electron density to, the acid metal centre. In addition, the more deshielded *N*-methyl group is *syn* oriented with respect to the oxo linkage (anisotropic contact shift), and the less deshielded one is *anti* positioned facing the alkoxo group. Similarly, the ^{31}P signal of the equatorially co-ordinated chelate moves downfield from δ −16.2 for free L to δ 1.2–2.3 for the oxo-alkoxo derivatives.

All of the rhenium(III) complexes have been characterised by (*i*) elemental analyses, (*ii*) conductivity measurements, (*iii*) spectroscopic measurements, *i.e.* IR, scanning electron microscopy (SEM)-EDX, positive ion FAB mass, NMR (see Table 2) and a crystal structure determination for **8**. Their IR spectra show a number of absorptions characteristic of the phenylphosphino moieties, but the ν(Re=O) bands are absent. The SEM-EDX analyses are in agreement with the 1:2:3 Re:P:X (X = Cl or Br) ratios proposed for $[ReX_2L']X$ and the 1:2:2:1 Re:P:Cl:S ratios for $[ReCl_2L_2][CF_3SO_3]$ complexes.

Octahedral rhenium(III) complexes are paramagnetic, as they usually possess a low-spin d^4 electronic configuration; the two unpaired electrons are responsible for the spreading of the proton NMR signals over a wide ppm range. Nevertheless, successful observation of ^1H NMR spectra is due to the extremely short electron-spin-relaxation time ($T_{1e} < 10^{-11}$ s) of the rhe-

Table 1 Spectroscopic data for rhenium(V) complexes

		NMR[a] (δ)				
		^1H				
Compound	IR (cm^{-1}) ν(Re=O)	NMe	OR	^{31}P-{^1H}	UV/VIS λ/nm (ε/dm^3 mol^{-1} cm^{-1})	Positive-ion FAB[b] (*m/z*)
L	—	2.59 (s)		−16.2 (s)		
1 $[ReOCl_3L]$	982	4.07 (s), 3.43 (s)		−16.6 (s)	680 (30), 350 (950), 275 (sh)	614 (20, M^+), 579 (100, $M^+ - Cl$), 544 (18, $M^+ - 2Cl$)
2 $[ReOCl_2(OMe)L]$	940	4.07 (s), 3.25 (s)	2.63 (s)	1.2 (s)	530 (40), 360 (750), 275 (sh)	610 (37, M^+), 575 (100, $M^+ - Cl$), 544 (18, $M^+ - Cl - OMe$)
3 $[ReOCl_2(OEt)L]$	915	4.09 (s), 3.26 (s)	2.93 (m), 0.49 (t)	1.3 (s)	520 (40), 360 (600), 275 (sh)	624 (40, M^+), 589 (100, $M^+ - Cl$), 544 (35, $M^+ - Cl - OEt$)
4 $[ReOBr_2(OEt)L]$	918	4.19 (s), 3.28 (s)	2.89 (m), 0.48 (t)	2.3 (s)	520 (40), 370 (600), 250 (sh)	
5 $[ReOI_2(OEt)L]$	918	4.27 (s), 3.28 (s)	2.84 (m), 0.40 (t)	1.6 (s)	530 (60), 395 (1300), 255 (sh)	
6 $[ReO_2L_2][BPh_4]$	821[c]	3.18 (s)		9.7 (s)		
L′	—	4.12 (s)[d]		−22.2 (s)		
12 $[ReOCl_3L']$	992	4.11 (s)[d]		−9.2 (s)	475 (80), 360 (1000), 270 (sh)	

[a] Chemical shifts with multiplicities in parentheses: s = singlet, t = triplet, m = multiplet. [b] Relative intensities in % in parentheses. [c] ν(O=Re=O). [d] NH.

Table 2 Spectroscopic data for rhenium(III) complexes

Compound	^{1}H NMR (δ)[a]								UV/VIS λ/nm (ε/dm^3 mol^{-1} cm^{-1})	Positive-ion FAB (*m/z*)
	α (d)	β (t)	γ (t)	δ (d)	NCH$_3$ (s)	a (d)	b (t)	c (t)		
7 [ReCl$_2$L$_2$][CF$_3$SO$_3$][b]	17.36	9.45	10.16	14.64	10.30	15.93	8.47	8.73		
8 [ReCl$_3$L(PPh$_3$)]	16.59	9.33	8.63	12.12	11.00	12.74, 15.18[c]	8.10, 8.74[c]	8.66, 8.11[c]	350 (3900), 285 (sh), 260 (9000)	860 (20, M^+), 825 (100, $M^+ - $ Cl)
9 [ReCl$_3$L′(PPh$_3$)]	16.59	9.85	8.29	11.77	—	13.30, 14.58[c]	8.04, 9.19[c]	7.93, 8.33[c]	460 (sh), 350 (3500), 285 (sh), 255 (9900)	
10 [ReCl$_2$L′$_2$]Cl	16.75	9.27	8.52	12.41	—	14.70	8.86	7.62	445 (sh), 380 (2500), 315 (sh), 285 (sh)	812 (100, M^+), 777 (45, $M^+ - $ Cl), 742 (55, $M^+ - $ 2Cl)
11 [ReBr$_2$L′$_2$]Br	15.73	9.38	8.73	12.44	—	15.15	8.75	7.68	450 (sh), 390 (5400), 345 (sh), 290 (sh)	902 (100, M^+), 822 (58, $M^+ - $ Br), 742 (3, $M^+ - $ 2Br)

