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Coordination Chemistry of 1,1,1, Tris(diphenylphosphinomethyl)ethane. I. Complexes of Rhenium(III) and (V)

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New six and seven coordinate complexes of rhenium(V) have been prepared with the triphosphine ligand, 1,1,1,tris(diphenylphosphinomethyl)ethane. In the former case the phoshpine is acting as a bidentate and in the latter as a tridentate ligand. Reduction to rhenium(III) can be achieved to give six coordinate complexes ReX_3phosphine ($X = Cl, Br$). The infrared, nmr and electronic spectra of the complexes have been investigated and assignments made to various absorptions. At least six infrared vibrations of the ligand show modification on coordination which can be used as a guide to complex formation. The nmr spectra of the paramagnetic rhenium(III) complexes show interesting differences between the chloro- and bromo- compounds. The chloro-complex shows ^{31}P–H coupling of the CH_2 resonance ($J_{P-H} = 12\text{-}14$ cps) while the bromo-complex shows no coupling at all.

Introduction

The preparation of the triphosphine 1,1,1,tris(diphenylphosphinomethyl)-ethane (TDPME) has been described by Hewertson and Watson.[1] Little is known however, of its coordinating properties. Complexes with group VIB metal carbonyls have been reported[2,3] in which the phosphine is acting as a tridentate ligand. However, with such a ligand it is possible that it may act as a bidentate with one phosphine donor uncoordinated. Therefore its reaction with the entity $ReOCl_3$ existing in a wide range of compounds $ReOCl_3L_2$ (L is monodentate or L_2 is bidentate) is of interest as the compounds produced may be either six coordinate with one uncoordinated phosphine or seven coordinate. In fact evidence is found for both types of compounds.

The complexes formed by the triphosphine with rhenium(III) have also been investigated and it is interesting that whereas the quadridentate and tridentate arsine ligands tris-(*o*-diphenylarsinophenyl)arsine and bis(*o*-diphenylarsinophenyl)phenylarsine[4] stabilise rhenium(II) the triphosphine ligand stabilise rhenium(III).

Experimental Section

Reagents. 1,1,1,tris(diphenylphosphinomethyl)ethane was obtained from Strem Chemicals Inc. and used without further purification.

Potassium perrhenate was prepared by oxidation of rhenium metal powder with 100 volume hydrogen peroxide, followed by addition of potassium hydroxide solution and crystallisation.

Rhenium trichloride was prepared by thermal decomposition of silver hexachlororhenate(IV) at 500°C.

1,1,1,tris(diphenylphosphinomethyl)ethanetrichloro-oxo-rhenium(V). $ReOCl_3$(TDPME) (Blue Isomer). To a solution of potassium perrhenate (0.5 g, 1.73 m. moles) in water (5 ml) and concentrated hydrochloric acid (10 ml) was added TDPME (1.1 g, 1.74 m moles) in acetone (150 ml), followed immediately by hypophosphorous acid (5 ml). The solution was heated under reflux for 2 hours during which time it became blue in colour. After evaporation of the solvent to a small volume, blue crystals separated from the solution on cooling in ice. The product was filtered off washed with water and dried under vacuum. Yield 1.29 g, 80%.

Anal. Calcd. for $C_{41}H_{39}Cl_3OP_3Re$; Re, 19.8; Cl, 11.3; C, 52.5; H, 4.14. Found: Re, 19.3; Cl, 12.4; C, 51.5; H, 4.23.

1,1,1tris(diphenylphosphinomethyl)ethanetrichloro-oxo-rhenium(V). $ReOCl_3$(TDPME) (Green Isomer). Prolonged refluxing of the above reaction mixture for periods up to 24 hours, yielded the same blue solution along with a small amount of an insoluble green material. This was filtered off, washed with water and acetone and dried under vacuum. Yield, 0.17 g, 10.5%.

Anal. Calcd. for $C_{41}H_{39}Cl_3OP_3Re$; Re, 19.8; Cl, 11.3; C, 52.2; H, 4.14. Found: Re, 20.0; Cl, 11.2; C, 51.8; H, 4.51.

