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Synthesis, characterization and structural investigation of new rhenium-oxo complexes containing bidentate phosphine ligands: an exploration of chirality and conformation in chelate rings of small and large bite angle ligands

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The new rhenium complexes, $[ReOCl_3(L_2)]$, incorporating bidentate organophosphorus ligands [L_2 = dppe-F_{20} (the perfluorinated analog of dppe), xantphos, *rac*-BINAP, biphep and DPEphos] were successfully synthesized using $[ReOCl_3(AsPh_3)_2]$ as the precursor. The complexes were characterized by IR, ^1H and ^{31}P NMR, elemental analysis and X-ray diffraction. The X-ray structures reveal a distorted octahedral geometry with a facial arrangement of chloro ligands and an axial rhenium-oxo group.

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Introduction

Metal-oxo complexes play many important roles as oxygen transfer agents, both in a variety of biological systems[1,2] and in the laboratory.[3,4] The more recent application of rhenium complexes as radiopharmaceutical agents,[5–8] as well as their role as models for technetium complexes, which are also extensively used as radiopharmaceuticals,[9,10] has given rise to a significant area of research. Oxorhenium(v) complexes of the type $[ReOX_3L_2]$ (X = halogen; L = triaryl or alkyl phosphine, arsine or stibine ligands) are versatile precursors in the synthesis of a wide variety of rhenium complexes[11–16] and also display activity as oxygen transfer agents.[17–26]

Organophosphorus compounds continue to gain in popularity as ligands in synthetic inorganic chemistry since, by varying the substituents on the phosphorus, the chemical behavior of both the ligand and the resultant complex can be altered.[27–32] The number of different phosphines available to the coordination chemist is vast and continues to increase. The interplay of the differing electronic and steric characters of these ligands influences the behavior of their metal complexes and can be employed to help synthesize novel coordination compounds and more effective catalytic systems. As an example with particular significance for this paper, hydroformylation reactions catalyzed by platinum-diphosphine complexes comprising chelating diphosphines are greatly affected by the bite angle of the diphosphine ligand.[30,31] A comparative study showed that complexes with bis(diphenylphosphino)ethane (dppe, natural bite angle β_n = 85°) had lower activities than complexes with bis(diphenylphosphino)butane (dppb, β_n = 98°). Thus, by introducing a diphosphine ligand with a larger bite angle in this particular system, the catalytic activity of the complex was enhanced.[30]

We have extended the range of known rhenium-oxo species by preparing examples comprising diphosphines with a range of bite angles and variable flexibility and electronic characteristics in order to study the effect of these changes on the corresponding complexes (Fig. 1). We report here the synthesis and structural characterization of five new rhenium-oxo complexes supported by diphosphine ligands of varying bite angle (β = 80–105°).

Experimental

General

The anhydrous solvents (methylene chloride, diethyl ether and hexanes), BINAP and triphenylarsine were obtained from Aldrich. Potassium perrhenate and the diphosphines were purchased from Strem and used as received. $[ReOCl_3(AsPh_3)_2]$ was prepared according to the literature method.[33] All manipulations were carried out using standard Schlenk techniques under an argon atmosphere.

NMR spectroscopy was carried out on a GE Omega 500 MHz instrument at 298 K. Proton spectra were measured in $CDCl_3$ or CD_2Cl_2 and referenced internally using the residual solvent protons as a reference. The ^{31}P NMR spectra were referenced externally to 85% phosphoric acid. All chemical shifts are quoted in δ (ppm) and coupling constants in Hz. IR spectra were obtained on a Mattson Genesis Series FTIR using a mull on sodium chloride plates.

Synthesis of $[ReOCl_3(L_2)]$ complexes

$[ReOCl_3$(dppe-F_{20})] (1). To a 100 ml Schlenk flask, 530 mg (0.575 mmol) of $[ReOCl_3(AsPh_3)_2]$ were added, followed by 20 ml of methylene chloride. To the resulting bright yellow-green slurry, approximately 1 equiv. of 1,2-bis(dipentafluorophenylphosphino)ethane (442 mg, 0.584 mmol) was then added. After 12 h at room temperature, the resulting green-blue slurry was filtered to obtain a lavender solid and a green solution. Crystals obtained from the green solution were identified as $[ReOCl_3(OAsPh_3)(AsPh_3)]$, which has been previously reported.[34] The lavender solid, **1**, was washed with methylene chloride (2 × 10 ml) and dried *in vacuo*. Yield: 365 mg (60%). Blue crystals of X-ray quality were obtained by diffusion of hexanes into an ethyl acetate solution of the product. The complex crystallizes with half a molecule of hexane. Anal. calcd for