[a] Protons α, β, γ, δ, a, b and c as in Fig. 1. [b] In CD$_3$CN solution. [c] Signal arising from the PPh$_3$ coligand.

nium(III) centre.[22] The spectra of all [ReX$_2$L$_2$]$^+$ or [ReX$_2$L′$_2$]$^+$ (X = Cl or Br) derivatives exhibit two sets of aromatic signals arising from the four phenyl groups attached to the phosphorus atoms (A$_2$B$_2$C system) and from the two phenyl rings interposed between the P and N donors (ABCD system). The coupling of the aromatic protons is evidenced in Fig. 1 for complex **7**. Moreover, the proton spectra of **8** and **9** show a further set of aromatic protons due to the presence of the monodentate PPh$_3$ group. As outlined in Table 2, all of the proton signals are shifted downfield with respect to the corresponding resonances of the unco-ordinated phosphinoamines, and the larger deshielding is experienced by those protons (α and δ) close to co-ordinated P and N donors. Similar rhenium(III) complexes having one PPh$_3$ coligated in an octahedral arrangement, as in [ReCl$_3$(CNCMe$_3$)$_2$(PPh$_3$)], *fac*-[ReCl$_3$(PhCOCOPh)(PPh$_3$)] and *mer*-[ReCl$_3$(py)$_2$(PPh$_3$)] (py = pyridine), exhibit aromatic proton signals of the triphenylphosphine group in the same range as that observed for our [ReCl$_3$(P–N)(PPh$_3$)] derivatives,‡,[23] indicating that the Re^{III}Cl$_3$(PPh$_3$) group constitutes a rather stable moiety.

Cyclic voltammetric studies on representative rhenium(III) complexes were performed in dichloromethane solutions. The electrochemistry of the bis-substituted [ReX$_2$L′$_2$]$^+$ complexes **10** (X = Cl) and **11** (Br) is dominated by the quasi-reversible[24] Re^{III}–Re^{II} couple ($E^\circ_{\frac{1}{2}}$ at −1.06 and at −0.94 V for **10** and **11**, respectively). As expected on the basis of the π-acid character of halides, the dibromo derivative is easier to reduce than the corresponding dichloro compound by 120 mV, in agreement with previously reported data on analogous [Re^{III}X$_2$(P–P)$_2$]$^+$ species [P–P = 1,2-bis(dimethylphosphino)ethane].[25] Moreover our complexes, which contain a P$_2$N$_2$X$_2$ donor set, are far more difficult to reduce (*ca.* 500 mV) than the above-mentioned compounds,[25,26] in which a larger number of phosphorus atoms in the co-ordination sphere (P$_4$X$_2$) ensures a better π-back bonding and stabilises Re^{II} relative to Re^{III}.[25] Conversely, the cyclic voltammogram of the monosubstituted complex [ReCl$_3$L(PPh$_3$)] shows a quasi-reversible Re^{III}–Re^{IV} wave at +0.25 V. No other redox processes are observable in the detectable window.

Table 3 Selected bond lengths (Å) and angles (°)

Complex **2**

Re–Cl(1)	2.383(4)	Re–Cl(2)	2.438(5)
Re–P	2.367(4)	Re–O(1)	1.70(1)
Re–O(2)	1.84(1)	Re–N	2.28(1)
P–C(1)	1.82(1)	P–C(10)	1.80(1)
P–C(16)	1.83(1)	O(2)–C(9)	1.39(2)
N–C(2)	1.47(2)	N–C(7)	1.52(2)
N–C(8)	1.51(2)		
Cl(1)–Re–Cl(2)	88.3(2)	O(1)–Re–N	86.4(4)
Cl(1)–Re–O(1)	94.5(3)	Re–P–C(10)	114.1(4)
Cl(1)–Re–O(2)	91.4(3)	C(1)–P–C(16)	105.0(6)
O(1)–Re–O(2)	173.2(4)	Re–N–C(2)	113.5(8)
P–Re–N	82.4(3)	Cl(2)–Re–P	173.8(1)
Re–P–C(1)	101.0(4)	P–Re–O(1)	88.8(3)
Re–P–C(16)	120.2(4)	P–Re–O(2)	87.1(3)
Re–O(2)–C(9)	111(1)	Cl(2)–Re–N	93.0(3)
Re–N–C(8)	108.5(8)	O(2)–Re–N	87.6(4)
Cl(1)–Re–P	96.2(1)	C(1)–P–C(10)	108.5(6)
Cl(2)–Re–O(1)	95.1(4)	C(10)–P–C(16)	106.9(6)
Cl(2)–Re–O(2)	88.5(3)	Re–N–C(7)	107.7(8)
Cl(1)–Re–N	178.4(3)		