1,1,1,tris(diphenylphoshpinomethyl)ethanedichloro-ethoxy-oxo-rhenium(V). $ReO(OEt)Cl_2$(TDPME). $ReOCl_3$(TDPME) (blue or green isomer) (0.25 g) was suspended in ethanol (50 ml) and the mixture refluxed for 5 hours (longer periods of about 40 hours were found necessary for the green isomer). The starting material dissolved completely and produced a pale mauve solution. Evaporation of excess ethanol to small volume, followed by the addition of 50-70° pe-

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troleum ether gave a grey-mauve precipitate. The product was filtered, washed with 50-70° petroleum ether and dried under vacuum. Yield, 0,25 g, 100%.

Anal. Calcd. for $C_{43}H_{44}Cl_2O_2P_3Re$ Re, 19.6; Cl, 7.45; C, 54.1; H, 4.73. Found: Re, 20.2; Cl, 8.10; C, 54.5; H, 4.80.

1,1,1,tris(diphenylphosphinomethyl)ethanetrichlororhenium(III). ReCl$_3$(TDPME). To a solution of $ReOCl_3$(TDPME) (blue isomer) (0.25 g, 0.266 m moles) in acetone (50 ml) was added a solution of sodium dithionite (0.087 g, 0.50 m moles) in water (10 ml). The solution immediately turned yellow-brown accompanied by the evolution of sulphur dioxide and was allowed to stand for 3 hours at room temperature to ensure complete reaction. Excess sodium dithionite, precipitated from the solution, was filtered off and the filtrate evaporated to small volume. On cooling in ice, a buff coloured solid was precipitated. Recrystallised from chloroform-50-70° petroleum ether. Yield, 0.135 g, 55%.

Anal. Calcd. for $C_{41}H_{39}Cl_3P_3Re$ Re, 20.1; Cl, 11.5; C, 53.1; H, 4.22. Found: Re, 21.5; Cl, 11.95; C, 52.4; H, 4.75.

1,1,1,tris(diphenylphoshpinomethyl)ethanetribromorhenium(III). ReBr$_3$(TDPME). To a solution of $ReCl_3$(TDPME) (0.5 g, 0.54 m moles) in a chloroform (50 ml) was aded a solution of lithium bromide (0.188 g, 2.18 m moles) in water (25 ml). The mixture was vigorously shaken for 48 hours, after which time the organic layer was run off in a separating funnel and evaporated to small volume. Addition of 50-70° petroleum ether gave a dark brown solid, which was filtered, washed with 50-70° petroleum ether and dried under vacuum. Recrystallised from chloroform 50-70° petroleum ether. Yield, 0.55 g, 96%.

Anal. Calcd. for $C_{41}H_{39}Br_3P_3Re$ Re, 17.6; Br, 22.7; C, 46.5; H, 3.68. Found: Re, 18.0; Br, 22.5; C, 47.2; H, 4.00.

1,1,1,tris(diphenylphosphinomethyl)ethane-hexachloro-tri-μ-chlorotrirhenium(III). Re$_3$Cl$_9$(TDPME). To a solution of rhenium trichloride (0.55 g, 0.628 m moles) in dry tetrahydrofuran (20 ml) was added TDPME (0.398 g, 0.630 m moles) in dry tetrahydrofuran (15 ml). On standing at room temperature a crop of deep red crystals was precipitated. These were filtered and dried under vacuum. Yield, 0.218 g, 23%.

Anal. Calcd. for $C_{41}H_{39}Cl_9P_3Re_3$; Re, 37.0; Cl, 21.2; C, 32.6; H, 2.58. Found: Re, 37.7; Cl, 20.9; C, 32.8; H, 3.01.

Solvents. All solvents were purified by standard techniques. Acetone was fractionally distilled retaining only the fraction boiling at 56°C to remove ethanol and methanol impurities.

Physical measurements. Conductivities were measured in a dip type cell with bright platinum electrodes using a Philips type P.R. 9500 conductivity bridge. Magnetic moments were measured by the Gouy method.

Infra-red spectra (4000-400 cm^{-1}) were recorded as KBr discs on a Shimadzu IR-27G spectrophotometer. Infra-red spectra (400-40 cm^{-1}) were recorded as nujol mulls on polythene plates on a RIIC Fourier F.S.-720 spectrophotometer.

Electronic spectra were recorded on a Shimadzu M.P.S-50 L spectrophotometer using solution cells or the diffuse reflectance attachment.

