Complexes of Rhenium with Alkyl and Cyclic Phosphites

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Some complexes of the type $[ReX_3L_3]$ and $[ReX_3(O)(PPh_3)L]$ $\{X = Cl$ or Br; $L = P(OMe)_3$, $P[(OCH_2)_3CMe]$, or $P[(OCH_2)_3CEt]\}$ have been prepared by treating $[ReX_3(O)(PPh_3)_2]$ with the corresponding phosphite in a suitable solvent. The preparations and reactions of these complexes and also their i.r. and ^1H n.m.r. spectra are reported.

ALTHOUGH the chemistry of transition-metal–phosphine complexes has been extensively studied, relatively little work has been undertaken on the corresponding complexes of phosphites. The only previously well characterised rhenium–phosphite complexes were $[ReI_3\{P(OPh)_3\}_3]$ [1] and $[ReH_3(PPh_3)_2\{P(OPh)_3\}_2]$ and $[ReH_3(PPh_3)\{P(OPh)_3\}_3]$.[2] However, complexes of the type $[ReX_3(O)(PPh_3)_2]$ (X = Cl, Br, or I) [3,4] are known to undergo reactions with a large number of ligands. These and the related ethoxo-species $[ReX_2(O)(OEt)(PPh_3)_2]$ [5] have been used in the synthesis of Re^{III},[6-8], Re^{IV},[9,10] Re^{V},[4,5] Re^{VI},[11] and Re^{VII} [12] complexes involving such ligands as $PEtPh_2$, $PMePh_2$, CN^-, pentane-2,4-dione, *etc.*

We have treated $[ReX_3(O)(PPh_3)_2]$ with $P(OMe)_3$ and compounds of the type $P[(OCH_2)_3CR]$ (R = Me or Et) and have isolated complexes of the type $[ReX_3(O)(PPh_3)\{P[(OCH_2)_3CR]\}]$ and also $[ReX_3\{P[(OCH_2)_3CR]\}_3]$ together with the trimethyl phosphite analogues. However, attempts to isolate any complex corresponding to the formula $[ReX_3(O)\{P[(OCH_2)_3CR]\}_2]$ have proved unsuccessful. Reactions of $[ReX_3(O)(PPh_3)_2]$ with $P(OR')_3$ (R' = Et or Ph) led to intractable oils. We describe the preparation, properties, and spectral data of these two types of complex. In the case of the paramagnetic species of Re^{III} we have investigated the nature of the paramagnetic effect, using a variable-temperature ^1H n.m.r. probe in conjunction with the Evans method [13-15] for magnetic-susceptibility measurement and compare the paramagnetic effects with those shown by their phosphine analogues.[4,16,17]

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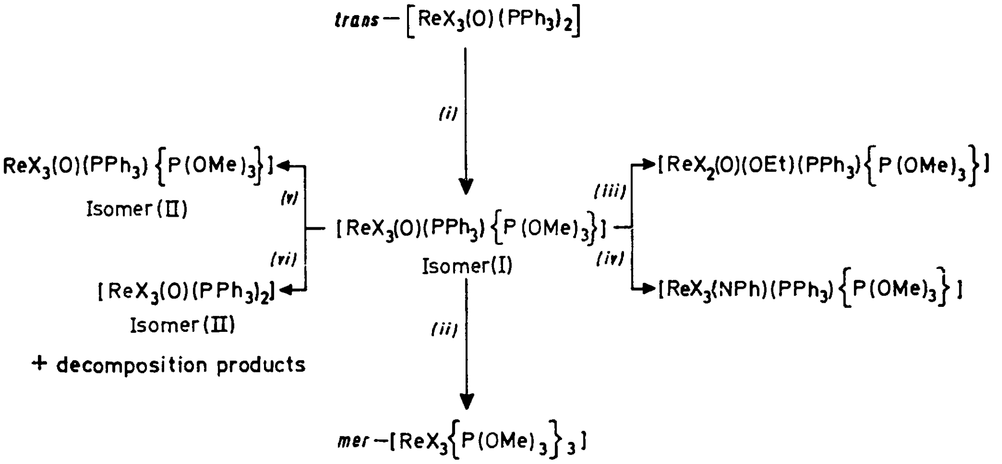
RESULTS AND DISCUSSION

The most easily isolated products were obtained using trimethyl phosphite. The reactions are summarised in the Scheme which also holds for the bicyclic phosphites.