Complex **8**

Re–Cl(1)	2.427(3)	Re–Cl(2)	2.336(4)
Re–Cl(3)	2.337(4)	Re–P(1)	2.388(3)
Re–P(2)	2.423(3)	Re–N	2.34(1)
P(1)–C(1)	1.80(1)	P(1)–C(9)	1.82(1)
P(1)–C(15)	1.83(1)	P(2)–C(21)	1.83(1)
P(2)–C(27)	1.84(1)	P(2)–C(33)	1.83(1)
N–C(2)	1.46(2)	N–C(7)	1.53(2)
N–C(8)	1.46(2)		
Cl(1)–Re–Cl(2)	90.9(1)	Re–P(1)–C(1)	101.0(4)
Cl(1)–Re–Cl(3)	90.9(1)	Re–P(1)–C(9)	125.9(4)
Cl(1)–Re–P(1)	170.4(1)	Re–P(1)–C(15)	115.1(4)
Cl(1)–Re–P(2)	85.1(1)	Re–P(2)–C(21)	113.6(4)
Cl(1)–Re–N	91.8(3)	Re–P(2)–C(27)	117.0(4)
Cl(2)–Re–Cl(3)	175.7(1)	Re–P(2)–C(33)	115.0(4)
Cl(2)–Re–P(1)	86.7(1)	Re–N–C(2)	112.1(7)
Cl(2)–Re–P(2)	94.9(1)	Re–N–C(7)	108.2(7)
Cl(2)–Re–N	83.5(3)	Re–N–C(8)	112.3(8)
Cl(3)–Re–P(1)	90.9(1)	P(1)–C(1)–C(2)	118.4(9)
Cl(3)–Re–P(2)	89.2(1)	N–C(2)–C(1)	120(1)
Cl(3)–Re–N	92.5(3)		

Crystal structures

The Re^V and Re^{III} in complexes **2** and **8** (Figs. 2 and 3, respectively) exhibit approximately octahedral co-ordination geometry, the maximum deviations from regularity occurring at the angles subtended by the nitrogen and phosphorus donors of the L ligands. In effect, the neutral chelate co-ordinates in the bidentate mode *via* phosphorus [Re–P 2.367(4) in **2** and 2.388(3) Å in **8**, respectively] and nitrogen atoms [Re–N 2.28(1) and 2.34(1) in **2** and **8**, respectively] (Table 3). The five-membered chelate ring thus formed, *i.e.* RePCCN, is roughly planar within ±0.08 Å in **2** (pertinent torsion angles in the range −9.7 to 11.8°) but severely rippled up to ±0.20 Å in **8** (torsion angles from −27.7 to 23.6°), the PCCN ring forming a dihedral angle with the square plane about the Re atom of 9.3° in **2** and 28.7° in **8**. Bidentate co-ordination of the ligand L has been previously observed in the structures of four-co-ordinate

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‡ The aromatic protons of the phenyl groups of co-ordinated PPh$_3$ fall at δ 13.42, 7.95 and 7.61 for [ReCl$_3$(CNCMe$_3$)$_2$(PPh$_3$)] in C$_6$D$_6$ solutions;[23] analogously, they occur at δ 13.54, 8.85 and 8.49 for *mer*-[ReCl$_3$(py)$_2$(PPh$_3$)] and at δ 14.25, 8.69 and 8.49 for *fac*-[ReCl$_3$(PhCOCOPh)(PPh$_3$)] in CDCl$_3$ solutions.