Melting points were measured on a calibrated Kofler hot-stage microscope. NMR spectra were obtained using a Varian Associates A-60 spectrometer at 60 Mc/s and 40°C.

Results and Discussion

The preparative interrelations of the compounds are given in Figure 1.

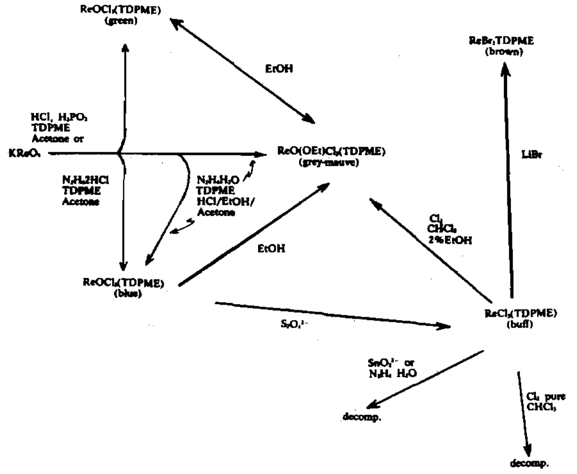

Figure 1.

Rhenium(V) complexes ReOCl$_3$(TDPME). The reaction of the perrhenate ion with TDPME in the presence of HCl and H_3PO_2 yields only complexes of rhenium(V). This is analogous to results reported by Chatt,[5] who isolated a series of complexes of the type $ReOX_3(R_3P)_2$ where X=Cl, Br, I or SCN and R=Ph, Et or *n*–Pr. No tendency was observed for the above reaction involving TDPME to proceed further, yielding tervalent complexes of the type $ReCl_3$(TDPME), in contrast to the case in which the ligand used was diarsine.[6]

The only seven coordinate complexes of the type $ReOX_3(L_3)$ previously reported were $ReOCl_3$(TAS) and $ReOBr_3$(TAS), where TAS=bis-(*o*-diphenylarsinophenyl)phenylarsine,[4] and in this case the bromo complex showed a marked tendency to dissociate in solution, presumably to [$ReOBr_2$(TAS)]Br.

It is of interest that in the case of the reaction involving TDPME, two isomers are in fact isolated. The blue isomer is non-conducting in nitromethane solution, but in the presence of excess methyl iodide, the conductivity rises to the value expected for a 1:1 electrolyte after about 5 hours. This arises by qua-

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Table I. Physical Data for the Complexes

Compound	Oxidation State	Colour	M.P.	Conductivity ohm^{-1} mole^{-1} cm^2	μ_{eff} at 24°C		
ReOCl$_3$(TDPME)	V	Green	214° (with decomp)	1.48^a (with MeI, 0.8)	—	984 cm^{-1} (M—O str.)	V. insol. in most organic solvents 7-coordinate
ReOCl$_3$(TDPME)	V	Blue	130°-160° (turns green) melts 214° (with decomp.)	2.9^a (with MeI, 78.0)	—	986 cm^{-1} (M—O str.)	Soluble in most organic solvents 6-coordinate
ReO(OEt)Cl$_2$(TDPME)	V	Grey-mauve	194-5°	1.9^a (with MeI, 88.2)	—	946 cm^{-1} (M—O str.) 909 cm^{-1} (OEt deform)	6-coordinate
ReCl$_3$(TDPME)	III	Buff	154-6°	2.5^a (with MeI, 4.6)	1.68		
ReBr$_3$(TDPME)	III	Brown	190-3°	3.7^a (with MeI, 8.2)	1.71		
Re$_3$Cl$_9$(TDPME)	III	Red	72.5^b 85.5^a (151.0 after 2 hours) 175.0^c				Formulated as [Re$_3$Cl$_8$(TDPME)]Cl in ethanol

^{a} In nitromethane. ^{b} In ethanol. ^{c} In dimethylformamide.