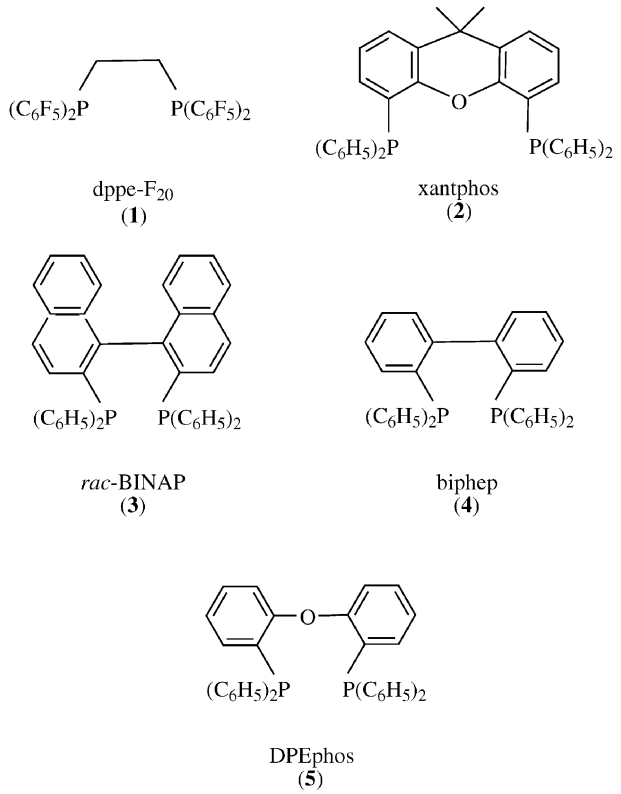


Fig. 1 Diphosphine ligands used in this study. The numbers in parentheses indicate the corresponding $[ReOCl_3(L_2)]$ complex.

$C_{26}H_4Cl_3F_{20}OP_2Re \cdot 0.5C_6H_{14}$: C, 31.4; H, 1.00; found: C, 31.6; H, 0.98. IR (Nujol): $\nu_{Re=O}$ 978 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.39 (br s, 2H, $-CH_2-$), 3.21 (br s, 2H, $-CH_2-$). ^{31}P NMR (CD_2Cl_2): δ −18.7 (s).

$[ReOCl_3$(xantphos)] (2). To a 100 ml Schlenk flask, 108 mg (0.117 mmol) of $[ReOCl_3(AsPh_3)_2]$ was added, followed by 20 ml of methylene chloride. One equivalent of xantphos (70.2 mg, 0.121 mmol) was then added. The resulting turquoise-green solution was stirred under argon for 5 h. The volume of the solution was reduced *in vacuo* and hexanes (20 ml) was added to induce precipitation. The blue-green solid, **2**, was washed with hexanes (2 × 10 ml) and dried *in vacuo*. Yield: 61.5 mg (59%). Green crystals of X-ray quality were obtained by diffusion of diethyl ether into a methylene chloride solution of the product. Anal. calcd for $C_{39}H_{32}Cl_3O_2P_2Re$: C, 52.8; H, 3.64; found: C, 52.6; H, 3.48. IR (Nujol): $\nu_{Re=O}$ 986 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.72–6.91 (br m, 26H, aromatic H), 1.48 (s, 3H, $-CH_3$), 1.88 (s, 3H, $-CH_3$). ^{31}P NMR (CD_2Cl_2): δ −36.6 (s).

$[ReOCl_3$(*rac*-BINAP)] (3). To a 100 ml Schlenk flask 146 mg (0.158 mmol) of $[ReOCl_3(AsPh_3)_2]$ was added, followed by 20 ml of methylene chloride. One equivalent of BINAP (racemic, 86 mg, 0.159 mmol) was then added. The bright green solution was allowed to stir under argon for 5 h. The volume of the solution was reduced *in vacuo* and hexanes (20 ml) was added to induce precipitation. The green solid was washed with hexanes (2 × 10 ml) and dried *in vacuo*. Yield: 109 mg (74%). Green crystals of X-ray quality were obtained by diffusion of benzene into a methylene chloride solution of the product. Anal. calcd for $C_{36}H_{28}Cl_3O_2P_2Re$: C, 56.7; H, 3.46; found: C, 56.9; H, 3.53. IR (Nujol): $\nu_{Re=O}$ 967 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.79–6.57 (br m, 32H, aromatic H). ^{31}P NMR (CD_2Cl_2): δ −17.8 (d, AB, 1P, J_{PP} = 30 Hz); −21.4 (d, AB, J_{PP} = 30 Hz).