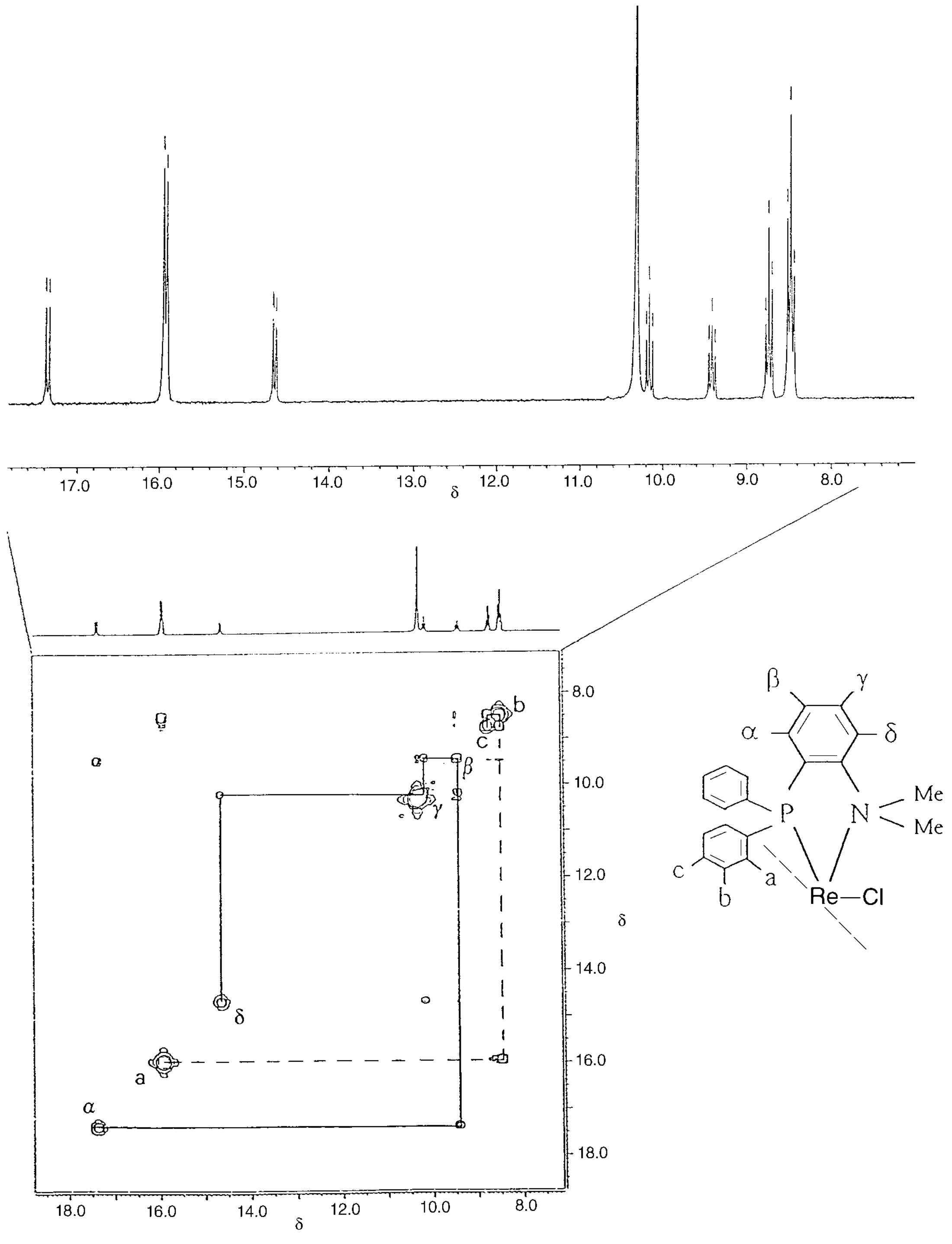

Fig. 1 Two-dimensional COSY-90 ^1H NMR contour map of complex **7** in CD_3CN over the region δ 7.00–19.00

[IrCl(CO)L],[9] five-co-ordinate $[RuCl_2L(PPh_3)]\cdot C_6H_6$[10] and six-co-ordinate $[IrClH\{CH_2NH(Me)C_6H_4PPh_2\}L]\cdot 0.5CH_2Cl_2$.[11] The bidentate ligands show P···N distances of 3.06 and 3.00 Å in **2** and **8**, respectively, which is shortened to 2.95, 2.95 and 2.89 Å in the three compounds mentioned above. The corresponding 'bite' angles are 82.4° in **2**, 78.6° in **8**, and 84.8, 79.6 and 81.8° in the other three species. In all of these complexes the angles about the phosphorus and nitrogen atoms have an approximately tetrahedral arrangement. The methyl groups at the nitrogen atoms are symmetrically placed above and below the equatorial co-ordination plane by 1.19 and −1.28 Å in **2**, while they are 0.73 and −1.34 Å further from the plane in **8**.

The structures of complexes **2** and **8** are roughly superimposable (Fig. 4) with a weighted root-mean-square (r.m.s.) deviation, derived from the BMFIT program,[28] of 0.10 Å, when the fitting is performed using the equatorial atoms. In **2** the metal atom is displaced from the mean plane of the Cl_2PN donor atom set by 0.05 Å towards the oxo O(1) atom and in **8** it is 0.03 Å from the mean Cl_2PN plane towards Cl(3). The Re atom in the co-ordination polyhedron of **2** is 1.25 Å from the O(2), N, Cl(2) plane and −1.13 Å from the O(1), P, Cl(1) plane, the angle between the two triangular faces being 5.3°. The corresponding values for **8** are 1.40, −1.25 Å and 4.7°. In **2** the chloride ligands occupy mutually *cis* positions with a Cl(1)–Re–Cl(2) angle of 88.3(2)°, while in **8** the chlorine atoms adopt a meridional arrangement. The Re–Cl bonds *trans* to P [Re–Cl(2) in **2** and Re–Cl(1) in **8** are of comparable length, 2.438(5) and 2.427(3) Å, respectively] but longer than that *trans* to the amino-nitrogen in **2** [2.383(4) Å] and than those involving the mutually *trans* positions in **8** [2.336(4) and 2.337(4) Å]. This result confirms the lower *trans* influence of the amino relative to the phosphine group.[29] On the other hand, the Re^V–P and Re^{III}–P(1) bonds *trans* to Cl are only slightly different [2.367(4) and 2.388(3) Å, respectively], while the Re^{III}–P(2) distance, *trans* to the amino