Table II. Electronic Spectra for Re^V and Re^{III} Complexes

	Charge Transfer and/or Intraligand Bands cm^{-1}		Ligand Field Bands cm^{-1}	
	Solution	Solid^d	Solution	Solid^d
ReOCl$_3$(TDPME)^{a,b} blue isomer	38,000 (6710) (sh)	40,000?	20,700 (7.4)	
	37,300 (7910)		16,500 (21.2)	16,400
	36,200 (6570) (sh)	36,200	12,800 (17.2)	12,700
	32,100 (5340) (sh)	31,700		
	28,200 (1330)			
ReOCl$_3$(TDPME) green isomer		31,300 (br)		16,300
				12,400
ReO(OEt)Cl$_2$(TDPME)^a	37,300 (22,000) (sh)		20,500 (25)	
	36,400 (18,000) (sh)		16,300 (15)	
	34,100 (14,000)		14,900 (8)	
	28,600 (3100) (br)			
ReCl$_3$(TDPME)^a	33,300 (3700)		16,700 (139) (sh)	16,100
			10,900 (21.4)	11,300
			10.500 (16.1) (sh)	
			9,700 (17.1)	9,800
ReBr$_3$(TDPME)^a	32,800 (3550) sh	34,500	16,500 (119)	16,300
		32,800	10,300 (26.5)	12,500
Re$_3$Cl$_9$(TDPME)^c	21,700 (570) (sh)	19,500 (787)	13,200 (264)	

^{a} chloroform; ^{b} acetone; ^{c} ethanol; br = broad; sh = shoulder. Molar extinction coefficients are given in parenthesis. ^{d} diffuse reflectance.

ternisation of an unbound or very weakly bound phosphorus atom and is similar to a method used previously to indicate the presence of uncoordinated arsenic atoms in complexes containing a polydentate arsine ligand.[6] Thus the blue isomer is presumed to contain a six coordinate rhenium atom and its colour and the position of the metal-oxygen stretching frequency in the infra-red spectrum indicate that the coordination around the metal is similar to that in ReOCl$_3$(Et$_2$PhP)$_2$, the structure of which has been determined by X-ray diffraction,[7] the oxygen atom being *trans* to chlorine rather than a phosphorous atom.

The green isomer of ReOCl$_3$(TDPME) is also nonconducting in nitromethane solution, but in this case no rise in the conductivity of such a solution is observed in the presence of excess methyl iodide, even over a period of several days. It is therefore likely that this isomer contains a seven cordinate rhenium atom. The close similarity of the metal-oxygen stretching vibration to that observed for the blue isomer (Table I) indicates that the oxygen atom is again essentially *trans* to chlorine rather than phosphorus.

Attempts to form nitrido-complexes of rhenium(V) containing the ligand TDPME by reduction of the perrhenate ion with hydrazine hydrate, mono-or dihydrochloride were unsuccessful, in contrast to similar reactions involving other organo-phosphorus ligands.[8] The products obtained from the hydrazine TDPME reactions were found to be dependant on the solvent

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employed, but in no case was there any indication of a stable nitrido-complex being formed. When perrhenate was reduced in pure acetone, the blue and green isomers of $ReOCl_3(TDPME)$ were isolated. Similar reductions in an acetone-ethanol mixture yielded a mixture of blue $ReOCl_3(TDPME)$ and $ReO(OEt)Cl_2(TDPME)$.

The electronic spectrum of blue $ReOCl_3(TDPME)$ has been recorded in solution and in the solid while that of $ReOCl_2(OEt)(TDPME)$ is recorded in solution. The spectrum of the green isomer $ReOCl_3(TDPME)$ was recorded in the solid only, as it did not prove to be sufficiently soluble in organic solvents to allow measurements to be made in solution. These results are recorded in Table II.

The electronic spectra of complexes of the type $[ReOCl_5]^{2-}$ have not been extensively studied, but electronic spectra of compounds of the type $[MOCl_5]^{2-}$ (where M = Cr and Mo) have been reported and assigned on the basis of a molecular orbital scheme.[9] This assignment has been extended to complexes of the type $MOCl_3L_2$ (where M = Mo or W and L can be a variety of ligands).[10,11]

The weak bands in spectra of the three compounds reported here have similarities to those mentioned above.[9,10,11] Yet assignments on the basis of the molecular orbital energy level scheme used for $[MoOCl_5]^{2-}$ would be at the most very tentative particularly in view of the lower symmetry of the complexes (*viz.* C_s) and also because the spectra reported for Cs_2ReOCl_5 [12] and for the species $[ReOX_4]^-$ (X = Cl, Br)[13] are more complex than for the molybdenum and tungsten complexes. Considerably more complexes need to be studied and this is in the process of investigation.

