DALTON
FULL PAPER

Synthesis and characterisation of oxo- and phenylimido-rhenium(V) complexes containing bidentate phosphinoenolato ligands

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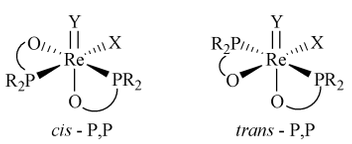
Reacting 1-phenyl-2-(diphenylphosphino)ethanone (P_1~OH), 1-*tert*-butyl-2-(diphenylphosphino)ethanone (P_2~OH) and 1-phenyl-2-(diphenylphosphino)propanone (P_3~OH) with $ReOCl_3(PPh_3)_2$ and $Re(NPh)Cl_3(PPh_3)_2$ in toluene and ethanol in the presence of NEt_3 yields complexes in which these ligands bind as monoanionic enolato chelating agents. Bromo and iodo analogues are prepared similarly. The reactions are solvent dependent. The disubstituted $ReOCl(P\sim O)_2$ compounds obtained in toluene adopt the 'twisted' *cis*-(P,P) octahedral structure. With $Re(NPh)Cl_3(PPh_3)_2$, P_1~OH and P_2~OH give the corresponding $Re(NPh)Cl(P\sim O)_2$ compounds and the *trans*-(P,P)-*trans*-(Cl,Cl) isomer of monosubstituted $Re(NPh)Cl_2(PPh_3)(P\sim O)$ as the major products, together with small amounts of 'twisted' *trans*-(P,P) $Re(NPh)Cl(P\sim O)_2$. The monosubstituted complex is the only species isolated with P_3~OH. The major structural difference between the two systems is the small stability gap between the *cis*- and the *trans*-(P,P) isomers of the imido complexes. In ethanol, unexpected *cis*-ethoxo-oxo complexes $ReO(OEt)(P\sim O)_2$ are isolated, resulting from stereoselective substitution of the halide in the 'twisted' *cis*-(P,P) octahedral complexes. The reactions with $Re(NPh)Cl_3(PPh_3)_2$ are less selective and give rise to mixtures of complexes. The *trans*-ethoxo-phenylimido compound $Re(NPh)(OEt)(P_1\sim O)_2$ is obtained in good yield. A crystallographic study reveals an unexpected 'equatorial' *trans*-(P,P) structure with the ethoxo ligand *trans* to the Re=NPh bond. ^{1}H NMR indicates that the ethoxo ligand acts as an electron reservoir in these complexes, since its protons are strongly deshielded in the *cis*-oxo-ethoxo species and strongly shielded in the *trans*-phenylimido-ethoxo complex.

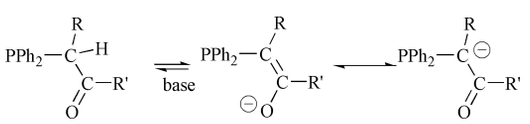
Introduction

Over the recent years, we and others have been investigating the reactions of bidentate phosphinophenols with Re(V) oxo, imido and nitrido complexes and with various Re(III) precursors.[1–10] The interest in these dissymmetric bidentate ligands originates in the presence of soft and hard donor atoms, which impart good co-ordinative capability toward metals in a variety of oxidation states and stereoelectronic control of the co-ordination sphere of the metal. They react with the Re(V) complexes $ReOCl_3(PPh_3)_2$ and $Re(NPh)Cl_3(PPh_3)_2$ by ligand exchange processes, invariably behaving as bidentate four-electron donor anionic ligands and leading to species including *trans* O=Re–O~P and PhN=Re–O~P moieties. The high stability of these two units, due to electron delocalisation, is of particular significance since it reduces the lability of the site *trans* to the multiple bond and decreases significantly the number of geometric isomers obtained. For instance, in the case $ReYCl(P\sim O)_2$ (Y = O, NPh), the 'twisted' *cis*-(P,P) or *trans*-(P,P) isomers shown in Scheme 1 are by far the major products. This point has crucial implications in the area of radiopharmaceuticals, where systems giving stoichiometric and stereospecific reactions are actively desired.[11,12]



Scheme 1

Alkyl- and aryl-functionalised phosphinoketones belong to the family of P~O bifunctional ligands. In the field of organometallic chemistry, they give rise to a variety of stable complexes, in which they are neutral and usually co-ordinated as a monodentate phosphine or as a bidentate phosphinoketone.[13–22] Interestingly, phosphinoketones containing an acidic hydrogen in the α position to the keto function can be converted into their enol tautomer[23] upon addition of a strong base, and the resulting enolate ions (Scheme 2) bind mainly in the monoanionic



Scheme 2

chelating P~O$^-$ form. Several examples have been reported for Ni,[13,24] Co,[16,17] Fe,[18] Pt, Pd,[13,15,25] Rh,[21,22] and Ru.[19,20,26] However, strong electrophilic alkali metals give only monodentate O-bonded compounds,[27] whereas a few cases of co-ordination as a bridging bidentate anionic P~C ligand have been achieved with late transition-metal complexes when phosphinoester ligands were used.[28]

The co-ordinative properties of $Ph_2PCH_2C(O)Ph$ have been tested already toward rhenium in low oxidation states. An

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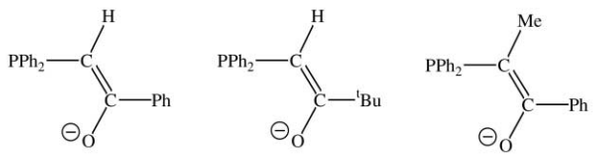
earlier work described the synthesis of Re(I) complexes with the non-deprotonated phosphinoketone bonded as a unidentate (P-bonded) or chelating (P,O-bonded) ligand, and a Re(II) complex containing a chelating phosphinoenolate unit.[29] We reported previously the crystal structures of the Re(V) enolate complexes $ReOCl(Ph_2PCH{=}CO(Ph))_2$ and $ReN(PPh_3)(Ph_2PCH{=}CO(Ph))_2$.[30] However, no imido–Re complexes with ligands of this type have yet been synthesised.

We describe here the reactions of three differently substituted diphenylphosphinoketones (Scheme 3) with $ReOCl_3(PPh_3)_2$ and $Re(NPh)Cl_3(PPh_3)_2$. This study was undertaken to collect information on the structure and stability of the new complexes and to evaluate the potential of these ligands for the preparation of radiopharmaceuticals. The reactions were run in toluene and in ethanol, in the presence of the NEt_3 base as proton quencher. The new oxo and phenylimido reaction products were found to be solvent dependent. Although monochloro species formed in toluene, ethanol gave halo and ethoxo products. Furthermore, with the rhenium–imido core, the stereochemistry of the resulting complexes was found to be sensitive to the P~O ligand used, and the $Re(NPh)(OEt)(P_1{\sim}O)_2$ compound isolated was shown by X-ray diffraction to have an unexpected *trans*-(P,P) arrangement of two phosphinoenolate chelate rings lying in the 'equatorial' plane.



Scheme 3

Experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. $ReOX_3(PPh_3)_2$,[31] $Re(NPh)Cl_3(PPh_3)_2$,[32] 1-phenyl-2-(diphenylphosphino)ethanone ($P_1{\sim}OH$),[15] 1-*tert*-butyl-2-(diphenylphosphino)ethanone ($P_2{\sim}OH$),[19] 1-phenyl-2-(diphenylphosphino)propanone ($P_3{\sim}OH$)[19] and $ReOCl(P_1{\sim}O)_2$ (**1**)[30] were prepared as described in the literature. The preparation of $ReO(OEt)Cl_2(PPh_3)_2$ was adapted from the literature by using NH_4ReO_4 (Strem Chemicals) as the starting material.[33] Infrared spectra (4000–400 cm^{-1}) were recorded as KBr pellets on a Vector 22 Bruker spectrophotometer. ^1H NMR spectra were obtained at room temperature on Bruker AMX 400 and WM 250 instruments. The residual solvent signals (δ = 5.20 ppm for CD_2Cl_2 and 7.30 for $CDCl_3$) were used as internal standard and the chemical shifts are reported with respect to Me_4Si. For the $^{31}P\{^1H\}$ NMR spectra, the AC 200, AMX 300 and ARX 400 instruments were used and the external standard was H_3PO_4 (82% D_2O, δ = 0.0 ppm). Mass spectra were measured with a NERMAG R10–10 spectrometer. Elemental analyses were carried out at the Laboratoire de Contrôle de l'École Nationale Supérieure de Chimie de Toulouse.

Syntheses

***cis*-(P,P)-[ReOBr($P_1{\sim}O)_2$] (2).** To a green suspension of 0.50 g (0.52 mmol) of $ReOBr_3(PPh_3)_2$ in 40 mL of ethanol were added 0.32 g (1.06 mmol) of $P_1{\sim}OH$ and 0.13 g (1.25 mmol) of NEt_3. Refluxing the mixture for 1.5 h gave a clear green solution. Upon cooling, a green solid was deposited, which was filtered off, washed with ethanol and diethyl ether, and dried *in vacuo* (yield 50%). Anal. calc. for $C_{40}H_{32}BrO_3P_2Re$: C, 54.06; H, 3.63. Found: C, 54.90; H, 3.60%. IR (KBr, cm^{-1}): 971 ν(Re=O), 1537 ν(C⋯C⋯O). MS DCI/NH_3 (*m*/*z*, %): 889 (100%) $[M + H]^+$, 826 (20%) $[M - Br + NH_4]^+$.

***cis*-(P,P)-[ReOCl($P_2{\sim}O)_2$] (3).** Same method as above for **2**: 1.08 g (1.3 mmol) of $ReOCl_3(PPh_3)_2$, 0.74 g (2.6 mmol) of $P_2{\sim}OH$, 0.279 g (2.76 mmol) of NEt_3, 50 mL of ethanol. Green solid (yield 85%). Anal. calc. for $C_{36}H_{40}ClO_3P_2Re$: C, 53.76; H, 5.01. Found: C, 53.95; H, 4.94%. IR (KBr, cm^{-1}): 967 ν(Re=O), 1535 ν(C⋯C⋯O). MS DCI/NH_3 (*m*/*z*, %): 805 (100%) $[M + H]^+$.