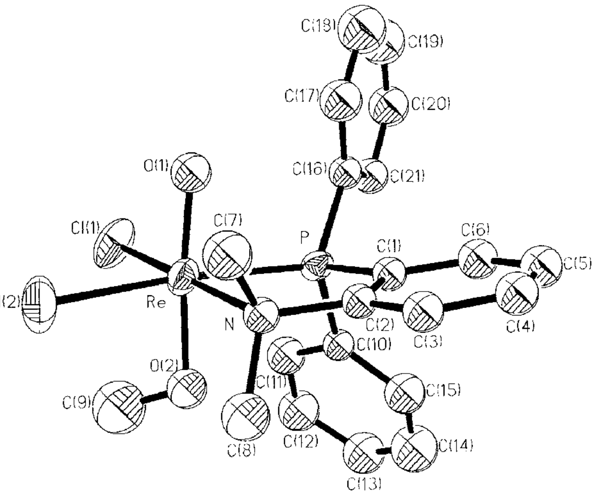

Fig. 2 An ORTEP[27] view of complex **2** showing the atom-labelling scheme; thermal ellipsoids are drawn at 50% probability and hydrogen atoms are omitted for clarity

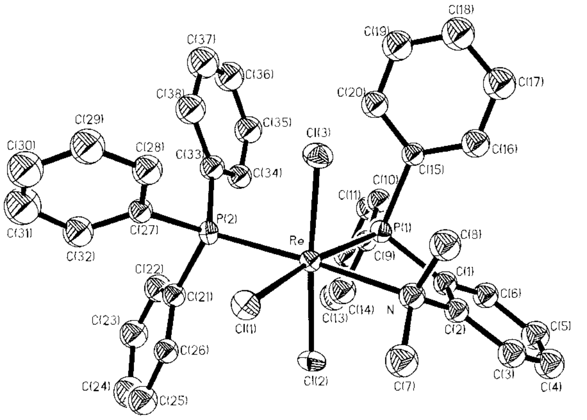

Fig. 3 An ORTEP[27] diagram of complex **8** with 50% probability ellipsoids

nitrogen donor, is somewhat longer [2.423(3) Å]. The shortening of the Re^{V}–N distance *trans* to Cl(1) [2.28(1) Å] compared to the Re^{III}–N bond length *trans* to P [2.34(1) Å] may be ascribed to the greater *trans* influence exhibited by an organophosphine with respect to a chloride ligand. The mean value of 2.31 Å represents the greatest value for an Re–N distance, dramatically greater than the mean of 2.00 Å observed for the Re–N (amido) bonds in [ReO(L′ − H)$_2$X] (X = OEt or Cl).[15] A similar trend has been encountered for Pt–N$_{amino}$ *vs.* Pt–N$_{amido}$ distances in four-co-ordinate *cis/trans*-[PtL′$_2$]$^{2+}$ and [Pt(L′ − H)$_2$] complexes,[30] but in those cases the difference is restricted to 0.08 Å. In any case, the extreme length of the Re–N bonds parallels that found, for example, in trigonal-bipyramidal [NiCl$_2$L(PMe$_2$Ph)] and [NiCl$_2$L(PMePh$_2$)] complexes [2.353(4) and 2.325(8) Å, respectively], where the dimethylamino nitrogen of L still faces a phosphorus donor of a tertiary-phosphine coligand.[31,32] This distance shortens to 2.056(8) Å in the square-planar compound [NiClL(PMePh$_2$)]$^+$,[32] indicating that a less-crowded configuration allows for a stronger metal–nitrogen interaction.