The reaction of either blue or green $ReOCl_3(TDPME)$ with ethanol leads to the formation of the same product, although reaction time for the latter is considerably longer. The product is formulated as $ReO(OEt)Cl_2(TDPME)$ and is non-conducting in nitromethane solution. However, in the presence of excess methyl iodide, the conductivity of such a solution rises to the value expected for a 1:1 electrolyte after 5 hours and such behaviour is again taken to indicate the presence of one uncoordinated phosphino- group. No evidence was ever found for a seven coordinate complex of this type.

The position of the metal-oxygen stretching frequency is now observed at 946 cm^{-1} and appears together with a very strong band at 909 cm^{-1}, assigned to an ethoxy-deformation mode. The lowering of the metal-oxygen stretching frequency on replacement of one chlorine atom by an ethoxy-group suggests that the oxo-and ethoxo-ligands are *trans* to each other, as has been reported for analogous complexes.[5,14]

Rhenium(III) Complexes Re(TDPME)X₃ (X=Cl or Br)

No reaction was observed between blue $ReOCl_3(TDPME)$ in acetone and either titanous chloride solution or a suspension of sodium borohydride in ethanol. However, the reaction between blue $ReOCl_3(TDPME)$ in acetone and aqueous sodium dithionite solution gave the complex $Re(TDMPE)Cl_3$ in good yield.

The reaction between $Re(TDPME)Cl_3$ and LiBr is also found to proceed with good yield to give $Re(TDPME)Br_3$.

Both complexes are soluble in most organic solvents, with the exception of petroleum ether, and are found to be non-electrolytes in nitromethane solution. In the presence of excess methyl iodide, such solutions show no change in conductivity over a period of several days and are deduced to contain a six coordinate rhenium atom, the three phosphorus atoms being, of necessity, *cis* to each other and *trans* to the halogen atoms. A molecular model shows that such a configuration is possible.

The magnetic moments observed for these complexes are well below the spin- only value for $Re^{III}(d^4)$ of 2.83 B.M. However, this figure is reduced as a consequence of spin-orbit coupling ($\zeta = 2500\ cm^{-1}$ for Re^{III}) and the observed values are in accord with those reported for other Re^{III} mononuclear complexes.[15]

The electronic spectra of the two complexes are given in Table II. The spectra consist of weak bands around 10,000 cm^{1-} and 16,500 cm^{-1}. The first set may be assigned to the spin forbidden transition $^3T_1 \rightarrow {}^5E$ and the second to $^3T_1 \rightarrow {}^1T_2$, ^1E assuming octahedral symmetry. In fact the symmetry is C_3 and the T_1 and T_2 states will both be split into A and E. Hence the lower symmetry than octahedral together with spin-orbit coupling cause considerable modification to the spectral bands predicted for octahedral symmetry. The bands are in fact broad and for $ReCl_3(TDPME)$ the group around 10,000 cm^{-1} show considerable splitting.

Reduction of $Re(TDPME)Cl_3$ with hydrazine hydrate or sodium stannite solution, in an attempt to obtain the corresponding complex of divalent rhenium, as reported for $[Re(diarsine)_2Cl_2]^+$,[6] proved unsuccessful and resulted in the isolation of decomposition products only.

Oxidation of $Re(TDPME)Cl_3$ in pure chloroform solution by means of chlorine gas, in an attempt to obtain the corresponding chloro-complexes of either tetravalent rhenium as reported for $Re(Et_2PhP)_3Cl_3$ [16] or pentavalent rhenium as reported for $[Re(diarsine)_2Cl_2]^+$,[6] also proved unsuccessful. Again decomposition products only were isolated. The oxidation of $Re(TDPME)Cl_3$ in reagent grade chloroform (containing 2% ethanol) yielded the complex $ReO(OEt)Cl_2(TDPME)$.

Re₃Cl₉(TDPME). The reaction between Re_3Cl_9 and TDPME in a 1:1 mole ratio yields the complex $Re_3Cl_9(TDPME)$. The electronic spectrum of this complex in ethanol shows bands at 513 and 760 mμ (Ratio of extinction coefficients = 3:1), charac-

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Table III. NMR Data for TDPME and its complexes Chemical Shift (in p.p.m. from T.M.S.)