***cis*-(P,P)-[ReOBr($P_2{\sim}O)_2$] (4).** Same method as **2**: 0.498 g (0.5 mmol) of $ReOBr_3(PPh_3)_2$, 0.28 g (0.98 mmol) of $P_2{\sim}OH$, 0.142 g (1.40 mmol) of NEt_3, 40 mL of ethanol. Green solid (yield 91%). Anal. calc. for $C_{36}H_{40}BrO_3P_2Re$: C, 50.94; H, 4.75. Found: C, 50.27; H, 4.55%. IR (KBr, cm^{-1}): 968 ν(Re=O), 1534 ν(C⋯C⋯O). MS DCI/NH_3 (*m*/*z*, %): 849 (55%) $[M + H]^+$.

***cis*-(P,P)-[ReOI($P_2{\sim}O)_2$] (5).** Same method as **2**: 0.443 g (0.40 mmol) of $ReOI_3(PPh_3)_2$, 0.24 g (0.84 mmol) of $P_2{\sim}OH$, 0.094 g (0.93 mmol) of NEt_3, 35 mL of ethanol. The green complex was recrystallised from diethyl ether (yield 51%). Anal. calc. for $C_{36}H_{40}IO_3P_2Re$: C, 48.27; H, 4.50. Found: C, 47.98; H, 4.12%. IR (KBr, cm^{-1}): 968 ν(Re=O), 1532 ν(C⋯C⋯O). MS DCI/NH_3 (*m*/*z*, %): 897 (100%) $[M + H]^+$, 285 (7%) $[P_2{\sim}OH + H]^+$, 786 (3%) $[M - I + NH_4]^+$.

***cis*-(P,P)-[ReOCl($P_3{\sim}O)_2$] (6).** A mixture of 0.306 g (0.37 mmol) of $ReOCl_3(PPh_3)_2$, 0.234 g (0.74 mmol) of $P_3{\sim}OH$ and 0.306 g (0.37 mmol) of NEt_3 in 40 mL of toluene was refluxed for 4 h. The solvent was evaporated *in vacuo*, the dark-green solid was redissolved in 20 mL of diethyl ether and precipitated with pentane (30 mL). The green solid was filtered off, washed with pentane and dried *in vacuo*. Recrystallisation from ethanol–pentane afforded green crystals (yield 49%). Anal. calc. for $C_{42}H_{36}ClO_3P_2Re$: C, 57.79; H, 4.16. Found: C, 56.96; H, 3.67%. IR (KBr, cm^{-1}): 958 ν(Re=O), 1545 ν(C⋯C⋯O), 320 ν(Re–Cl). MS DCI/NH_3 (*m*/*z*, %): 873 (17%) $[M + H]^+$, 854 (100%) $[M - Cl + NH_4]^+$, 837 (23%) $[M - Cl + H]^+$, 890 (11%) $[M + NH_4]^+$.

***cis*-(P,P)-[ReO(OEt)($P_1{\sim}O)_2$] (7).** To a brown suspension of 0.202 g (0.24 mmol) of $ReO(OEt)Cl_2(PPh_3)_2$ in 20 mL of ethanol were added 0.219 g (0.72 mmol) of $P_1{\sim}OH$ and 0.073 g (0.72 mmol) of NEt_3. The mixture was refluxed for 4 h, giving a brown solution and a brown precipitate. The solution was cooled to increased the amount of precipitate and the brown solid was filtered off, washed with diethyl ether and dried *in vacuo* (yield 40%). Anal. calc. for $C_{42}H_{37}O_4P_2Re$: C, 59.08; H, 4.37. Found: C, 58.80; H, 4.40. IR (KBr, cm^{-1}): 965 ν(Re=O), 1527 ν(C⋯C⋯O). MS DCI/NH_3 (*m*/*z*, %): 855 (100%) $[M + H]^+$, 826 (34%) $[M - EtOH + NH_4]^+$, 809 (7%) $[M - EtOH + H]^+$.

***cis*-(P,P)-[ReO(OEt)($P_2{\sim}O)_2$] (8).** A mixture of 0.202 g (0.24 mmol) of $ReO(OEt)Cl_2(PPh_3)_2$, 0.274 g (0.96 mmol) of $P_2{\sim}OH$, and 0.101 g (1.00 mmol) of NEt_3 in 20 mL of ethanol was refluxed for 4 h, giving a brown solution. Evaporation of the solvent *in vacuo* gave a solid residue, which was extracted with a toluene–pentane mixture to eliminate the ammonium salt. Filtration and evaporation of the solvent gave a brown solid, which was recrystallised from acetonitrile (yield 40%). Anal. calc. for $C_{38}H_{45}O_4P_2Re$: C, 56.07; H, 5.57. Found: C, 56.24; H, 5.58%. IR (KBr, cm^{-1}): 959 ν(Re=O), 1524 ν(C⋯C⋯O). DCI/NH_3 (*m*/*z* %): 815 (42%) $[M + H]^+$, 786 (100%) $[M - EtOH + NH_4]^+$, 769 (13%) $[M - EtOH + H]^+$.

***cis*-(P,P)-[ReO(OEt)($P_3{\sim}O)_2$] (9).** A mixture of 0.202 g (0.24 mmol) of $ReO(OEt)Cl_2(PPh_3)_2$, 0.160 g (0.50 mmol) of

P_3~OH, and 0.050 g (0.50 mmol) of NEt_3 in 30 mL of ethanol was refluxed for 4 h. After cooling, a green solid was deposited, which was filtered off, washed with ethanol and diethyl ether, and dried *in vacuo* (yield 43%). Anal. calc. for $C_{44}H_{41}O_4P_2Re$: C, 59.85; H, 4.68. Found: C, 58.84; H, 4.01%. IR (KBr, cm^{-1}): 959 ν(Re=O), 1545 ν(C⋯C⋯O). MS DCI/NH_3 (*m*/*z*, %): 883 (24%) $[M + H]^+$, 854 (100%) $[M - EtOH + NH_4]^+$, 837 (19%) $[M - EtOH + H]^+$.

***cis*-(P,P)-[Re(NPh)Cl(P_1~O)$_2$] (13).** To a green suspension of 0.18 g (0.20 mmol) of $Re(NPh)Cl_3(PPh_3)_2$ in toluene (20 mL) were added 0.30 g (0.98 mmol) of P_1~OH and 0.10 g (1.00 mmol) of NEt_3. The mixture was refluxed for 24 h, giving a green solution from which a green solid was deposited upon cooling. The solid was filtered off, washed with diethyl ether, and dried *in vacuo* (yield 15%). Anal. calc. for $C_{46}H_{37}ClO_2P_2NRe$: C, 60.09; H, 4.06; N, 1.52. Found: C, 61.85; H, 4.39; N, 1.28%. IR (KBr, cm^{-1}): 1536 ν(C⋯C⋯O). DCI/NH_3 (*m*/*z*, %): 920 (100%) $[M + H]^+$, 901 (14%) $[M - HCl + NH_4]^+$, 884 (4%) $[M - HCl + H]^+$.

***cis*-(P,P)-[Re(NPh)Cl(P_2~O)$_2$] (14).** The procedure used for **13** was applied, with 0.208 g (0.23 mmol) of $(ReNPh)Cl_2(PPh_3)_2$, 0.26 g (0.91 mmol) of P_2~OH and 0.094 g (0.93 mmol) of NEt_3 in 20 mL of toluene. The mixture was refluxed for 1 day. The brown solution was reduced to half volume. Adding pentane and cooling to 4 °C gave a brown-violet solid, which was filtered off, washed with pentane, and dried *in vacuo* (yield 30%). Anal. calc. for $C_{42}H_{45}NO_2P_2ClRe$: C, 57.36; H, 5.16; N, 1.59. Found: C, 57.78; H, 5.38; N, 1.49%. IR (KBr, cm^{-1}): 1527 (br) ν(C⋯C⋯O). MS DCI/NH_3 (*m*/*z*, %): 880 (100%) $[M + H]^+$, 861 (25%) $[M - HCl + NH_4]^+$, 884 (5%) $[M - HCl + H]^+$.

***trans*-(P,P)-[Re(NPh)Cl(P_2~O)$_2$] (15).** The procedure used for **13** was applied, with 0.208 g (0.23 mmol) of $Re(NPh)Cl_3(PPh_3)_2$, 0.26 g (0.91 mmol) of P_2~OH, and 0.94 g (0.93 mmol) of NEt_3 in 20 mL of ethanol. The mixture was refluxed for 5 h. After cooling, the solution deposited a green solid, which was filtered off, washed with pentane, and dried *in vacuo* (yield 60%). Anal. calc. for $C_{42}H_{45}NO_2P_2ClRe$: C, 57.36; H, 5.16; N, 1.59. Found: C, 56.26; H, 5.15; N, 1.60%. IR (KBr, cm^{-1}): 1536 ν(C⋯C⋯O). DCI/NH_3 (*m*/*z*, %): 880 (100%) $[M + H]^+$.

***trans*-(P,P)-[Re(NPh)(OEt)(P_1~O)$_2$] (16).** A mixture of 0.185 g (0.20 mmol) of $Re(NPh)Cl_3(PPh_3)_2$, 0.30 g (0.98 mmol) of P_1~OH, and 0.10 g (1.00 mmol) of NEt_3 in 20 mL of ethanol was refluxed for 16 h. Upon cooling a green solid was deposited, which was filtered off, washed with diethyl ether and dried *in vacuo* (yield 60%). Crystals suitable for X-ray work were grown from chloroform. Anal. calc. for $C_{48}H_{42}O_3P_2NRe$: C, 62.06; H, 4.56; N, 1.51. Found: C, 62.00; H, 4.77; N, 1.48%. IR (KBr, cm^{-1}): 1512 ν(C⋯C⋯O). MS DCI/NH_3 (*m*/*z*, %): 930 (7%) $[M + H]^+$, 901 (100%) $[M - EtOH + NH_4]^+$, 884 (9%) $[M - EtOH + H]^+$.