Experimental

Physical measurements

Elemental analyses (C, H, N) were performed on a Fisons model EA 1108 elemental analyser. Only for rhenium(III) compounds, spot or selected area analyses, to determine the Re : P : X : S (X = Cl or Br) ratios, were performed by integral counting of the back-scattered X-ray fluorescence radiation from a Philips model XL 40 scanning-electron microscope equipped with an EDX model data station following the procedure described elsewhere.[14] Infrared spectra were recorded on a Mattson 3030 Fourier-transform spectrometer (4000–400 cm^{-1}) using KBr pellets, ^{1}H and ^{31}P NMR spectra on a Bruker AC-200 instrument using SiMe$_4$ (^{1}H) as internal and 85% aqueous H$_3$PO$_4$ (^{31}P) as external reference and UV/VIS spectra in CH$_2$Cl$_2$ using a Cary 17D spectrophotometer (750–220 nm). Conductivity measurements were made in MeCN at 25 °C using a Metrohm Herison E518 conductometer. Fast-atom bombardment mass spectra in the positive mode were recorded by using 3-nitrobenzyl alcohol or glycerol matrices on a VG ZAB-2F spectrometer. Xenon was used as the primary beam gas, and the ion gun was operated at 8 keV (*ca.* 1.28×10^{-15} J). Data were collected over the mass range *m/z* 100–1000 at 0.7 s per scan. Cyclic voltammetry measurements were performed on a BAS (Bioanalytical System Inc.) CV-IB cyclic voltammograph at room temperature under an atmosphere of nitrogen by using a conventional three-electrode cell. A platinum-disc electrode (area *ca.* 10^{-3} cm^2) was used as the working electrode, a platinum wire as the counter electrode and a silver wire as a quasi-reference electrode. The measurements of the complexes (*ca.* 5 mmol dm^{-3}) were done in dry and degassed CH$_2$Cl$_2$ solutions (Aldrich gold label) with 0.2 mol dm^{-3} NBu$_4$ClO$_4$ as supporting electrolyte. Potentials were calculated at the midpoint between the anodic and cathodic peaks of the cyclic voltammetric waveform scanned at 0.2 V s^{-1}, and were referenced internally to the ferrocenium–ferrocene couple.[24,33] All electron-transfer processes measured in this work are monoelectronic, as qualitatively established by comparison of the current peaks of an equimolar amount of the internal ferrocenium–ferrocene standard.

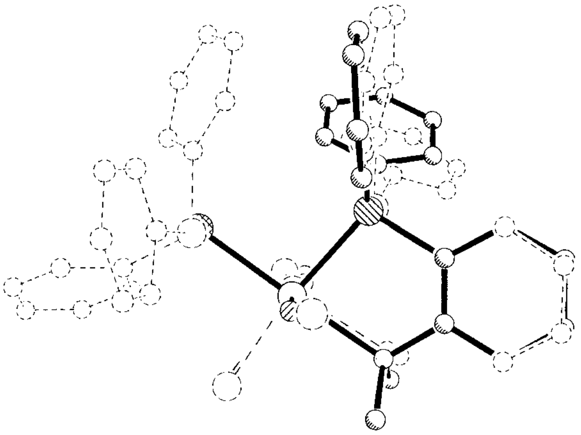

Fig. 4 Superimposition of the structures of complexes **2** and **8** (- - -)

Materials

Unless otherwise stated, all chemicals and solvents were of reagent grade used without further purification. The compounds [NBu$_4$][ReOCl$_4$] and [ReOX$_2$(OEt)(PPh$_3$)$_2$] were prepared as reported elsewhere[34] starting from fine metal rhenium powder (a gift from H. C. Starck GmbH, Goslar, Germany), which was oxidised to Re^{VII} prior to use. The compounds L and L′ were prepared according to the literature.[35,36]

Syntheses

[ReOCl$_3$L] 1. The salt [NBu$_4$][ReOCl$_4$] (96 mg, 0.19 mmol) was dissolved in MeOH (10 cm^3). To the pale green solution solid L (58 mg, 0.19 mmol) was added with stirring at room temperature. The solution turned blue and a precipitate was suddenly deposited. After 30 min the pale blue solid was filtered off, washed with MeOH (5 cm^3) and Et$_2$O (10 cm^3), and dried under vacuum (yield 90 mg, 78%) (Found: C, 39.4; H, 3.3; N, 2.4. C$_{20}$H$_{20}$Cl$_3$NOPRe requires C, 39.1; H, 3.3; N, 2.3%). Molar conductivity, $\Lambda_M = 11\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Table 4 Structure determination summary for complexes **2** and **8***

	2	**8**
Empirical formula	$C_{21}H_{23}Cl_2NO_2PRe$	$C_{38}H_{35}Cl_3NP_2Re$
M	Violet parallelepipeds	Orange parallelepipeds
Colour, habit	0.30 × 0.40 × 0.10	0.15 × 0.20 × 0.30
Crystal size/mm	*Pbca*	*Pna*2_1
Space group	15.967(7)	19.636(7)
a/Å	14.976(6)	17.570(5)
b/Å	18.658(10)	10.172(6)
c/Å	4462(4)	3510(3)
U/Å^3	8	4
Z	1.815	1.628
D_c/Mg m^{-3}	5.8	3.8
μ/mm^{-1}	2368	1704
F(000)	4.0–45.0	4.0–50.0
2θ Range/°	0–17, 0–16, 0–20	0–23, 0–20, 0–12
hkl Ranges	2879	3291
Independent reflections	1611	2522
Observed reflections [$F_o > 4\sigma(F_o)$]	$\sigma^2(F) + 0.0023F^2$	$\sigma^2(F) + 0.0015F^2$
Weighting scheme, w^{-1}	134	211
Number of parameters refined	0.042, 0.050	0.035, 0.043
Final *R*, *R′* (observed data)	0.78	0.83
Goodness of fit	1.00, −1.54	1.33, −0.69
Largest difference peak, hole/e Å^{-3}		