$[ReOCl_3$(biphep)] (4). To a 100 ml Schlenk flask, 106 mg (0.116 mmol) of $[ReOCl_3(AsPh_3)_2]$ was added, followed by 20 ml of methylene chloride. Approximately 1 equiv. of biphep (63.3 mg, 0.122 mmol) was then added. The clear blue solution was allowed to stir under argon for 4 h. The volume of the solution was reduced *in vacuo* and hexanes (20 ml) was added to induce precipitation. The pale blue solid was washed with hexanes (2 × 10 ml) and dried *in vacuo*. Yield: 78.5 mg (82%). Blue crystals of X-ray quality were obtained by diffusion of diethyl ether into a methylene chloride solution of the product. Anal. calcd for $C_{36}H_{28}Cl_3OP_2Re \cdot C_4H_{10}O$: C, 53.5; H, 3.64; found: C, 54.2 H, 3.85. IR (Nujol): $\nu_{Re=O}$ 969 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.68–6.80 [m, 20H, P–$(C_6H_5)_2$], 6.43 (m, 8H, aromatic H from biphenyl). ^{31}P NMR (CD_2Cl_2): δ −18.6 (d, AB, 1P, J_{PP} = 12 Hz); −22.2 (d, AB, 1P, J_{PP} = 12 Hz).

$[ReOCl_3$(DPEphos)] (5). To a 100 ml Schlenk flask, 217 mg (0.236 mmol) of $[ReOCl_3(AsPh_3)_2]$ was added, followed by 20 ml of methylene chloride. One equivalent of DPEphos (127 mg, 0.236 mmol) was then added. The turquoise-green solution was allowed to stir under argon for 5 h. The volume of the solution was reduced *in vacuo* and hexanes (20 ml) was added to induce precipitation. The turquoise-green solid, **3**, was washed with hexanes (2 × 10 ml) and dried *in vacuo*. Yield: 165 mg (83%). Blue crystals of X-ray quality were obtained by diffusion of diethyl ether into a methylene chloride solution of the product. Anal. calcd for $C_{36}H_{28}Cl_3O_2P_2Re$: C, 51.0; H, 3.30; found: C, 50.6; H, 3.23. IR (Nujol): $\nu_{Re=O}$ 967 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.18–7.35 (br m, 28H, aromatic H). ^{31}P NMR (CD_2Cl_2): δ −31.0 (br s).

Structure determination and refinement of 1–5

Data were collected with a Nonius Kappa CCD (MoKα monochromatic radiation, λ = 0.71069 Å) and scaled using HKL 2000.[35] Compound **2** was specifically corrected for absorption (SORTAV);[36,37] the others were corrected for absorption *via* the spherical harmonics correction inherent in the scaling within Scalepack.[38] The structures were solved by Patterson methods[39,40] and refined on *F* for all reflections using the teXan package.[41] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions. Solvent inclusion was present in crystals of **1**, **3**, **4** and **5**. Crystals of **3**, when crystallized from methylene chloride and diethyl ether, rapidly lost solvent and yielded a poor structure; however, those crystallized from methylene chloride and benzene were well-behaved and provided a high quality structure showing the presence of both solvents. The disordered solvent could not be adequately modelled in **1** and **4**. The program SQUEEZE in PLATON[42] was used to compensate for scattering from the solvent for **1** and **4**. Relevant crystal and data parameters are presented in Table 1.†

Results and discussion

Synthesis

The rhenium(v) complex $[ReOCl_3(AsPh_3)_2]$ reacts with chelating diphosphines to form complexes **1–5**, with the general formula $[ReOCl_3(L_2)]$ (Scheme 1). The complexes formed are air-stable solids with spectroscopic properties consistent with other known $[ReOCl_3L_2]$ complexes.