Crystallographic measurements and structure determination for 16

Green crystals suitable for X-ray diffraction work appeared overnight in an NMR tube containing a $CDCl_3$ solution of **16**. A specimen was glued on to a glass fibre and mounted on an Enraf-Nonius CAD-4 diffractometer. Low-angle spots in an axial photograph led to a reduced triclinic cell,[34] for which no higher Laue symmetry was detected. A whole sphere of data was collected, corrected for absorption and averaged to provide the basic four-octant data set. The structure refined normally in the centric space group $P\bar{1}$.

The structure was solved by the direct methods of SHELXS-86[35] and ΔF syntheses of SHELXL-93.[36] The non-hydrogen atoms of the complex were readily located. The asymmetric unit contained one severely disordered chloroform molecule. Four sites with separations of 2.34–2.39 Å were found in the ΔF map, consistent with fractional Cl atoms, but they could not be assembled into sets of three sites for a chloroform unit. Thus, in addition to positional disorder, the solvent showed high thermal motion, probably rocking about a Cl–Cl vector, so that two of the Cl sites of each fractional chloroform unit were relatively well defined, whereas the third Cl and the C atoms could not be distinguished from the general background. By refining the U_{iso} and occupancy factors of these sites for a few cycles, occupancies close to 0.50 were obtained. They were fixed to 0.50 for the rest of the refinement. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealised positions and refined as riding atoms with C–H distances of 0.93 (sp^2) or 0.96 Å (methyl). Their isotropic temperature factors were adjusted to 20% (sp^2) or 50% (methyl) above the value for the supporting atom. The VOID routine of the PLATON software[37] was used to check that no holes remained in the structure. Crystal data are collected in Table 1.

Table 1 Crystal data for compound **16**

Empirical formula	$C_{48}H_{42}NO_3P_2Re{\cdot}CHCl_3$
M	1048.33
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	12.027(3)
b/Å	12.377(3)
c/Å	17.916(3)
α/°	72.09(3)
β/°	80.05(2)
γ/°	63.03(2)
V/Å^3	2260.0(9)
Z	2
T/°C	20
λ/Å	1.54178 (CuKα)
D_c/g cm^{-3}	1.541
μ/mm^{-1}	7.86
Crystal dimensions/mm	0.74 × 0.34 × 0.11
$R1$ [$I > 2\sigma(I)$]	0.0419
$wR2$ [$I > 2\sigma(I)$]	0.1186
S	1.118

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [c] $S = [\Sigma[w(F_o^2 - F_c^2)^2]/(N_{reflns} - N_{params})]^{1/2}$.

CCDC reference number 178319.

See http://www.rsc.org/suppdata/dt/b1/b106306p/ for crystallographic data in CIF or other electronic format.

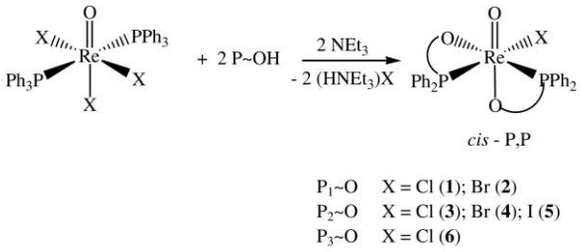
Results

Synthesis of the *cis*-(P,P)-ReOX(P~O)$_2$ complexes (X = Cl, Br, I, OEt)

The oxo Re(v) phosphinoenolato complexes were obtained in good yield *via* ligand exchange of P~OH with the halide precursors $ReOX_3(PPh_3)_2$ and $ReO(OEt)Cl_2(PPh_3)_2$. Since the nature of the complexes was found to depend on the solvent polarity, the reactivity in toluene and in ethanol was investigated.

Reactions in toluene. Reacting two equivalents of the diphenylphosphinoketones (P~OH) with $ReOX_3(PPh_3)_2$ (X = Cl, Br, I) in refluxing toluene (110 °C) in the presence of two equivalents of the NEt_3 base produced quantitatively the 'twisted' *cis*-(P,P)-ReOX(P~O)$_2$ complexes (Scheme 4) as insoluble products. Since simultaneous precipitation of $(HNEt_3)Cl$ occurred, recrystallisation from ethanol was needed to get pure samples.

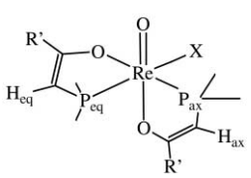
The compounds were characterised by elemental analysis, whereas mass spectrometry (DCI/NH_3) indicated monomeric molecular species. The $[M + H]^+$ parent ions give the



Scheme 4

predominant peaks for **1**–**5**, whereas the highest peaks for **6** correspond to $[M - Cl + H]^+$ and $[M - Cl + NH_4]^+$, which indicates that the halogen is less strongly bonded in the latter complex. In all cases, the ν(Re=O) stretch appears clearly in the 958–973 cm^{-1} range. Ligand co-ordination in the enol form is confirmed by the presence of ν(C⋯C⋯O) bands in the 1530–1545 cm^{-1} range and the disappearance of the typical ν(C=O) stretch of the free ligand in its keto form at *ca.* 1650 cm^{-1}. A small, but significant, decrease of ν(Re=O) in the series P_1~$O^- > P_2$~$O^- > P_3$~O^- suggests that the nucleophilic character of the enol oxygen *trans* to the Re=O bond varies in the reverse order.[38]

The *cis*-(P,P) 'twisted' structure observed in the crystals of **1**[30] is retained in solution for **1**–**6**, as evidenced from NMR spectroscopy. In all cases, the $^{31}P\{^1H\}$ spectra show resonances for two non-equivalent enolato ligands. Both P donors must be co-ordinated, since the signals have moved downfield considerably upon co-ordination to the strongly acidic $[Re=O]^{3+}$ core and formation of the five-membered metallacycles.[39,40] AX-type spectra are observed, consisting of two doublets with $^2J_{PP}$ values of *ca.* 11 Hz characteristic of two P atoms occupying *cis* positions in octahedral Re(v) complexes[1,3–11] (Table 2). Assigning the individual doublets to P_{ax} or P_{eq} (Scheme 5) is not



Scheme 5

straightforward. Crystal structures of analogous Re(v) complexes with P~O ligands indicated that, in the absence of particular steric effects, the Re–P_{eq} bonds are generally shorter than the Re–P_{ax} bonds.[1–3,8,30] On this basis, the downfield doublet was assigned to P_{eq} and the upfield one to P_{ax} in earlier studies. This generalisation is assumed to hold here, although it raises a problem for the related ethoxo complexes **7**–**9** to be discussed below. No *trans* effect of the halide is detected (Table 2), since the P_{eq} chemical shift is not halide sensitive, but a small *cis* effect is observed on P_{ax}, which may be steric in origin.

The presence of the two non-equivalent enolato P~O ligands is confirmed by ^1H NMR spectroscopy. Compounds **1**–**5** show signals for two ethylenic protons H_{ax} and H_{eq} in the range 4.1–5.6 ppm, appearing as doublets due to coupling to the nearby phosphorus atom (Scheme 5). These protons are assigned individually from the 2D $^{31}P/^1H$ spectrum of **3** (Fig. 1), where coupling is unambiguously found to occur between the low-field P_{eq} nucleus (16.1 ppm), the high-field ethylenic proton H_{eq} (4.52 ppm) and the low-field CH_3 group of the ^{t}Bu substituent (1.39 ppm), on the one hand, and between the high-field P_{ax} (8.3 ppm), the low-field ethylenic H_{ax} (4.98 ppm) and the high-field ^{t}Bu methyl group (0.64 ppm), on the other hand. These large chemical shift differences between the two ligands illustrate the importance of electron delocalisation in stabilising these Re(v) complexes. For **6**, the two methyl groups appear as doublets near 1.8 ppm. Replacing the electron-releasing *t*-butyl substituent on the enol carbon in **3** by an electron-withdrawing

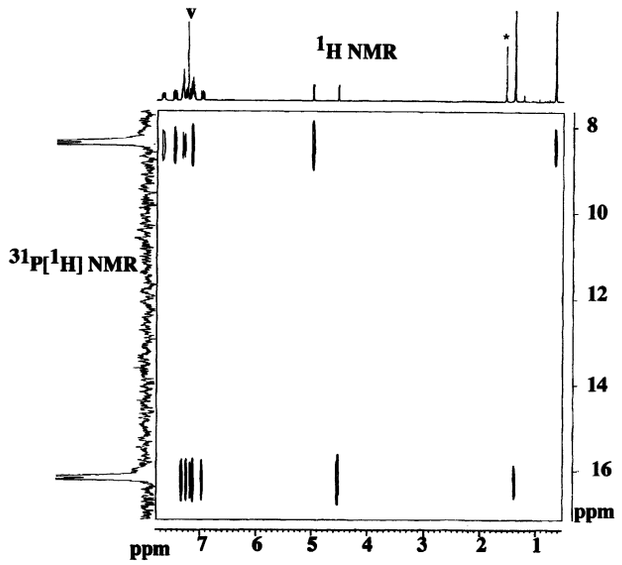


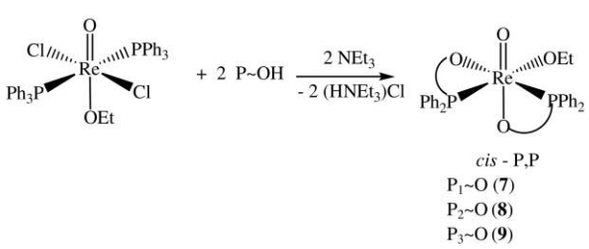
Fig. 1 2D $^{31}P/^1H$ NMR spectrum of $ReOCl(P_2$~$O)_2$ (**3**) in $CDCl_3$.

phenyl group in **1** produces the expected deshielding of the ethylenic protons (4.98/4.52 ppm for **3** *versus* 5.60/5.28 ppm for **1**).