* Details in common: orthorhombic; Siemens R3m/V diffractometer; Mo-Kα radiation (λ = 0.710 73 Å); ω–2θ scans; variable scan rate 2.49–14.65° min^{-1} in ω; scan range 1.05° + Kα; stationary crystal–stationary counter at beginning and end of each scan, each for 25% of total scan time; two standard reflections every 150; SHELXTL PLUS;[37] full-matrix least squares minimising $\Sigma w(|F_o| - |F_c|)^2$; data to parameter ratio 12 : 1.

[ReOCl$_2$(OR)L] (R = Me 2 or Et 3). The salt [NBu$_4$][ReOCl$_4$] (136 mg, 0.27 mmol) was dissolved in MeOH (10 cm^3) (or EtOH) and solid L (166 mg, 0.54 mmol) was added with stirring. The mixture was refluxed for 3 h until a clear violet solution gave a violet precipitate. After cooling, the solid was filtered off, washed with MeOH (3 cm^3) (or EtOH) and Et$_2$O (10 cm^3) and dried under vacuum. Complex **2**: yield 130 mg (79%) (Found: C, 41.5; H, 3.9; N, 2.5. $C_{21}H_{23}Cl_2NO_2PRe$ requires C, 41.4; H, 3.8; N, 2.3%); $\Lambda_M = 8\ \Omega^{-1}\ cm^2\ mol^{-1}$. Complex **3**: yield 83% (Found: C, 41.5; H, 3.9; N, 2.5. $C_{22}H_{25}Cl_2NO_2PRe$ requires C, 42.35; H, 4.05; N, 2.25%); $\Lambda_M = 17\ \Omega^{-1}\ cm^2\ mol^{-1}$.

[ReOX$_2$(OEt)L] (X = Cl 3, Br 4 or I 5). These complexes were prepared in EtOH as described for **2** and **3** but using different starting materials: [ReOCl$_2$(OEt)(PPh$_3$)$_2$] for **3**, [ReOBr$_2$(OEt)(PPh$_3$)$_2$] for **4** and [ReOI$_2$(OEt)(PPh$_3$)$_2$] for **5**. Complex **4**: yield 64% (Found: C, 37.5; H, 3.7; N, 2.1. $C_{22}H_{25}Br_2NO_2PRe$ requires C, 37.1; H, 3.55; N, 1.95%); $\Lambda_M = 20\ \Omega^{-1}\ cm^2\ mol^{-1}$. Complex **5**: yield 51% (Found: C, 33.5; H, 3.5; N, 1.8. $C_{22}H_{25}I_2NO_2PRe$ requires C, 32.75; H, 3.1; N, 1.75%); $\Lambda_M = 23\ \Omega^{-1}\ cm^2\ mol^{-1}$.

[ReO$_2$L$_2$][BPh$_4$] 6. The salt [AsPh$_4$][ReOCl$_4$] (105 mg, 0.14 mmol) was suspended in MeCN (5 cm^3) and solid L (44 mg, 0.14 mmol) was added with stirring. The mixture was left to stand at room temperature for 5 min until it was green. Additional L (44 mg, 0.14 mmol) and an ethanolic solution (2 cm^3) containing 0.2 mol dm^{-3} sodium ethoxide were added. The solution darkened and was stirred overnight at room temperature. Then the solvent was removed by a gentle stream of dinitrogen and the residue treated with water–dichloromethane (1 : 1, 6 cm^3). The organic phase was separated, reduced in volume and treated with ethanol–hexane (10 cm^3). After vigorous stirring a cream solid precipitated. It was washed twice with hexane (5 cm^3) and dried under vacuum. Yield 36 mg (28%) (Found: C, 68.3; H, 6.0; N, 2.5. $C_{68}H_{70}BN_2O_2P_2Re$ requires C, 67.7; H, 5.85; N, 2.3%). $\Lambda_M = 186\ \Omega^{-1}\ cm^2\ mol^{-1}$.