Using $P(OPh_3)_3$, no complex containing the mixed phosphine–phosphite ligand system could be isolated. The only products were $[ReCl_4(PPh_3)_2]$ and a red intractable oil. However, for comparison studies we looked at $[ReI_3\{P(OPh)_3\}_3]$ prepared as previously.[1] We conclude that the reduction from Re^V to Re^{III} [reaction (*ii*) of Scheme] is carried out by the phosphite, and that the phosphine does not enter into the reaction for the following reasons: (*a*) no triphenylphosphine oxide could be isolated from reaction solutions; (*b*) more than 2 moles of phosphite per mole of rhenium were needed for complete reaction; and (*c*) the ^1H n.m.r. of reaction solutions showed a doublet centred at 3.70 p.p.m. downfield from $SiMe_4$, corresponding to trimethyl phosphate. The initial step to $[ReX_3(O)(PPh_3)\{P(OMe)_3\}]$ [reaction (*i*) in the Scheme] took *ca.* 5 min at 20 °C and the reduction of this to Re^{III} [reaction (*ii*) in the Scheme] is slower, taking several hours at 20 °C. No evidence was found for the existence of $[ReX_3(O)\{P(OMe)_3\}_2]$ and attempts to make it by a method similar to the preparation of $[ReX_3(O)(PPh_3)_2]$ [3] proved unsuccessful.



SCHEME (*i*), 1 mol of $P(OMe)_3$ per mol of Re (X = Cl or Br); (*ii*), 3 mol of $P(OMe)_3$ per mol of Re (X = Cl or Br); (*iii*), heat under reflux in EtOH (X = Cl or Br); (*iv*), heat under reflux with aniline in benzene (X = Cl); (*v*), u.v. light (X = Cl or Br); (*vi*), heat under reflux in benzene (X = Cl).

Rhenium(V) *Complexes*.—The complexes are listed in Table 1. The complexes of the type $[ReX_3(O)(PPh_3)\{P(OMe)_3\}]$ (X = Cl or Br) and $[ReX_3(O)(PPh_3)\{P[(OCH_2)_3CR]\}]$ (R = Me or Et) are all diamagnetic despite being octahedral, d^2. The reason for this has been adequately described before.[3,18] The diamagnetism is almost certainly due to a distortion of the t_{2g} orbitals caused by the nature of the Re=O bond.

The i.r. spectra contained a sharp band at 1 090 cm^{-1} characteristic of co-ordinated PPh_3. All the oxo-complexes showed ν(Re=O) in the range 945—960 cm^{-1}. The complexes underwent the following reactions similar to their phosphine analogues. They formed ethoxo- and phenylimido-complexes when allowed to react with EtOH and $PhNH_2$. They isomerised in hot solvents or when exposed to u.v. light. They were reduced to the rhenium(III) species by further addition of phosphite. However, unlike the phosphine analogues, they decomposed when heated under reflux in benzene for 2 h to form isomer (II) $[ReCl_3(O)(PPh_3)_2]$.[4] They are soluble in acetone, dichloromethane, and ethanol and insoluble in light petroleum and diethyl ether.

Rhenium(III) *Complexes*.—The complexes listed in Table 2 all have the general formula $[ReX_3\{P(OR')_3\}_3]$. ^1H N.m.r. studies show them to be octahedral with meridional geometry. They are extremely soluble in most solvents and show evidence of decomposition in moist air.

The most interesting feature of their chemistry is in their ^1H n.m.r. spectra, where the following features were observed: (*a*) they are paramagnetic and hence show Knight shifts;[16] (*b*) they nevertheless give narrow lines (<1 Hz); and (*c*) ^{31}P–^1H couplings are absent. The spectrum of $[ReCl_3\{P(OMe)_3\}_3]$ consisted of two singlets in the ratio 2 : 1 at 11.2 and 10.9 p.p.m. downfield from $SiMe_4$, consistent with a meridional structure, and the spectrum of $[ReI_3\{P(OPh)_3\}_3]$ [1] (prepared for comparison studies) showed a multiplet structure where the shift was generally *ortho* > *para* > *meta*.[16] Features (*a*)—(*c*) had previously been shown [16] for the analogous phosphine complexes and it had been suggested that the narrow line spectra were in fact general for the d^4 system. Variable-temperature studies on the ^1H n.m.r. spectra of these phosphine complexes showed the paramagnetism to be entirely of a second order or Van Vleck type: *i.e.*, (*a*) the Knight shift was a linear function of temperature; (*b*) the temperature gradient was positive and smaller than for normal paramagnetics which give a reciprocal function of temperature.