Reactions in ethanol. When the above reactions with $ReOCl_3(PPh_3)_2$ were performed in refluxing ethanol (78 °C) for 2 h in the presence of NEt_3, besides $ReOCl(P$~$O)_2$ (**1**, **3**, **6**), a new species appeared, which was shown to be the 'twisted' *cis*-(P,P)-$ReO(OEt)(P$~$O)_2$ complex (**7**–**9**) (*vide infra*) in which the Re–Cl bond has ethanolysed. The ratio of the two complexes was ligand dependent: $ReOCl(P$~$O)_2$ was the major species for P_1~O and P_2~O, but only the minor product for P_3~O, as though ethanolysis occurred faster for the P_3~O complex. At this stage, concentrating the solutions gave exclusively **1**, **3**, **6** as microcrystalline solids.

In order to cast some light on the fact that $ReO(OEt)(P_3$~$O)_2$ formed as the major species, the reaction between $ReOCl_3(PPh_3)_2$ and P_3~OH/NEt_3 in refluxing ethanol was monitored by $^{31}P\{^1H\}$ NMR (Fig. 2). $ReO(OEt)(P_3$~$O)_2$ was obtained as the only species after 1 h, showing complete ethanolysis of the Re–Cl bond. After 4 h, the mixture consisted of a *ca.* 1 : 3 ratio of the chloro (**6**) and ethoxo (**9**) compounds, whereas heating for 11 extra hours produced the chloro complex **6** as the only species. Therefore, **6** is the thermodynamic complex, while **9** is the kinetic species. On the other hand, adding HCl to an ethanol solution of **9** at room temperature for 2 h produced **6** quantitatively.

This contrasts with the exchange reactions performed with $ReO(OEt)Cl_2(PPh_3)_2$. In these cases, complexes **7**–**9** were obtained quantitatively (Scheme 6), and under all the experi-



Scheme 6

mental variations applied, the $ReOCl(P$~$O)_2$ complexes never formed. This suggests that HCl is an active species in this process, since the acid formed is completely quenched as $(HNEt_3)Cl$ in the present case, whereas 1 equivalent of HCl is liberated when starting with $ReOCl_3(PPh_3)_2$.

Table 2 Selected spectroscopic properties of the complexes

	Compound	$^{31}P\{^1H\}$ NMR (ppm; Hz)[a] P_{ax}	P_{eq}	$^2J_{PP}$	^1H NMR (ppm; Hz)[a] H [or Me]	IR ν(Re=O)/cm^{-1}
1	$ReOCl(P_1{\sim}O)_2$	8.1	16.2	11.0	5.28 (d, $^2J_{HP}$ = 3.5); 5.60 (d, $^2J_{HP}$ = 4.9) [C=CH]	973
2	$ReOBr(P_1{\sim}O)_2$	7.4	17.3	11.7	5.00 (d, $^2J_{HP}$ = 4.0); 5.35 (d, $^2J_{HP}$ = 4.9) [C=CH]	971
3	$ReOCl(P_2{\sim}O)_2$	8.3	16.1	11.8	4.52 (d, $^2J_{HP}$ = 5.1); 4.98 (d, $^2J_{HP}$ = 6.2) [C=CH] 0.64 (s); 1.39 (s) [*t*-Bu]	967
4	$ReOBr(P_2{\sim}O)_2$	7.1	16.5	11.8	4.39 (d, $^2J_{HP}$ = 5.3); 5.07 (d, $^2J_{HP}$ = 6.1) [C=CH] 0.66 (s); 1.40 (s) [*t*-Bu]	968
5	$ReOI(P_2{\sim}O)_2$	5.6	16.1	11.8	4.14 (d, $^2J_{HP}$ = 4.0); 5.17 (d, $^2J_{HP}$ = 5.6) [C=CH] 0.61 (s); 1.38 (s) [*t*-Bu]	968
6	$ReOCl(P_3{\sim}O)_2$	19.6	29.7	11.0	1.74 (d, $^3J_{HP}$ = 10.0); 1.80 (d, $^3J_{HP}$ = 10.0) [C=CMe]	958
7	$ReO(OEt)(P_1{\sim}O)_2$	3.4	14.9	7.5	5.22 (d, $^2J_{HP}$ = 4.4); 5.35 (d, $^2J_{HP}$ = 1.3) [C=CH] 5.38 (ABH_3P, m, $^2J_{AB}$ = 10.7; $^3J_{AH}$ = 6.9; $^4J_{AP}$ = 4.1); 5.45 (ABH_3P, m, $^2J_{AB}$ = 10.9; $^3J_{BH}$ = 6.9; $^4J_{BP}$ = 2.0) [ethoxo CH_2] 1.25 (t, $^3J_{HH}$ = 6.9) [ethoxo CH_3]	965
8	$ReO(OEt)(P_2{\sim}O)_2$	5.0	16.1	8	4.68 (dd, $^2J_{HP}$ = 5.7; $^4J_{HP}$ = 0.5); 4.69 (d, $^2J_{HP}$ = 2.4) [C=CH] 0.56 (s); 1.36 (s) [*t*-Bu] 5.14 (qd, $^3J_{HH}$ = 7.0; $^4J_{HP}$ = 2.6) [ethoxo CH_2] 1.16 (t, $^3J_{HH}$ = 7) [ethoxo CH_3]	959
9	$ReO(OEt)(P_3{\sim}O)_2$	17.2	22.5	8.0	1.67 (d, $^3J_{PH}$ = 10.0); 1.74 (d, $^3J_{PH}$ = 10.0) [C=CCH_3] 5.30 (ABH_3P, m, J_{AB} = 11.0; $^3J_{AH}$ = 7.0; $^4J_{AP}$ = 1.8); 5.39 (ABH_3P, m, $^2J_{AB}$ = 11.0; $^3J_{BH}$ = 7.0; $^4J_{BP}$ = 3.7) [ethoxo CH_2] 1.33 (t, $^2J_{HH}$ = 7.0) [ethoxo CH_3]	959
10	$Re(NPh)Cl_2(PPh_3)(P_1{\sim}O)$	−5.7	21.2	273		
11	$Re(NPh)Cl_2(PPh_3)(P_2{\sim}O)$	−6.8	21.9	273		
12	$Re(NPh)Cl_2(PPh_3)(P_3{\sim}O)$	29.0	34.4	272		
13	$Re(NPh)Cl(P_1{\sim}O)_2$ ('twisted' *cis*-PP)	9.6	18.7	7.0	5.30 (d, $^2J_{HP}$ = 3.5); 5.38 (d, $^2J_{HP}$ = 4.4) [C=CH]	
14	$Re(NPh)Cl(P_2{\sim}O)_2$ ('twisted' *cis*-P,P)	14.9	19.0	7.0	4.56 (d, $^2J_{HP}$ = 5.2); 4.91 (d, $^2J_{HP}$ = 4.2) [C=CH] 0.83 (s); 1.40 (s) [*t*-Bu]	
15	$Re(NPh)Cl(P_2{\sim}O)_2$ ('twisted' *trans*-P,P)	14.2	28.4	236	4.49 (dd, $^2J_{HP}$ = 5.4, $^4J_{HP}$ = 1.0); 4.50 (dd, $^2J_{HP}$ = 2.4, $^4J_{HP}$ = 1.3) [C=CH] 0.65 (s); 1.07 (s) [*t*-Bu]	
16	$Re(NPh)(OEt)(P_1{\sim}O)_2$ ('equatorial' *trans*-P,P)	3.6			5.40 (t, $^2J_{HP}$ = $^4J_{HP}$ = 1.2) [C=CH] 2.72 (ABH_3P_2, m, $^2J_{AB}$ = 11.2; $^3J_{AH}$ = 7.0; $^4J_{AP}$ = 1.7); 2.95 (ABH_3P_2, m, $^2J_{AB}$ = 11.2; $^3J_{BH}$ = 7.0; $^4J_{BP}$ = 2.0) [ethoxo CH_2] −0.14 (t, $^2J_{HH}$ = 7) [ethoxo CH_3]	
17	$Re(NPh)(OEt)(P_2{\sim}O)_2$ ('equatorial' *trans*-P,P)	4.5				

[a] In $CDCl_3$. Multiplicity in parentheses: s = singlet; d = doublet; t = triplet; m = multiplets.

Compound **7** is stable under the conditions prevailing in the mass spectrometer, since the $[M + H]^+$ parent peak is predominant. This is not the case for **8** and **9**, whose main peaks are $[M - EtOH + NH_4]^+$, thus indicating a decreased stability of the Re–OEt bond. The ν(Re=O) stretch is observed at 959–965 cm^{-1}, as expected, and the presence of the ν(C···C···O) stretches in the 1520–1550 cm^{-1} range confirms the coordination of both ligands in their enolato form. The ethoxo ligand is characterised by its strong ν(C–C–O) asymmetric stretch at *ca.* 1050 cm^{-1}.[41] The ν(Re=O) frequency follows the order $P_1{\sim}O > P_2{\sim}O = P_3{\sim}O$. With the $P_3{\sim}O$ ligand, the ν(Re=O) frequencies are identical for the chloro and ethoxo complexes, whereas the frequency is *ca.* 8 cm^{-1} lower for the ethoxo compounds of $P_1{\sim}O$ and $P_2{\sim}O$, indicating that in these two cases the Re=O bond gets weaker when Cl is regioselectively replaced by OEt.