Group	Free ligand [a]	$ReOCl_3(TDPME)$ [a]	$ReO(OEt)Cl_2(TDPME)$ [a]	$ReCl_3(TDPME)$ [b]	$ReBr_3(TDPME)$ [b]
CH_3	−1.01	−0.92	−0.90	−0.90	−0.90
CH_2 (bonded)		−3.00 to −4.00	−3.00 to −4.00	−1.38 and +0.92	−1.26 and +1.00
CH_2 (non-bonded)	−2.53	−2.50	−2.50	—	—
o—phenyl	−7.40	−7.80	−7.84	−7.84	−7.85
p—phenyl *m*—phenyl	−7.27	−7.34	−7.44	−7.3 to −7.64	−7.28 to −7.65
non bonded phenyl		−7.27	−7.27		
CH_2 (OEt)			−3.55		
CH_3 (OEt)			−1.22		

[a] Recorded in deuteroacetone; [b] Recorded in deuterochloroform

teristic of a complex containing the triangular species Re_3Cl_3.[15] The conductivity of the complex in ethanol (Table I) indicates it to be and «11-type» complex, *i.e.* a total of eleven ligands positions occupied around the rhenium triangle. The infra-red spectrum of the complex gave no indication of the presence of coordinated water, as is the case for $Re_3Cl_9(Et_2S)_2H_2O$.[15] Conductivity measurements in nitromethane and dimethylformamide indicated further dissociation in these solvents. Initial values obtained in nitromethane indicated the presence of a 1:1 electrolyte, however, if the solution was allowed to stand for two hours or longer, the conductivity rose to that expected for a 2:1 electrolyte. Initial readings in dimethylformamide always indicated the presence of a 3:1 electrolyte in this solvent. These higher conductivity values may arise by replacement of one or two terminal chlorine atoms by solvent molecules. However, attempts to recover solid samples from these solutions lead only to the formation of black gums.

Attempts to prepare mononuclear rhenium(III) complexes by refluxing the trinuclear complex in acetone were not successful and yielded only the trinuclear complex unchanged. This is in contrast to the complex $[Re_3Cl_9(diarsine)_2]$ which readily yields $(Re(diarsine)_2Cl_2]Cl$.[17]

N.M.R. Spectra. The NMR spectra of the free ligand, TDPME, and the complexes blue $ReOCl_3$ (TDPME), $ReO(OEt)Cl_2(TDPME)$, $Re(TDPME)Cl_3$ and $Re(TDPME)Br_3$ have been examined and the chemical shifts observed are shown in Table III.

Free Ligand. The free ligand spectrum resonances are in the expected positions. The phenyl region is complex and ortho-, meta- and para-multiplets cannot be distinguished with any certainty. The methylene signal shows a remarkably large splitting due to ^{31}P coupling of 2.4 c.p.s compared to values of less than 0.5 c.p.s. in triethylphosphine[18] and diethylphenylphosphine.[19] The methyl resonance is the predicted singlet.

Blue $ReOCl_3(TDPME)$. The approximately octahedral complex, $ReOCl_3(TDPME)$ is inferred as being diamagnetic by analogy with similar known complexes.[5] The spectrum is expected to show resonances due to protons associated with bonded and non-bonded phosphino-groups. This effect is observed for the phenyl resonances, which are complex and show signals due to ortho protons of bonded phosphino-groups at −7.80 p.p.m. and to meta- and para- protons of bonded phosphino groups at −7.34 p.p.m. « Non-bonded » proton signals are observed at −7.27 p.p.m., as in the free ligand. Such non-equivalence of resonance positions is also expected for signals arising from methylene protons. However, other complications arise for these resonances such as $^{31}P–CH_2$ coupling. In addition to this, the two sets of « bonded » methylene protons become magnetically inequivalent on coordination.[19] The pattern observed as a result of these effects should show a signal at about −2.5 p.p.m., split by ^{31}P coupling, arising from the «non-bonded» CH_2 group and a complex resonance due to the magnetic inequivalence and $^{31}P–CH_2$ coupling of « bonded » CH_2 protons. The pattern observed for these resonances is a weak signal at −2.50 p.p.m. assigned to « non-bonded » CH_2, but showing no $^{31}P–CH_2$ coupling and a series of weak signals in the region −3.00 to −4.00 p.p.m. assigned to « bonded » CH_2 groups. Definite assignment of these signals was only made possible by use of integration. Similar weak but complex resonances have been observed for $IrCl_3(Et_2PhP)_3$.[19] The single methyl resonance is observed in the expected region.