Variable-temperature studies on our phosphite analogues have given some anomalous results. We measured

[18] D. Loft and A. Symons, *J. Chem. Soc.*, 1960, 973.

TABLE 1

Rhenium(V) complexes

Complex	Colour	Analysis (%) *		Melting range (θ_c/°C)	I.r. bands (cm^{-1})	
		C	H		ν(Re=O)	ν(Re–Hal)
$[ReCl_3(O)(PPh_3)\{P(OMe)_3\}]$, Isomer (I)	Blue	36.1 (36.3)	3.45 (3.45)	172—174	965	333, 290, 274
$[ReCl_3(O)(PPh_3)\{P(OMe)_3\}]$, Isomer (II)	Green	36.15 (36.3)	3.40 (3.45)	180—182	964	325, 280
$[ReBr_3(O)(PPh_3)\{P(OMe)_3\}]$, Isomer (I)	Green	30.1 (30.3)	3.00 (2.90)	165—167	960	
$[ReCl_3(O)(PPh_3)\{P[(OCH_2)_3CEt]\}]$, Isomer (I)	Blue	38.9 (38.9)	3.40 (3.35)	170—172	959	
$[ReCl_2(O)(OEt)(PPh_3)\{P(OMe)_3\}]$	Black	40.5 (40.7)	3.45 (3.40)	140—142	945	302, 270
$[ReBr_2(O)(OEt)(PPh_3)\{P(OMe)_3\}]$	Brown	34.6 (34.8)	3.60 (3.70)	134—136	950	
$[ReCl_2(O)(OEt)(PPh_3)\{P[(OCH_2)_3CEt]\}]$	Brown	42.0 (42.05)	4.00 (4.20)	146—148	948	
$[ReCl_2(NPh)(PPh_3)\{P(OMe)_3\}]$	Green	44.1 (44.15)	3.80 (3.95)	174—176		

* Calculated values are given in parentheses.

TABLE 2

Rhenium(III) complexes

Complex	Colour	Analysis (%) [a]		Melting range (θ_c/°C)	$\mu_{eff.}$ [b]/B.M.	ν(Re–Hal)/cm^{-1}
		C	H			
mer-$[ReCl_3\{P(OMe)_3\}_3]$	Yellow	16.25 (16.15)	4.05 (4.10)	118—120	1.84	317, 298, 278
mer-$[ReBr_3\{P(OMe)_3\}_3]$	Orange	13.5 (13.5)	3.30 (3.40)	122—127	1.74	270, 225, 214
mer-$[ReI_3\{P(OPh)_3\}_3]$	Blue	43.4 (43.3)	3.15 (3.05)	134—136	1.68 [c]	195
mer-$[ReCl_3\{P[(OCH_2)_3CMe]\}_3]$	Yellow	22.5 (22.45)	3.95 (3.90)	184—186	1.59	330, 280, 269
mer-$[ReBr_3\{P[(OCH_2)_3CMe]\}_3]$	Orange	20.55 (20.7)	3.40 (3.10)	174—176	1.48	274, 234, 220

[a] Calculated values are given in parentheses. [b] At 20 °C; 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2. [c] Ref. 1.

χ_m as a function of temperature for $[ReCl_3\{P(OMe)_3\}_3]$ and $[ReI_3\{P(OPh)_3\}_3]$ using the Evans method, incorporating acetonitrile as an external lock and $SiMe_4$ as external and internal reference. In both cases, the shift difference between the two $SiMe_4$ peaks was independent of temperature in the range −20 to 40 °C. Hence χ_m and the magnetic moment for the two complexes appeared to be independent of temperature. However, for $[ReCl_3\{P(OMe)_3\}_3]$ the Knight shifts measured as a function of temperature showed a very slight negative temperature gradient, although not large enough for the dependence to be proportional to T^{-1}, and for $[ReI_3\{P(OPh)_3\}_3]$ the Knight shifts appeared to be independent of temperature in the range −30 to 56 °C within experimental error.

We suggest that these results, which are intermediate between those expected for first- and second-order paramagnetics, are caused by there being both a first- and a second-order contribution to the total Knight shift.