Complexes **7**–**9** show AX-type $^{31}P\{^1H\}$ NMR spectra with chemical shifts following the same trends as the halogen analogues (**1**–**5**) and $^2J_{PP}$ constant of *ca.* 8 Hz, consistent with the 'twisted' *cis*-(P,P) structure. The spectra of **7** and **8** exhibit distinct signals for the ethylenic proton of the axial and equatorial ligands, respectively, whereas two signals for methyl substituents are similarly found for **9** (Table 2). The ethoxo methyl protons give a triplet at *ca.* 1.25 ppm, whereas the diastereotopic methylene protons produce a complex multiplet in the 5.0–5.5 ppm range. For **7** and **9**, this multiplet actually consists of two overlapping $H_AH_BH_3P$ patterns, each due to the non-equivalent methylene protons H_A and H_B coupling together (*ca.* 11 Hz), with the methyl protons (*ca.* 7 Hz) and one phosphorus atom ($^4J_{P–HA/HB}$ 2–4 Hz). The presence of such patterns and the significant downfield shifts experienced by these protons agree with a *cis*-oxo-ethoxo structure, since these effects are not found for the methylene protons in the related *trans*-oxo-ethoxo *cis*-(P,P) complexes.[8,42] Surprisingly, complex **8** gives a single multiplet, as if H_A and H_B were equivalent. Since the ^{31}P data indicate that **8** has the same structure as **7** and **9**, the equivalence of these protons likely results either from an accidental chemical shift coincidence or some dynamic exchange process. In the three compounds, the ethoxo CH_2 protons are coupled to a ^{31}P nucleus, as noted for $ReO(OEt)(Ph_2PCH_2C_6H_4O)_2$.[8] The 2D $^{31}P/^1H$ NMR spectrum of **7** (Fig. 3) proves that this coupling involves only the upfield ^{31}P signal, which has been assigned to the P_{ax} donor sitting *cis* to the ethoxo group. This is rather surprising, since the couplings observed so far occurred with a *trans* P atom and we have no explanation at this time for this different behaviour.

The ethoxo signals are significantly deshielded as compared with those of various Re–oxo complexes containing a *trans* O=Re–OEt unit with different types of chelating ligands (Table 3). However, they compare well with those observed for the *cis*-oxo-ethoxo $ReO(OEt)(Ph_2PCH_2C_6H_4O)_2$ complex[8] and indicate a large ethoxo-to-rhenium electron transfer, thereby decreasing the nucleophilicity of the ethoxo group, which thus behaves like a chloro ligand.

Synthesis of *cis*- and *trans*-(P,P)-Re(NPh)X(P~O)$_2$ (X = Cl, OEt)

The solvent dependence noted above for the reactions of P~OH with the oxo precursor is also found to affect the reactivity of $Re(NPh)Cl_3(PPh_3)_2$. As generally observed, in the latter case, the reactions are slower and less selective, higher ligand : Re

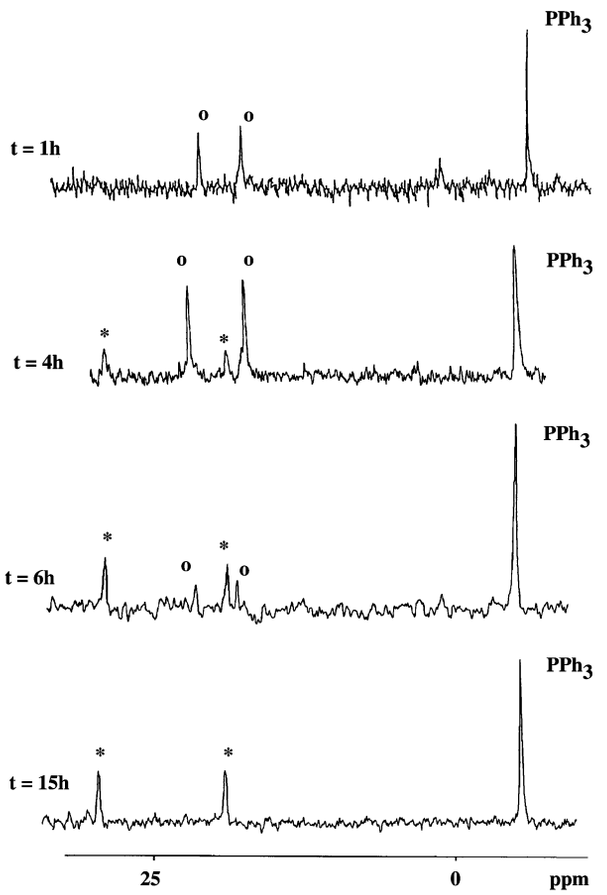


Fig. 2 Monitoring the reaction of $ReOCl_3(PPh_3)_2$ with P_3~OH and NEt_3 (complex : ligand molar ratio = 1 : 2) in ethanol by $^{31}P\{^1H\}$ NMR (80.0 MHz). o = $ReO(OEt)(P_3{\sim}O)_2$ (**9**), * = $ReOCl(P_3{\sim}O)_2$ (**6**).

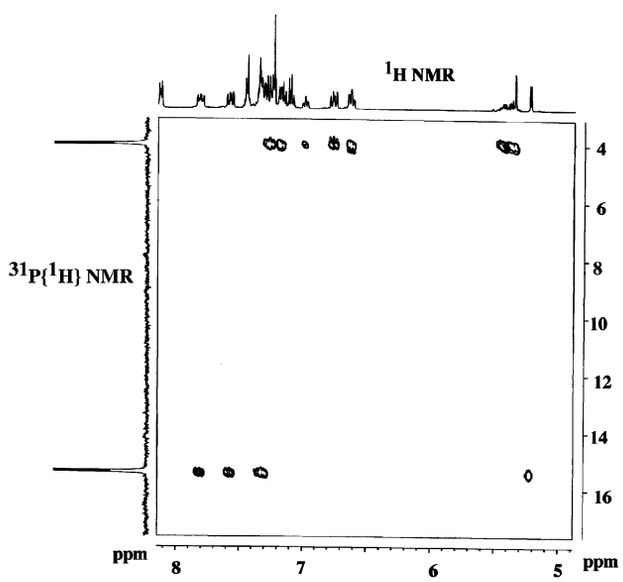


Fig. 3 2D $^{31}P/^1H$ NMR spectrum of $ReO(OEt)(P_1{\sim}O)_2$ (**7**) in $CDCl_3$.

ratios are needed for the substitution to go to completion, and the influence of the ligand is more pronounced.

Reactions in toluene. Considering that the oxo complexes were efficiently generated in toluene *via* ligand exchange, the similar reactions starting from $Re(NPh)Cl_3(PPh_3)_2$ and phosphinoenols in basic media was checked by $^{31}P\{^1H\}$ NMR. The three main species detected (Scheme 7) gave characteristic AX- or AB-type spectra, from which the *cis*- or *trans*-(P,P) configuration of the octahedral species was determined *via* the $^2J_{PP}$ constant (Table 2).

Thus, refluxing a 4 : 4 : 1 ratio of P_1~OH, NEt_3 and $Re(NPh)Cl_3(PPh_3)_2$ in toluene for 4 h gave a clear green solution. Concentration of this solution *in vacuo* produced a mixture of compounds which was soluble in $CDCl_3$ and analyzed by $^{31}P\{^1H\}$ NMR. The spectrum showed signals for PPh_3 (−4 ppm), the free neutral ligand in its keto form (−16 ppm) and two new complexes. The major product exhibited doublets at 9.6 and 18.7 ppm with a $^2J_{PP}$ constant of 7 Hz, consistent with the 'twisted' *cis*-(P,P) disubstituted $Re(NPh)Cl(P_1{\sim}O)_2$ complex (**13**). The monosubstituted *trans*-(P,P)-$Re(NPh)Cl_2(PPh_3)$-(P_1~O) species (**10**), showing doublets at −5.7 and 21.2 ppm with a $^2J_{PP}$ constant of 273 Hz, formed in slightly smaller amount. By increasing the reactant ratio to 5 : 5 : 1 and the reaction time to 24 h, a green solid was precipitated, which was found to be the pure *cis*-(P,P) complex **13**.

P_2~OH was reacted under the same conditions for 4 h and the reaction was followed as above. The monosubstituted *trans*-(P,P) complex $Re(NPh)Cl_2(PPh_3)(P_2{\sim}O)$ (**11**) (doublets at −6.8 and 21.9 ppm, $^2J_{PP}$ = 273 Hz) appeared as the major species, whereas *cis*-(P,P)-$Re(NPh)Cl(P_2{\sim}O)_2$ (**14**) (doublets at 14.9 and 19.0 ppm, $^2J_{PP}$ = 7 Hz) formed in smaller amount. Traces of a third species, the 'twisted' *trans*-(P,P) complex Re(NPh)Cl-(P_2~O)$_2$ (**15**), were detected from the doublets at 14.2 and 28.4 ppm ($^2J_{PP}$ = 236 Hz). Twenty-four hours later, the monosubstituted complex **11** had decreased significantly, while the *cis*-(P,P) disubstituted compound **14** had become the major species. The proportion of the *trans*-(P,P) isomer **15** had not changed. Reducing the volume of the solution and adding pentane precipitated, as above, the 'twisted' *cis*-(P,P) compound **14** as a brown-violet solid.

Refluxing P_3~OH for 4 h gave only the *trans*-(P,P) monosubstituted complex $Re(NPh)Cl_2(PPh_3)(P_3{\sim}O)$ (**12**), showing ^{31}P doublets at 29.0 and 34.4 ppm with a $^2J_{PP}$ constant of 272 Hz. No new species appeared in the solution as heating was pursued.