[ReCl$_2$L$_2$][CF$_3$SO$_3$] 7. Complex **2** (50 mg, 0.08 mmol) was dissolved in a CH_2Cl_2–MeOH (1 : 1, 5 cm^3) in a test-tube. Water (1 cm^3) and an excess of neat trifluoromethanesulfonic acid (0.5 cm^3) were added. The tube was capped and after several days yellow crystals separated. They were filtered off and dried under vacuum (yield 11 mg, 14%) (Found: C, 50.4; H, 5.0; N, 2.6; S, 3.0. $C_{45}H_{50}Cl_2F_3N_2O_3P_2ReS$ requires C, 50.3; H, 4.7; N, 2.6; S, 3.0%). $\Lambda_M = 197\ \Omega^{-1}\ cm^2\ mol^{-1}$.

[ReCl$_3$L(PPh$_3$)] 8. The complex [ReCl$_3$(MeCN)(PPh$_3$)$_2$] (83 mg, 0.10 mmol) was suspended in MeOH (10 cm^3). Solid L (59 mg, 0.19 mmol) was added with stirring and the mixture refluxed under a dinitrogen atmosphere for 24 h. The hot yellow-orange solution containing a precipitate was filtered and the orange powder washed with MeOH (3 cm^3) and Et$_2$O (10 cm^3) and dried under vacuum. Yield 60 mg (67%) (Found: C, 53.8; H, 4.4; N, 1.7. $C_{38}H_{35}Cl_3NP_2Re$ requires C, 53.05; H, 4.10; N, 1.65%). $\Lambda_M = 15\ \Omega^{-1}\ cm^2\ mol^{-1}$.

[ReCl$_3$L′(PPh$_3$)] 9. The complex [ReCl$_3$(MeCN)(PPh$_3$)$_2$] (94 mg, 0.11 mmol) was suspended in EtOH–benzene solution (1 : 1, 10 cm^3). Solid L′ (61 mg, 0.22 mmol) and an excess of 37% HCl (0.5 cm^3) were added with stirring and then refluxed for 2 h. The solution turned red-brown and, after cooling, a brick-red solid was filtered off, washed with cold EtOH and Et$_2$O. Yield 30 mg (32%) (Found: C, 52.0; H, 3.6; N, 1.6. $C_{36}H_{31}Cl_3NP_2Re$ requires C, 51.9; H, 3.75; N, 1.7%).

[ReX$_2$L′$_2$]X (X = Cl 10 or Br 11). These two complexes were prepared in a similar way, detailed for **10**. The complex [ReCl$_3$(MeCN)(PPh$_3$)$_2$] (171 mg, 0.20 mmol) was suspended in EtOH–benzene solution (1 : 1, 10 cm^3). Solid L′ (110 mg, 0.40 mmol) and an excess of 37% HCl (0.5 cm^3) were added with stirring. This mixture was refluxed for 18 h and a brick-red solid was filtered off after cooling (see above). The yellow filtrate was reduced in volume by a gentle stream of dinitrogen until a yellow solid precipitated. This powder was filtered off, washed with EtOH (2 cm^3) and Et$_2$O (10 cm^3), and dried under vacuum. Yield 52 mg (30%) (Found: C, 51.7; H, 4.0; N, 3.2. $C_{36}H_{32}Cl_3N_2P_2Re$ requires C, 51.05; H, 3.8; N, 3.3%). Complex **11** was prepared starting from [ReBr$_3$(MeCN)(PPh$_3$)$_2$] and an excess of 48% HBr. Yield 24% (Found: C, 44.9; H, 3.5; N, 2.6. $C_{36}H_{32}Br_3N_2P_2Re$ requires C, 44.1; H, 3.3; N, 2.85%).

[ReOCl$_3$L′] 12. Solid L′ (189 mg, 0.68 mmol) and an excess of 37% HCl (1 cm^3) were added to a solution containing [NBu$_4$][ReOCl$_4$] (100 mg, 0.17 mmol) dissolved in MeCN

(5 cm^3) with stirring at room temperature. A pale blue solid was quickly deposited and was filtered off, washed with EtOH (5 cm^3) and Et_2O (5 cm^3), and dried under vacuum. Yield 85 mg (85%) (Found: C, 37.2; H, 2.7; N, 2.5. $C_{18}H_{16}Cl_3NOPRe$ requires C, 36.9; H, 2.75; N, 2.4%).

Crystallography

Room-temperature crystallisation over 2 d gave violet crystals of complex **2** which were washed with CH_2Cl_2 and dried. Crystals of **8** suitable for X-ray analysis were grown from a CH_2Cl_2 solution layered with EtOH. For both structures the structure determination data are summarised in Table 4. The structures were solved by conventional heavy-atom methods, the co-ordinates of the Re atoms being determined from the Patterson function and those of the remaining non-hydrogen atoms from subsequent Fourier syntheses. Anisotropic thermal parameters were applied only to the Re, Cl and P atoms; all H atoms were included in calculated positions and refined anisotropically using a riding model. The correct configuration of **8** was ascertained by the η test[38] [+1.07(12)]. Absorption correction was performed using the ψ-scan method[39] for fine reflections at χ *ca.* 90° and the refinement procedure was based on *F*.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/415.

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