The diphosphines (see Fig. 1) were chosen in order to vary either the electronic (*e.g.*, dppe-F_{20}) or the steric (*e.g.*, bite angle range β = 80–105°) parameters of the ligand set. In each

† CCDC reference numbers are 247679–83 for compounds **1–5**, respectively. See http://www.rsc.org/suppdata/nj/b4/b412818d/ for crystallographic data in .cif or other electronic format.

Table 1 Crystallographic data for complexes **1–5**

	1	**2**	**3**	**4**	**5**
Color and shape	Blue needle	Green needle	Green block	Blue needle	Blue needle
Empirical formula	$C_{29}H_{11}Cl_3F_{20}OP_2Re$	$C_{39}H_{32}Cl_3O_2P_2Re$	$C_{51}H_{40}Cl_5OP_2Re$	$C_{40}H_{38}Cl_3O_2P_2Re$	$C_{38}H_{32}Cl_7O_2P_2Re$
Formula weight	1109.89	887.19	1094.30	905.25	1017.00
T/K	183	183	173	173	173
Crystal system	Tetragonal	Orthorhombic	Triclinic	Triclinic	Triclinic
Space group	$I4_1/a$ (No. 88)	$Pbca$ (No. 61)	P–1 (No. 2)	P–1 (No. 2)	P–1 (No. 2)
a/Å	26.7896(5)	17.2122(2)	11.4133(2)	10.6209(3)	9.7531(2)
b/Å	26.7896(5)	14.1969(2)	12.1448(2)	11.6561(3)	13.2526(3)
c/Å	22.2608(4)	28.0146(5)	17.4349(3)	16.7301	17.0097(5)
α/°	90	90	84.6835(7)	69.9318(13)	71.8177(10)
β/°	90	90	72.1592(7)	85.4535(11)	74.7252(10)
γ/°	90	90	75.5004(7)	69.6000(13)	69.7270(10)
U/Å^3	15976.2(4)	6845.6(2)	2226.87(7)	1821.48(9)	1929.41(8)
Z	16	8	2	2	2
ρ_{calcd}/g cm^{-3}	1.846	1.722	1.632	1.650	1.750
μ/cm^{-1} (Mo Kα)	34.42	39.15	31.40	36.80	37.52
Total reflections	30476	36833	17475	13931	14760
Unique reflections	9125	8543	10111	8302	8598
R_{int}	0.045	0.113	0.033	0.049	0.049
Obs. reflections [$I > x\sigma(I)$][a]	5432	4279	7785	4162	5665
R^a	0.031	0.048	0.031	0.045	0.034
$R_w{}^b$	0.038	0.051	0.033	0.046	0.032

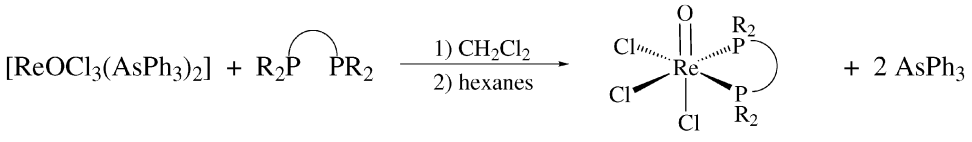
[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, for **1**, **3**, **4** and **5**: $I > 3\sigma(I)$; for **2**: $I > 2\sigma(I)$. [b] $R_w = [\sum[w(|F_o| - |F_c|)^2]/\sum[w(F_o)^2]]^{1/2}$.

case, the reaction of $[ReOCl_3(AsPh_3)_2]$ with 1 equiv. of diphosphine in methylene chloride at room temperature resulted in the formation of the corresponding chelating phosphine complex (**1–5**) in good yield. Except for complex **1**, reaction times were short with complete conversion observed after only a few minutes. The presence of a perfluorinated ligand system, where the donor capability of the phosphine is compromised due to the highly electron-withdrawing nature of fluorine, gave rise to longer reaction times (12 h) and a lower yield (60%) compared to the other ligands utilized in this study.