Only the *cis*-(P,P)-$Re(NPh)Cl(P{\sim}O)_2$ complexes with P_1~O (**13**) and P_2~O (**14**) were successfully isolated as powders stable in air and in solution. No attempts were made to obtain the monosubstituted complexes by using a lower ligand : metal ratio. The formulas proposed for **13** and **14** are consistent with the microanalyses and the mass spectra (DCI/NH_3), whose strongest features are the parent peaks $[M + H]^+$. However, small peaks are observed for $[M - HCl + H]^+$ and $[M - HCl + NH_4]^+$, resulting from chloride loss, showing that the Re–Cl bond is less stable here than it was in the Re=O analogues, where such peaks were absent. As usual, no ν(Re=NPh) stretch could be identified in the IR spectra, because these vibrations overlap with ν(C–N) and ν(C–P) ligand modes. P~O coordination in the enolato form is evidenced from the strong and broad IR ν(C···C···O) stretch at 1536 cm^{-1} for **13** and 1527 cm^{-1} for **14**. For both compounds, the ^1H NMR spectrum includes individual signals for the vinylic protons of the two non-equivalent ligands (5.30/5.38 ppm for **13**, 4.56/4.91 ppm for **14**), which appear as doublets due to coupling with the nearby phosphorus atom (Table 2). As noted for the related Re–oxo complexes, the vinyl protons of P_2~O appear upfield from those of P_1~O.

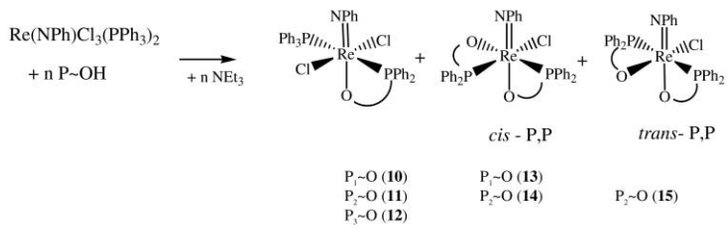
Reactions in ethanol. Refluxing a 5 : 5 : 1 ratio of P_1~OH, NEt_3 and $Re(NPh)Cl_3(PPh_3)_2$ in ethanol for 7 h precipitated quantitatively a green solid analysing as $Re(NPh)(OEt)(P_1{\sim}O)_2$ (**16**). Its ^{31}P NMR spectrum in $CDCl_3$ showed only one singlet at 3.6 ppm, consistent with the high-symmetry structure shown in Scheme 8. This complex is stable since the spectrum remained unchanged after refluxing the mixture for 40 h.

When P_2~OH was reacted under the same conditions, the $^{31}P\{^1H\}$ spectrum of the solution showed evidence for two complexes. The major species was the 'twisted' *trans*-(P,P)-$Re(NPh)Cl(P_2{\sim}O)_2$ complex (**15**), showing doublets at 14.2 and

Table 3 X-Ray and NMR data for the ethoxo co-ligand in Re(v) oxo and imido complexes

Compound	Structure	NMR data (ppm) CH_3; CH_2	X-Ray data	Ref.
$[ReO(OEt)(P_1{\sim}O)_2]$ (**7**)	*cis* O–Re–OEt 'twisted' *cis*-P,P	1.25 (t); 5.38, 5.45 (m)		This work
$[ReO(OEt)(P_2{\sim}O)_2]$ (**8**)	*cis* O–Re–OEt 'twisted' *cis*-P,P	1.16 (t); 5.14 (qd)		This work
$[ReO(OEt)(P_3{\sim}O)_2]$ (**9**)	*cis* O–Re–OEt 'twisted' *cis*-P,P	1.33 (t); 5.30, 5.39 (m)		This work
$[ReO(OEt)(P^*{\sim}O)_2]$ [a]	*cis* O–Re–OEt 'twisted' *cis*-P,P	1.05 (t); 5.03, 5.56 (m)		8
$[ReO(OEt)(cyclam)]^{2+}$ [b]	*trans* O–Re–OEt	1.17 (t); 3.68 (q)		55
$[ReO(OEt)Cl_2(P{\sim}N)$ [c]	*trans* O–Re–OEt 'equatorial' *cis*-P,P	0.49 (t); 2.93 (m)		54
$[ReO(OEt)(dppd)]$ [d]	*trans* O–Re–OEt 'equatorial' *cis*-P,P	0.15 (t); 2.56 (m)		10,43
$[ReO(OEt)(Hdpa)_2]$ [e]	*trans* O–Re–OEt 'equatorial' *cis*-P,P	0.00 (t); 2.91 (m)	Re–O: 2.004(7) Å Re–O–C: 124.6(6)°	42
$[ReOI_2(OEt)(PPh_3)_2]$	*trans* O–Re–OEt 'equatorial' *trans*-P,P	−0.26 (t); 1.51 (q)	Re–O: 1.880(9) Å Re–O–C: 176.2(14)°	51
$[Re(NPh)(OEt)(P_1{\sim}O)_2]$ (**16**)	*trans* N–Re–OEt 'equatorial' *trans*-P,P	−0.14 (t); 2.72, 2.95 (m)	Re–O: 1.951(3) Å Re–O–C: 135.0(3)°	This work
$[Re(NPh)(OEt)(dppd)]$ [d]	*trans* N–Re–OEt 'equatorial' *cis*-P,P	0.30; 3.06 (q)	Re–O: 2.003(8) Å (av.) Re–O–C: 125(1)° (av.)	10,44
$[Re(NPh)(OEt)(bipy)_2]^{2+}$	*trans* N–Re–OEt	0.35; 3.25 (q)	Re–O: 1.895(5) Å Re–O–C: 147.5(6)°	46

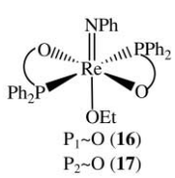
[a] P*~OH = 2-diphenylphosphino-4-methylphenol. [b] Cyclam = 1,4,8,11-tetraazacyclotetradecane. [c] P~N = *o*-(diphenylphosphino)-*N*,*N*′-dimethylaniline. [d] H_2dppd = *N*,*N*′-bis[2-(diphenylphosphino)phenyl]propane-1,3-diamine. [e] H_2dppa = (*o*-aminophenyl)diphenylphosphine.



Scheme 7

28.4 ppm with a $^2J_{PP}$ constant of 236 Hz. Re(NPh)(OEt)$(P_2{\sim}O)_2$ (**17**), similar to **16**, formed as a minor species, characterised by a singlet at 4.5 ppm. Again, increased refluxing time had no influence on the reaction. Concentration of the solution produced only green crystals of pure **15**.

P_3~OH reacted differently. The reaction mixture contained only PPh_3, free ligand and the monosubstituted *trans*-(P,P)-Re(NPh)$Cl_2(PPh_3)(P_3{\sim}O)$ compound (**12**) identified from its doublets at 29.0 and 34.4 ppm with a $^2J_{PP}$ constant of 272 ppm. This complex could not be precipitated. The formation of ethoxo species was not observed.



Scheme 8

Complex **16** was characterised as the 'equatorial' *trans*-(P,P)-Re(NPh)(OEt)$(P_1{\sim}O)_2$ isomer on the basis of elemental analysis, IR spectra, mass spectra, NMR data and crystal structure. The ethoxo ligand was detected from its medium intensity ν(O–C–C) IR stretching band at 1032 cm^{-1}. Co-ordination of P_1~O in its enolato form was confirmed by the absence of a ν(C=O) band and the presence of the ν(C⋯C⋯O) stretch at *ca.* 1512 cm^{-1}. In the mass spectrum, the strongest feature is the $[M - EtOH + NH_4]^+$ peak (100%), the low intensity of the parent peak $[M + H]^+$ (7%) being indicative of the low thermal stability of the Re–OEt bond. The equivalence of the two co-ordinated P~O ligands is deduced from the ^{31}P and ^{1}H NMR data (Table 2). The ^{31}P spectrum exhibits only one singlet. ^{1}H NMR signals are found for all the ligand protons, but there are only half as many as for the 'twisted' complexes. The two equivalent vinyl protons give a triplet at 5.40 ppm, due to virtual coupling with two phosphorus atoms, in agreement with the P atoms being *trans* to one another. The 'equatorial' *trans*-(P,P) structure adopted by **16** is quite unusual, since all 'equatorial' alkoxo species reported so far for Re–oxo complexes with P~O and P~N chelating ligands adopt the *cis*-(P,P) configuration.[42–44] Thus, the energy difference between the *cis*-(P,P) and the *trans*-(P,P) configurations should be small.

The ethoxo group *trans* to the Re=NPh bond gives a methyl triplet at −0.14 ppm, whereas the diastereotopic methylene protons give $H_AH_BH_3P_2$ multiplets at 2.72 and 2.95 ppm, respectively, due to coupling with one another, the methyl protons and two P nuclei. These $^4J_{HP}$ couplings of ~2 Hz to two *cis* P atoms are rather unusual for Re complexes. These signals have shifted upfield with respect to free EtOH (1.2 CH_3; 3.6 CH_2), but they remain in the range reported for groups *trans* to O=Re or PhN=Re units (Table 3). These upfield shifts confirm that an important electron transfer occurs from the PhN group into its *trans*-ethoxo ligand in accordance with the *trans* influence exerted by the phenylimido group. It could also result in part from the ethoxo group being located close to an enolate oxygen and undergoing an H/O through-space interaction.

The 'equatorial' ethoxo compound (**17**) could not be isolated with the P_2~O ligand, even though it was present in solution. Instead, the trans-(P,P) monochloro complex (**15**) was obtained.

It is noteworthy that the related chloro complex precipitated as the *cis*-(P,P) isomer (**14**) in toluene. The *trans*-(P,P) species obtained in ethanol appears to be the thermodynamic product, poor solubility being probably responsible for isolating the *cis* compound as the kinetic product from toluene. A subtle difference in phosphorus binding between these two isomers is revealed by the ^{31}P NMR spectra. The P_{eq} signal appears at much lower field for the *trans*-(P,P) complex **15**, thus indicating a stronger Re–P_{eq} bond than in the *cis* isomer.