EXPERIMENTAL

Analyses were carried out by the departmental analyst. I.r. spectra were recorded on a Perkin-Elmer 457 spectrophotometer as Nujol mulls between caesium iodide plates, and on a Beckmann-RIIC F.S. 720 spectrophotometer as vaseline mulls between Polythene plates at liquid-nitrogen temperature. ^1H N.m.r. spectra were obtained on a Varian T60 spectrometer using $CDCl_3$ as solvent. Solid-state magnetic moments were measured on a Gouy–Rankine balance.[19]

The complexes $[ReX_3(O)(PPh_3)_2]$ (X = Cl or Br) were prepared as previously,[3,4] as was $[ReI_3\{P(OPh)_3\}_3]$.[1] All preparations were carried out under nitrogen. Rhenium metal was supplied by B.D.H.

mer-*Trichlorotris(trimethyl phosphite)rhenium*(III), *mer*-$[ReCl_3\{P(OMe)_3\}_3]$.—(a) The complex *trans*-$[ReCl_3(O)(PPh_3)_2]$ (1.6 g) was suspended in a solution of $P(OMe)_3$ (0.64 cm^3) in dichloromethane (50 cm^3). The solution was stirred for *ca.* 8 h, becoming dark blue and then yellow. The reaction mixture was reduced (to 5 cm^3) at 20 °C on a rotary evaporator, and was eluted from a silica column (100—200 mesh) using light petroleum (b.p. 40—60 °C)–dichloromethane (1 : 1). The yellow fraction was evaporated to dryness, leaving an oily yellow solid which was recrystallised from light petroleum (b.p. 40—60 °C). The pale yellow needles were filtered off, washed with light petroleum (b.p. 40—60 °C), and dried *in vacuo* (yield 0.45 g).

(b) Isomer I, $[ReCl_3(O)(PPh_3)\{P(OMe)_3\}]$ (1.0 g) was dissolved in a solution of $P(OMe)_3$ (0.64 cm^3) in dichloromethane (50 cm^3). On stirring for 24 h the solution became orange-yellow. The solution was evaporated to dryness leaving a brown oil, which was extracted with boiling light petroleum (b.p. 40—60 °C) (100 cm^3). The extract was evaporated to 10 cm^3 and on cooling yielded pale yellow needles characterised by i.r., n.m.r., and m.p.

mer-*Tribromotris(trimethyl phosphite)rhenium*(III), *mer*-$[ReBr_3\{P(OMe)_3\}_3]$.—This complex was prepared as for the chloride [method (a)] using $[ReBr_3(O)(PPh_3)_2]$ (2.0 g) and $P(OMe)_3$ (0.6 g) and stirring for 1 h. The orange needles were washed as before and dried *in vacuo* (yield 0.43 g).

mer-*Trichlorotris(4-methyl-*2,6,7-*trioxa-*1-*phosphabicyclo-*[2.2.2]*octane)rhenium*(III), *mer*-$[ReCl_3\{P[(OCH_2)_3CMe]\}_3]$.—The complex *trans*-$[ReCl_3(O)(PPh_3)_2]$ (2.4 g) was suspended in a solution of the ligand (1.4 g) in dichloromethane (50 cm^3). The solution was stirred for 8 h becoming dark blue and then yellow. The solution was reduced to 5 cm^3 at 20 °C and the product was precipitated with benzene (10 cm^3). The crude product was recystallised from benzene to give pale yellow *microcrystals* (0.6 g) which were washed with cold benzene and dried *in vacuo*.

mer-*Tribromotris(4-methyl-*2,6,7-*trioxa-*1-*phosphabicyclo-*[2.2.2]*octane)rhenium*(III), *mer*-$[ReBr_3\{P[(OCH_2)_3CMe]\}_3]$.—This complex was prepared as for the chloride, using $[ReBr_3(O)(PPh_3)_2]$ (2.8 g) and giving orange *microcrystals* (0.3 g) which were washed with cold benzene and dried *in vacuo*.

Trichloro-oxo(trimethyl phosphite)(triphenylphosphine)-rhenium(V), $[ReCl_3(O)(PPh_3)\{P(OMe)_3\}]$ [*Isomer* (I)].—The complex $[ReCl_3(O)(PPh_3)_2]$ (2.0 g) was suspended in a solution of $P(OMe)_3$ (0.4 g) in dichloromethane (50 cm^3). The

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[19] D. F. Evans, *J. Chem. Soc.* (*A*), 1967, 1670.

mixture was stirred to give a blue solution (*ca.* 5 min), and was poured into light petroleum (b.p. 40—60 °C). The resulting blue precipitate was filtered off, washed with diethyl ether (5 × 20 cm^3), and dried *in vacuo*. The pale blue *microcrystals* (0.8 g) were not recrystallised due to isomerisation in hot solvents.