$ReO(OEt)Cl_2(TDPME)$. As expected, the spectrum of this complex shows resonances due to the ligand TDPME, at positions very similar to those observed for $ReOCl_3(TDPME)$. Additional signals at −1.22 p.p.m. (triplet) and −3.55 p.p.m. (quartet) ($J = 7$ c.p.s.) arise from the ethoxy-ligand.

$Re(TDPME)X_3$ ($X = Cl$ or Br). Despite the fact that these compounds are paramagnetic, sharp lines (width approx. 2 c.p.s.) are obtained in their spectra. Similar line widths have been reported for the paramagnetic complexes *cis* $ReCl_3(Et_2PhP)_3$ [19] and *cis* $ReCl_3(Me_2PhP)_3$.[20] Surprisingly, the chemical shifts for the phenyl and methyl resonances are not much different to those observed in the free ligand. Complete assignment of the complex phenyl multiplet was not possible, however, integration suggests that the resonance centred on −7.84 and −7.85 p.p.m. for the chloro- and bromo-complexes respectively may be assigned to the ortho-protons. The methylene resonances of the

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Table IV. Infra-red spectrum of TDPME

Frequency (cm^{-1})	Intensity	Assignment
3075	sh	C–H str. (Ar)
3050	m	
3010	sh	
2960	m	assym. C–H str. (CH$_3$)
2940	sh	sym. C–H str. (CH$_3$) or assym C–H str. (CH$_2$)
2895	m	sym. C–H str. (CH$_2$)
2325	w	(1483+843)
1960	w	(1003+958)
1885	w	(1069+918)
1800	w	(958+842)
1586	m	C–C str. (Ar)
1483	s	C–C str. (Ar)
1454	sh	assym. C–H def. (CH$_3$) or CH$_2$ scissors
1450	m	
1434	s	C–C str. (Ar)
1400	m	C–H def. (Ar)
1365	m	sym C–H def. (CH$_3$) X Xsensitive (a)
1323	w	C–C str. (Ar)
1297	w	C–H in plane def. (Ar)
1259	m	CH$_2$ wag (CH$_2$) X sensitive (b)
1174	w	C–H in plane def. (Ar)
1150	w	C–H in plane def. (Ar)
1116	w	CH$_3$ rock
1093	m	X sensitive (c)[a]
1069	m	C–H in plane def. (Ar)
1039	w	—
1028	m	C–H in plane def. (Ar)
1003	m	ring breathing (Ar)
958	w	C–H out of plane def. (Ar)
918	v.w.	C–H out of plane def. (Ar)
842	w	C–H out of plane def. (Ar)
830	m	C–H out of plane def. (Ar)
790	w	CH$_2$ rock (CH$_2$)
760	v.s.	C–H out of plane def. (Ar)
752		
742		
737		
702	v.s.	out of plane ring def. (Ar) and X sensitive (d)[a]
697		
620	w	in plane ring def. (Ar)
560	v.v.w.	—
570		
535	m	X sensitive (e)[b]
519	s	
480	m	
473	m	
431	w	X sensitive (f)[a]
416	w	

[a] Involves P–C stretching vibrations; [b] involves P–C bending vibrations. w = weak, sh = shoulder, m = medium; s = strong, v = very.

two complexes show some differences. The resonance positions for the chloro complex are −1.38 p.p.m. (doublet J = 14 c.p.s.) and +0.92 p.p.m. (doublet, J = 12 c.p.s.), whereas the bromo-complex shows two singlets only, at −1.26 and +1.00 p.p.m.