Complex **15** was characterised by elemental analysis. The highest peak in the mass spectra was that of the parent ion, confirming that the stable Re–Cl bond had resisted alcoholysis. The ν(C⋯C⋯O) stretches for the enolato group appeared at

1536 cm^{-1}. The ^1H NMR spectra confirmed the octahedral 'twisted' *trans*-(P,P) structure indicated by ^{31}P NMR (Table 2). In **14**, the vinyl proton of each ligand appears as a doublet (4.56, 4.91 ppm) resulting from an intraligand $^2J_{PH}$ coupling of *ca.* 5.5 Hz with the nearby phosphorus atom, no coupling being detected with the other P atom. In contrast, for **16**, these vinyl protons are coupled with the two mutually *trans* P atoms, giving $HP_{ax}P_{eq}$-type signals in both cases (Table 2).

Crystal structure of Re(NPh)(OEt)(P_1~O)$_2$ (16)

The crystal structure of **16** confirms that the stereochemistry of the molecule is the same in solution and in the solid state. ORTEP drawings are provided in Fig. 4 and 5. Selected bond lengths and angles are listed in Table 4.

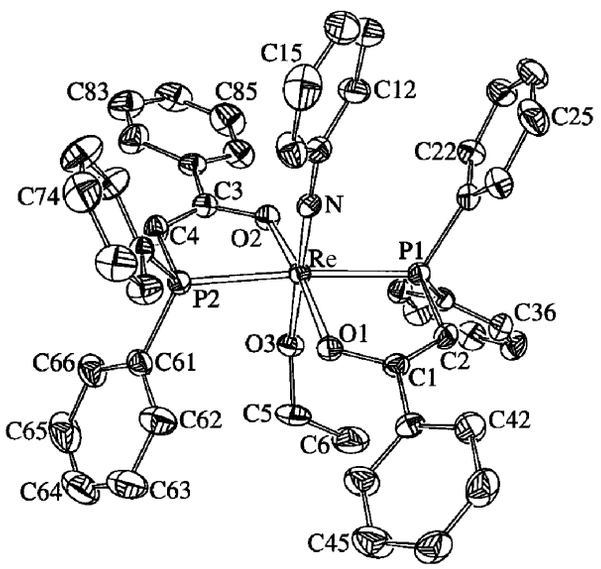


Fig. 4 ORTEP drawing of **16**. Ellipsoids correspond to 40% probability. Hydrogens are omitted for simplicity. In the ring-numbering scheme, the last digit corresponds to the position around the ring, starting with 1 for the *ipso* position.

The Re atom adopts a distorted octahedral co-ordination. The two phosphinoenolate ligands lie the equatorial plane (perpendicular to the Re=NPh multiple bond) with the P donors *trans* to one another, whereas the sixth co-ordination site is occupied by the oxygen of an ethoxo group.

The 'pinched' distortion in the octahedron is due to the small O–Re–P bite angles (*ca.* 80.5°), similar to those found in **1** and ReN(PPh_3)(P_1~O)$_2$,[30] but a few degrees smaller than those reported for various transition metals.[14–17,21–23,25–28] Most of the distortion is absorbed by the O1–Re–O2 angle [169.7(1)°], so that the two other *trans* angles remain closer to ideality [N–Re–O3 = 179.4(1)° and P1–Re–P2 = 175.6(3)°]. As usual, the equatorial ligands are displaced away from the Re=N multiple bond, as evidenced from the N–Re–L_{eq} angles ranging from 90.7 to 95.7° (mean 93.5°), whereas the O3–Re–L_{eq} angles involving the ethoxo oxygen lie in the 88.9–84.0° range (mean 86.5°). As a result, the Re atom lies 0.135(1) Å away from the P_2O_2 'equatorial' plane, on the Re=N side.

The Re–P distances [2.447(1) and 2.420(1) Å] are normal, similar to those observed in the related systems.[1–3,8,30] The geometry about the amide N atom is consistent with a triply-bonded N–Ph group. The Re–N–C(Ph) unit is essentially linear [178.4(3)°], whereas the Re–N and N–C distances of 1.745(4) and 1.378(6) Å, respectively, correspond with the mean values reported for phenylimido–alkoxo compounds.[44–50] The phenyl ring stands upright, roughly perpendicular to the equatorial plane. The phenyl plane bisects the O1–Re–P2 and O2–Re–P1 angles (dihedral angle of 48.5 and 50.9° with the Re–O1–O2–N–O3 and Re–P1–P2–N–O3 planes, respectively), which contrasts with the case of *cis*-(P,P)-Re(NPh)(OMe)(Hdpa)$_2$, [where $Hdpa^-$ is the monoanion of (*o*-aminophenyl)diphenylphosphine],[44] in which the N-phenyl ring is rotated above the chelate rings.

Table 4 Selected bond lengths (Å) and angles (°) for **16**

Re–P1	2.447(1)	P2–C61	1.805(5)
Re–P2	2.420(1)	P2–C71	1.835(5)
Re–N	1.745(4)	N–C11	1.378(6)
Re–O1	2.076(3)	O1–C1	1.328(5)
Re–O2	2.081(3)	O2–C3	1.323(5)
Re–O3	1.951(3)	O3–C5	1.420(6)
P1–C2	1.777(5)	C1–C2	1.341(7)
P1–C31	1.819(5)	C1–C41	1.494(6)
P1–C21	1.845(5)	C3–C4	1.362(7)
P2–C4	1.736(5)	C3–C81	1.517(6)
		C5–C6	1.498(9)
P1–Re–P2	175.61(3)	C21–P1–C31	103.0(2)
P1–Re–N	90.68(13)	Re–P2–C4	99.13(17)
P1–Re–O1	80.62(9)	Re–P2–C61	118.86(16)
P1–Re–O2	100.94(9)	Re–P2–C71	116.47(15)
P1–Re–O3	88.86(11)	C4–P2–C61	108.4(3)
P2–Re–N	93.32(13)	C4–P2–C71	108.6(2)
P2–Re–O1	97.25(9)	C61–P2–C71	104.8(2)
P2–Re–O2	80.47(9)	Re–N–C11	178.4(3)
P2–Re–O3	87.15(11)	Re–O1–C1	119.6(3)
N–Re–O1	94.47(15)	Re–O2–C3	119.2(3)
N–Re–O2	95.72(15)	Re–O3–C5	135.0(3)
N–Re–O3	179.38(14)	O3–C5–C6	112.8(5)
O1–Re–O2	169.67(12)	O1–C1–C2	125.8(4)
O1–Re–O3	85.86(13)	O1–C1–C41	111.6(4)
O2–Re–O3	83.97(14)	C2–C1–C41	122.6(4)
Re–P1–C2	98.09(16)	P1–C2–C1	115.8(3)
Re–P1–C31	118.32(15)	O2–C3–C4	124.7(4)
Re–P1–C21	119.16(15)	O2–C3–C81	112.7(4)
C2–P1–C21	108.8(2)	C4–C3–C81	122.5(4)
C2–P1–C31	109.0(2)	P2–C4–C3	116.2(4)

The axial Re–O3(ethoxo) bond [1.951(3) Å] is similar to those found for alkoxo groups *trans* to the Re=NPh bond.[44–50] Considering that distances of 2.04, 1.86 and 1.75 Å have been proposed for typical single, double and triple bonds, respectively,[51] the Re–O3 distance indicates a significant double-bond character. On the other hand, those with the P~O ligands [2.076(3) and 2.081(3) Å] correspond to typical single bonds.

Electron delocalisation in the co-ordinated enolate ligand is evidenced from various structural features discussed earlier:[14] the P–C bonds in the rings [1.777(5) and 1.736(5) Å] are much shorter than those (*ca.* 1.83 Å) found for the same ligand co-ordinated as the neutral keto form; multiple bond character makes the C–C bonds [1.341(7) and 1.362(7) Å] shorter than the single bonds in the keto form (*ca.* 1.51 Å); the opposite effect is noted for the C–O bonds [mean 1.325(7) Å], which have lost some double bond character compared with the keto form (*ca.* 1.20 Å).

The departure from planarity in the P–C–C–O part of the co-ordinated ligands, although significant, is not very large (mean deviations from least-squares plane of 0.008 Å for O1–C1–C2–P1 and 0.030 Å for O2–C3–C4–P2), but the Re atom lies considerably out theses planes, the Re-to-plane distances being 0.032 and 0.142 Å, respectively. It was noticed earlier[30] that the phenyl substituent on the double bond tends to be coplanar with the chelate ring, probably because this orientation favours extended electron delocalisation. This holds true here for one of the rings (dihedral angle of 11° for ring C81–86), but the resulting stabilisation is probably not great since the dihedral angle is *ca.* 40° for ring C41–46 in the other ligand.

The Re–O3–C5 bond angle of 135.0(3)° in the ethoxo group lies in the normal range.[44–54] Interestingly, the O3–C5 bond is nearly coplanar with the Re–O1 bond [C5–O3–Re–O1 torsion angle = 7.3(5)°] (Fig. 5). This orientation and the relatively large angle at the ethoxo oxygen create favourable conditions for

bonding interactions between the ethoxo π orbitals and the empty d_{xz} and d_{yz} orbitals on rhenium. This point will be further discussed below.

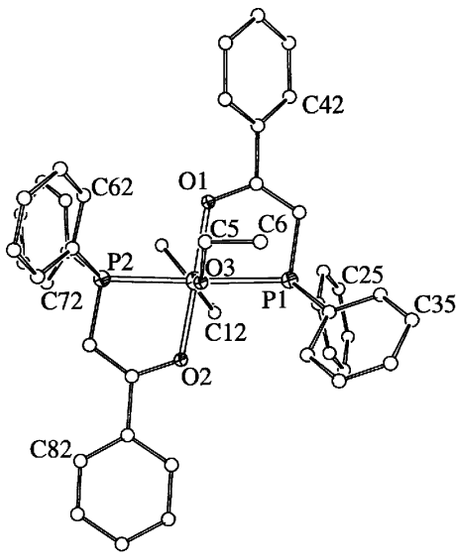


Fig. 5 Simplified ORTEP view of **16** showing the location of the *trans* OEt ligand. The atoms are numbered as in Fig. 4.