Trichloro-oxo(trimethyl phosphite)(triphenylphosphine)rhenium(v), $[ReCl_3(O)(PPh_3)\{P(OMe)_3\}]$ [*Isomer* (II)].—(*a*) Isomer (I) (0.2 g) was exposed to sunlight for 1 week, resulting in pale green *microcrystals* (0.02 g) which were characterised by i.r. and m.p.

(b) A suspension of isomer (I) (1.0 g) in benzene (30 cm^3) was heated under reflux until green. The resulting precipitate was filtered and dried *in vacuo*. The carbon analysis was always high due to the formation of small amounts of *trans*-$[ReCl_3(O)(PPh_3)_2]$ as a decomposition product. Its presence was shown by further heating which formed the insoluble *isomer* (II), $[ReCl_3(O)(PPh_3)_2]$,[4] which was characterised by i.r. spectra.

Tribromo-oxo(trimethyl phosphite)(triphenylphosphine)rhenium(v), $[ReBr_3(O)(PPh_3)\{P(OMe)_3\}]$.—The complex $[ReBr_3(O)(PPh_3)_2]$ (2.1 g) was suspended in a solution of $P(OMe)_3$ (0.42 g) in dichloromethane (30 cm^3). The solution was stirred until green (*ca.* 2 min) and poured into light petroleum (b.p. 40—60 °C) (250 cm^3). The green precipitate was recrystallised from benzene to give green *crystals* (0.6 g).

*Trichloro(4-ethyl-*2,6,7*-trioxa-*1*-phosphabicyclo*[2.2.2]*-octane)oxo(triphenylphosphine)rhenium*(v), $[ReCl_3(O)(PPh_3)\{P[(OCH_2)_3CEt]\}]$.—The complex $[ReCl_3(O)(PPh_3)_2]$ (1.6 g) was suspended in a solution of the ligand (1.4 g) in dichloromethane (50 cm^3). The solution was stirred until dark blue, and was poured into excess of light petroleum (b.p. 40—60 °C). The product was filtered off, washed with diethyl ether (5 × 20 cm^3), and dried *in vacuo* as blue *microcrystals* (0.9 g).

*Dichloroethoxo(4-ethyl-*2,6,7*-trioxa-*1*-phosphabicyclo*[2.2.2]*-octane)oxo(triphenylphosphine)rhenium*(v), $[ReCl_2(O)(OEt)(PPh_3)\{P[(OCH_2)_3CEt]\}]$.—The complex $[ReCl_3(O)(PPh_3)\{P[(OCH_2)_3CEt]\}]$ (1.0 g) was heated under reflux in ethanol (20 cm^3) for *ca.* 8 h resulting in a brown solution. On cooling, the product was precipitated. It was recrystallised from ethanol as brown *needles* (0.6 g) which were dried *in vacuo*.

Dichloroethoxo-oxo(trimethyl phosphite)(triphenylphosphine)rhenium(v), $[ReCl_2(O)(OEt)(PPh_3)\{P(OMe)_3\}]$.—Isomer (I) (0.5 g) was heated under reflux in ethanol (25 cm^3) for 2 h. The volume was reduced to 10 cm^3 by boiling off solvent. On cooling a black precipitate was formed. Recrystallisation from ethanol gave black *crystals* (0.4 g).

Dibromoethoxo-oxo(trimethyl phosphite)(triphenylphosphine)rhenium(v), $[ReBr_2(O)(OEt)(PPh_3)\{P(OMe)_3\}]$.—This complex was prepared as for the chloride using $[ReBr_3(O)(PPh_3)\{P(OMe)_3\}]$ and resulting in brown *crystals* (0.4 g).

Trichloro(phenylimido)(trimethyl phosphite)(triphenylphosphine)rhenium(v). $[ReCl_3(NPh)(PPh_3)\{P(OMe)_3\}]$.—Isomer (I) (1.0 g) and aniline (0.2 cm^3) were stirred for 48 h in benzene (50 cm^3) in a stoppered flask. The resulting brown solution was evaporated to dryness at 20 °C and washed with water–acetic acid (25 cm^3, 1 : 1). The brown oil was dissolved in benzene (20 cm^3), concentrated hydrochloric acid (5 cm^3) was added, and the mixture was heated under reflux overnight. Cooling gave green *crystals* (0.2 g) which were washed with cold benzene and dried *in vacuo*. The i.r. spectrum showed no absorption characteristic of ν(Re=O) or ν(N–H).

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