NMR and IR studies

Complexes **1–5** contain rhenium(v) centers, which are formally d^2 systems. For complexes exhibiting a pure octahedral geometry, such centers would be expected to be paramagnetic. However, **1–5** all show zero or near-zero magnetic moments at room temperature and well-resolved NMR spectra with typical chemical shift values. This observation is consistent with other reports of related rhenium(v) systems, which show significant distortions from octahedral geometries, leading to a pairing of the two d electrons.[3]

Comparison of proton and phosphorus NMR spectra for both the free and the coordinated diphosphines reveals the expected shifts upon coordination. The phosphorus resonance for compound **1**, at δ −18.7, shows a dramatic shift downfield compared to the free ligand resonance (δ −43.4), which is consistent with the formation of a five-membered ring upon chelation. Complex **1** is chiral due to the conformation of the backbone (Figs. 2 and 3), and the two phosphorus atoms are diastereotopic due to the C_1 symmetry of the molecule. However, as a single signal is observed at room temperature, the two enantiomers are rapidly equilibrating in solution and the chemical exchange interconverting the δ/λ isomers averages the chemical shifts of the two phosphorus atoms.[43] The phosphorus resonance for **2**, a singlet at δ −36.6 is shifted upfield from the free ligand (δ −17.8). For complexes **3** and **4**, chelation gives rise to seven-membered ring systems in both cases and an AB pattern in the phosphorus spectra, indicating that in each case the two phosphorus environments are not equivalent (Table 2). For these two complexes (**3** and **4**) the nature of the ligand backbone is such that interconversion of the enantiomers is not occurring on the NMR time scale and the configuration is effectively locked into position, giving rise to AB patterns in their phosphorus spectra, in contrast to complexes **1** and **2**. The phosphorus-phosphorus coupling of 30 Hz seen for compound **3** and of 12 Hz for compound **4** is indicative of cis ligand coordination, which is also observed in each of the solid state structures of **1–5** (Figs. 2–7). The phosphorus spectrum for complex **5** shows a single resonance at δ −31.0, which is shifted upfield from the free ligand resonance at δ −16.5. For compounds **2** and **5**, ligand coordination gives rise to complexes with eight-membered ring configurations, where the flexibility is affected by the linkage group of the diphosphine backbone (Fig. 1). For the DPEphos complex, the flexibility of the backbone can allow for the formation of analogs of the δ and λ conformers, which interconvert in solution at room temperature at moderate rates to give rise to the broad singlet resonance seen in the phosphorus spectrum. However, the additional ring in the xantphos



fac-cis

R_2P PR_2 = dppe-F_{20} (**1**); xantphos (**2**); *rac*-BINAP (**3**); biphep (**4**); DPEphos (**5**)

Scheme 1 Synthesis of $[ReOCl_3(L_2)]$ complexes.

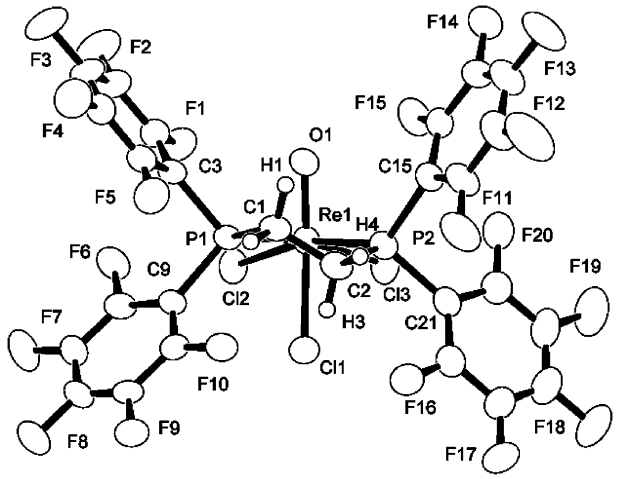


Fig. 2 Molecular structure of $[ReOCl_3(dppe\text{-}F_{20})]$ (**1**) showing the atom numbering scheme. The molecule represented has the chelate ring in the δ conformation.

backbone removes this flexibility and a single configuration is obtained, as evidenced by a single sharp resonance in the phosphorus spectrum.