The absence of ^{31}P–H coupling has been observed for the paramagnetic complexes ReCl$_3$(PR$_2$'R'')$_3$ (R' = Me or Et, R'' = Ph) and is said to be due to a decoupling mechanism involving the unpaired spins causing a rapid ^{31}P relaxation.[19] If this is so these results imply that the unpaired spins are nearer the phosphorus in ReBr$_3$(TDPME) than in ReCl$_3$(TDPME) which correlates with the lower electronegativity of bromine. This suggests the Re→P π-bond in weaker in the chloro-complex than in the bromo- complex. Similar reasoning suggests that the monodentate phosphine in ReCl$_3$(PR'$_2$R'')$_3$ forms stronger π-bonds than does the triphosphine.

Infra-red Spectra. The infra-red spectrum of the free ligand, TDPME, is given in Table IV together with assignments. The assignment of frequencies arising from the phenyl rings and the Ph$_2$P–C groups follows those given by Whiffen for chlorobenzene[21] and Deacon and Green for Ph$_3$P.[22]

X-sensitive modes arising from the Ph$_2$P–C groups are found in slightly higher positions to those of Ph$_3$P.[22] Additional X-sensitive modes arising from the CH$_3$C(CH$_2$)$_3$-group are also observed at 1365 cm^{-1} (sym. C–H str. of CH$_3$ group) and 1259 cm^{-1} (CH$_2$ wag of CH$_2$ groups). All the X-sensitive modes shift on complex formation. (see Table V). Similar shifts have been observed for triphenylphosphine complexes.[22] The bands at 519 and 535 cm^{-1} in the free ligand show remarkably large shifts on coordination but this would probably arise from the constrained

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(22) G. B. Deacon and J. H. S. Green, *Spectrochim. Acta*, *24 A*, 845 (1968).

Table V. X—sensitive and M—Hal. str. modes for Re^{III} and Re^{V} complexes in cm^{-1}

	$ReCl_3(TDPME)$	$ReBr_3(TDPME)$	$ReOCl_3(TDPME)$ (green)	$ReOCl_3(TDPME)$ (blue)	$ReO(OEt)Cl_2(TDPME)$
X-sens (a)	1387 (m)	1395 (m)	1378 (m)	1383 (m)	1375 (w)
X-sens (b)	1190 (m)	1190 (m)	1192 (m)	1190 (s)	1190 (m)
X-sens (c)	1100 (s)	1103 (s)	1095 (s)	1098 (s)	1097 (s)
	1120 (s)	1120 (m)	1115 (msh)	1120 (s)	1118 (s)
X-sens (d)	715 (m)	720 (m)	720 (m)	720 (s)	718 (m)
X-sens (e)	528 (m)	530 (m)	527 (s)	528 (m)	521 (s)
	572 (m)	580 (m)	560 (m)	571 (m)	570 (m)
			581 (m)	589 (m)	585 (m)
X-sens (f)	n.o.	n.o.	444	n.o.	n.o.
M—X	320 (br)	225	330	327.5	327
str.	295	212	310	302.5	320
			275	285	
				277.5	

n.o. = not observed.

nature of the ligand on complex formation giving rise to PC_3 deformation modes at higher frequency than those observed for triphenylphosphine. These modes give rise to two bands in $Re(TDPME)X_3$ complexes of A_1+E symmetry as would be expected for such complexes of C_3 symmetry. Lowering of the symmetry below C_3 should give rise to a splitting of the E mode giving 3 infra-red active modes and these are observed for the rhenium(V) complexes.

The infra-red spectra of the complexes in region 400-40 cm^{-1} have been examined. The free ligand shows strong bands at 377, 240, 232, 195 and 173 cm^{-1}. These are also observed in the complexes, although there are slight shifts in the frequencies. The bands tentatively assigned to metal-halogen stretching vibrations are given in Table V. The complexes $Re(TDPME)X_3$ show the two bands expected for this symmetry. Green $ReOCl_3(TDPME)$ gives rise to three bands, the E mode occurring under C_3 symmetry now being split as the symmetry is lowered. A further small splitting is observed in the 6-coordinate $ReOCl_3(TDPME)$, the origin of which is not clear.

The complex $ReO(OEt)Cl_2(TDPME)$ shows two bands assigned to metal halogen stretching frequencies. Additional bands at 295, 285 and 270 cm^{-1} are also observed in this complex, presumably arising from vibrations of the ethoxy-group.

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