^{99m}Tc complexes

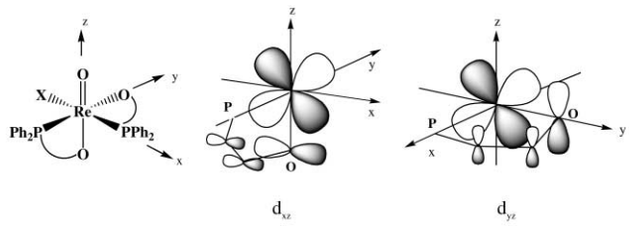
Preliminary results on the biodistribution of the neutral complexes resulting from the co-ordination of P_1~OH to the ^{99m}Tc(III), ^{99m}TcO and ^{99m}TcN centres, carried out by the procedures described elsewhere,[12] indicated that the species are taken up by the liver and the spleen due to their lipophilic character, whereas the uptake in other organs is unimportant.

Discussion

In the presence of NEt_3 acting as base and proton quencher, phosphinoketones give a new series of Re(V) oxo and imido complexes in which they are bonded to the metal centre in their enolate form *via* the enol oxygen and the phosphorus atoms. All these compounds share as a common feature the presence of an oxygen donor *trans* to the multiple Re=O or Re=NPh bond, which is a well-established trend in Re(V) chemistry.

Full characterisation of these complexes allowed us to make comparisons with the reactivity of the related phosphinophenol ligand toward the $[Re{=}O]^{3+}$ and $[Re{=}NPh]^{3+}$ cores. The first difference to be pointed out is the crucial role played by NEt_3 in the reactions involving phosphinoenols, since only a mixture of complexes was isolated without this reagent. In contrast, with phosphinophenol, NEt_3 accelerated the process, but the reaction occurred even in its absence. This agrees with the fact that phenols are easier to deprotonate than enols. A second major difference is the influence of the solvent. Phosphinophenol affords halide complexes, while phosphinoenols in ethanol give ethoxo compounds whose stability and structure depend on the ligand and the Re=Y core.

The $[Re{=}O]^{3+}$ core gives only disubstituted complexes, which all show a *cis*-(P,P) 'twisted' octahedral configuration with the two bidentate ligands located in mutually orthogonal planes. Molecular orbital calculations carried out on P_1~O^- indicate that the HOMO is a bonding π orbital (similar to that of an allylic system) highly localised on the enol oxygen atom.[27] This stereochemistry allows efficient electron delocalisation *via* π-bonding interactions to take place, since electron density can flow from the enol oxygens into the **two** empty rhenium d_{xz}/d_{yz} orbitals already involved in the Re=O π bonds (Scheme 9). It is noteworthy that in the electron-rich d^8 Ni(II) complex $Ni(P_1{\sim}O)_2$, where these d orbitals are not empty, electron



Scheme 9

density is delocalised in a different way: the complex reacts with the electrophilic CoI_2 to give the binuclear enolato-bridged complex $Ni(P_1{\sim}O)_2CoI_2$.[22]

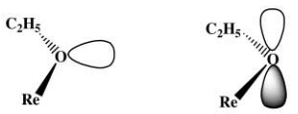
This same structure is retained in *cis*-(P,P)-$ReO(OEt)(P_1{\sim}O)_2$, as it was in *cis*-(P,P)-$ReO(OEt)(P^*{\sim}O)_2$ (where P*~OH = 2-diphenylphosphinomethyl-4-methylphenol),[8] and these two compounds belong to an unprecedented type of complexes with an alkoxo group *cis* to the Re=O bond. So far, *cis*-(P,P)-$ReY(OR)L_2$ (Y = O, NPh; L = P~N) have been observed only as the 'equatorial' isomers, while the corresponding 'twisted' *cis*-(P,P)-$ReYClL_2$ complexes were obtained by addition of HCl, thus indicating the preference of the OR group for the site *trans* to the Re=Y bond and of the Cl ligand for a *cis* site.[42] In the present phosphinoenol complexes with the $[Re{=}O]^{3+}$ core, the stereochemistry is the same for the chloro and the ethoxo complexes, that is, the OEt and the Cl ligands occupy the same co-ordination site and the exchange reaction is stereoselective. Furthermore, these compounds can be synthesised by reacting the phosphinoenolate with $ReO(OEt)Cl_2(PPh_3)_2$, whose *trans*-O=Re–OEt unit has to rearrange to position the ethoxo group on a *cis* site. Therefore, it must be concluded that the *cis*-(P,P) 'twisted' structure is very stable and that the phosphinoenolate oxygen competes efficiently with the OEt group for the position *trans* to the Re=O bond.

In contrast with this simple chemistry, the $[Re{=}NPh]^{3+}$ core leads to monosubstituted $Re(NPh)X_2(PPh_3)(P{\sim}O)$ and two disubstituted 'twisted' $Re(NPh)X(P{\sim}O)_2$ compounds. The first species is an intermediate in which one PPh_3 has been substituted and the P donors retain the mutually *trans* orientation of the starting $Re(NPh)Cl_3(PPh_3)_2$ compound. A Cl ligand is displaced and ring closure positions the phosphinoenolate oxygen *trans* to the Re=NPh bond. For the bulky P_3~O^- ligand, the reaction stops at this stage.

The $Re(NPh)Cl(P{\sim}O)_2$ complexes previously obtained with phosphinophenol usually adopted the 'twisted' *trans*-(P,P) structure in the solid state and this may ascribed, at least in part, to the steric effect from the imido phenyl substituent. With the phosphinoenolates P_1~O^- and P_2~O^-, the toluene solutions contained the *cis*-(P,P)-$Re(NPh)Cl(P{\sim}O)_2$ species as the main product. In ethanol, however, the only $Re(NPh)Cl(P{\sim}O)_2$ species detected were of the *trans*-(P,P) form and this was the major reaction product with P_2~O^-. Therefore, even though overall oxygen-to-metal π-bonding in the *trans*-(P,P) isomer is probably less efficient since it takes place with the **same** d orbital, the difference in thermodynamic stability between the *cis*-(P,P) and the *trans*-(P,P) isomers seems to be small for the Re–imido complexes: the balance between the electronic and steric factors is apparently more subtle and the structure of the complexes becomes solvent-dependent. Differences in the bonding in these two isomers are revealed by their ^{31}P NMR spectra: downfield shifts indicate stronger Re–P bonds in the *trans*-(P,P) complex, in agreement with the lower steric effects of the ligands adopting the *trans* arrangement.

The ethoxo compound $Re(NPh)(OEt)(P_1{\sim}O)_2$ was the only species precipitated from ethanol solutions. Its structure is 'equatorial' *trans*-(P,P). The site *trans* to the Re=NPh bond is occupied by the ethoxo group and steric hindrance is minimised by the phosphine groups adopting a *trans* arrangement. This molecule is stable toward halide substitution, whereas the

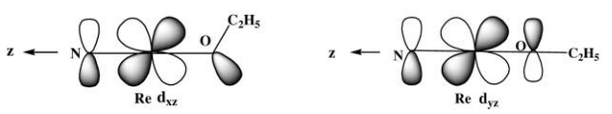
'twisted' *cis*-(P,P)-Re(NPh)Cl(P~O)$_2$ molecule does not ethanolyse. Interestingly, in the crystals of Re(NPh)(OEt)(P~O)$_2$, the Re–OCH$_2$ bond is nearly coplanar with the equatorial Re–O(enolate) bonds. This orientation favours overall oxygen-to-metal π-bonding, since the best ethoxo π orbital (p orbital perpendicular to the Re–O–C plane, Scheme 10) interacts with



Scheme 10

one of the d_{xz}/d_{yz} orbitals, while the other d orbital takes care of the π interactions with the equatorial enolate oxygens.

The binding versatility of the ethoxo group plays a major role in stabilising the novel 'twisted' *cis*-(P,P)-ReO(OEt)(P~O)$_2$ and 'equatorial' *trans*-(P,P)-Re(NPh)(OEt)(P~O)$_2$ complexes. In an ethoxo group occupying a site *cis* to the Re=Y multiple bond, one of the filled π orbitals can participate in π-bonding, whereas the other is involved in a four-electron destabilising interaction with the filled d_{xy} orbital (Scheme 11).[53] Large overall donation of the nucleophilic EtO$^-$ group



Scheme 11

to the Re(v) centre and concomitant decrease of its nucleophilic character are consistent with the rather large downfield ^{1}H chemical shifts of the methylene protons with respect to those of free ethanol. In contrast, an alkoxo ligand *trans* to the multiple bond has two filled π orbitals suitably oriented for donation into the d_{xz}/d_{yz} pair. If the EtO$^-$ group were linearly co-ordinated, these would actually be pure p orbitals. When the group is bent, one of these orbitals acquires sp^2 character, but since the Re–O–C angle is large, π-bonding ability is probably retained to a certain extent. At any rate, the other π-bonding orbital of a bent alkoxo group remains fully available and the orientation of the EtO$^-$ group in the crystal structure of Re(NPh)(OEt)(P~O)$_2$ suggests that it plays a significant role in bonding. The upfield ^{1}H NMR signal indicates that this group remains relatively electron-rich, in agreement with its own π-donating ability being counteracted by that of the very electron-rich Re=NPh (or Re=O) bond. The ability of OEt$^-$ to act as an electron reservoir and thus stabilise the Re(v) complexes is fully apparent in Table 3, where a wide range of O–C(R) distances and of Re–O–C(R) bond angles are observed.

The three phosphinoenols studied here show no drastic differences in reactivity, but the most sterically hindered P$_3$~O ligand is the less reactive and gives the least stable complexes. On the other hand, replacing Ph by ^{t}Bu as the enol substituent has no major effect.

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