The proton NMR for compound **1** shows two sets of multiplets at δ 4.39 and 3.21 for the methylene groups of the ligand backbone. The X-ray crystallographic study of this complex (*vide infra*), shows two nonequivalent methylene carbon atoms (C1 and C2), as well as nonequivalent phosphorus atoms (see Fig. 2), corresponding to one of the two contributing δ and λ conformations. Rapid interconversion of the δ and λ conformations on the NMR time scale, however, yields a single phosphorus resonance. Although one would anticipate that the methylene carbon atoms would also be equivalent on the NMR time scale, the protons proximal and distal to the oxo group are not interchanged. Thus, the methylene protons appear as complex multiplets because they exist as an AA'BB'XX' spin system at room temperature, with four magnetically nonequivalent protons and two magnetically nonequivalent phosphorus nuclei. For compound **2**, there are two sharp singlets at δ 1.48 and 1.88 corresponding to the two methyl groups, whereas in the free ligand, the methyl groups both resonate at δ 1.64, indicating that the equivalency of the two methyl groups in the free ligand is lost upon complexation. Based on the solid state structure (Fig. 4), the rigid xantphos backbone leads to a different environment for each of the methyl groups (endo, exo), consistent with the NMR spectrum. The aromatic protons in the coordinated xantphos ligand are found in the δ 6.91–7.72 range. Compounds **3** and **4** show typical proton resonances in the aromatic δ region: 6.57–7.79 for **3** and 6.43–7.68 for **4**. The aromatic region for the DPEphos compound (**5**) shows fairly broad peaks between δ 7.18 and 7.35 at room temperature. The poor solubility

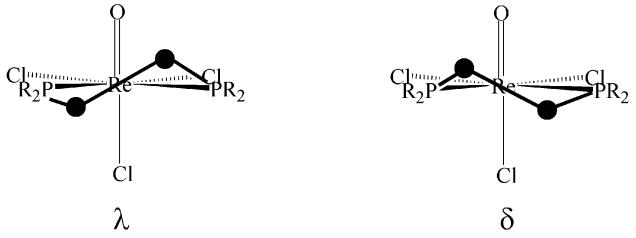


Fig. 3 Schematic for the enantiomeric conformations (λ and δ) of a generic 1,2-bis(diarylphosphino)ethane ligand (*e.g.*, **1**). The dark spheres indicate the location of the $-CH_2-$ groups along the ligand backbone (gauche configuration). These conformers are rapidly interconverting in solution.

Table 2 Selected spectroscopic data for complexes **1–5**

	1	**2**	**3**	**4**	**5**
$\nu_{Re=O}/cm^{-1}$ (Nujol mull)	978	986	971	969	967
^{31}P NMR[a]/ppm (CD_2Cl_2)	−18.7	−36.6	−21.4 (30 Hz); −17.8 (30 Hz)	−22.2 (12 Hz); −18.6 (12 Hz)	−31.0

[a] Referenced externally to 85% H_3PO_4

properties of **5** in suitable NMR solvents, however, precluded a full variable temperature ^1H NMR investigation of the fluxional process suggested by these broad resonances.

We have observed that the coordination of bidentate phosphine ligands can give rise to a fixed chiral conformation (complexes **3** and **4**) or a nonrigid chiral conformation (complexes **1** and **5**), where rapid interconversion takes place in solution on the NMR time scale with a barrier of ~10–16 kcal mol^{-1}.[44] The additional ring in the xantphos complex (**2**) removes the flexibility of the backbone and results in an achiral conformation.

The Re=O stretch in the infrared spectra of each of these complexes is found in the region 967–986 cm^{-1}, well within the range observed for other rhenium-oxo complexes.[3] A correlation between bite angle and metal-oxo stretch was not readily apparent, although the complexes comprising seven-membered chelate rings showed similar frequencies (969 and 971 cm^{-1} for **3** and **4**, respectively). The Re=O stretch for the complex of the fluoro-substituted ligand, dppe-F_{20}, at 978 cm^{-1} is the same as for the nonfluorinated ligand (dppe). This result is noteworthy in that the Re=O stretches might be expected to be different based upon the structural dissimilarities in Re=O bond lengths and the distortion of the Re=O bond (*vide infra*).

X-Ray crystallography

Crystals suitable for X-ray diffraction were grown by vapor diffusion of ethyl acetate–hexanes (**1**), methylene chloride–diethyl ether (**2**, **4**, **5**) and methylene chloride–benzene (**3**). Table 1 provides a summary of crystallographic data for complexes **1–5** and Table 3 shows selected bond lengths and angles for each complex. All complexes exhibit a distorted octahedral geometry, which is consistent with other *cis*-bis(phosphine) complexes of the type $[ReOX_3L_2]$.[45,46] The rhenium–oxo, rhenium–chloro and rhenium–phosphorus distances in compounds **1–5** are within the range observed for other reported fac-cis complexes of rhenium.[3,30,45]

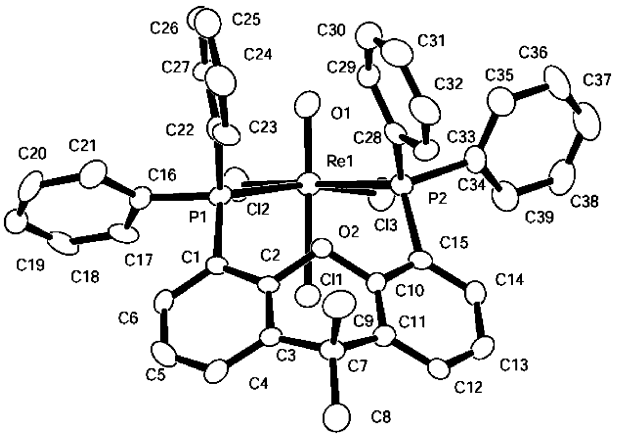


Fig. 4 Molecular structure of $[ReOCl_3(xantphos)]$ (**2**) showing the atom-numbering scheme.

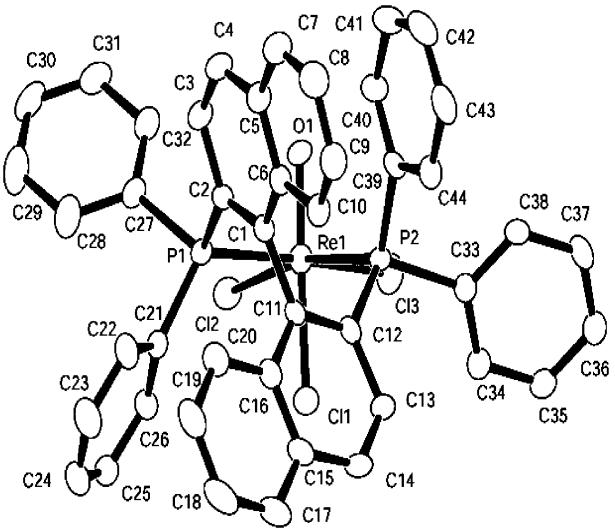


Fig. 5 Molecular structure of [$ReOCl_3$(*rac*-BINAP)] (**3**) showing the atom-numbering scheme.

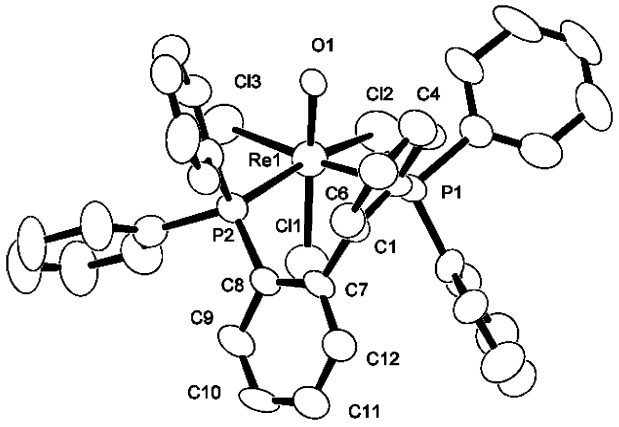


Fig. 6 Molecular structure of [$ReOCl_3$(biphep)] (**4**) showing the atom-numbering scheme. The molecule shown has a λ conformation of the ligand backbone.

The X-ray structure of **1** (Fig. 2) is, in large measure, similar to the structure of [$ReOCl_3$(dppe)], which has been reported previously.[45] In the five-membered ring formed upon coordination of the diphosphine to the metal, the backbone exhibits a gauche conformation. In addition, the oxo group appears to be tilted away from the equatorial ligands, away from the five-membered ring formed by coordination of diphosphine ligand to the rhenium center. This is consistent with nonequivalent methylene proton resonances seen in the ^{1}H NMR spectrum of **1**. The P1–Re–P2 angle measures 83.93(5)°, slightly larger than the corresponding angle in the dppe analog [83.29(2)°]. As a result of the difference in the electronic nature between dppe and dppe-F_{20}, the rhenium–oxo and rhenium–phosphine distances differ: Re═O is 1.665(4) Å in **1** and 1.680(5) Å in the nonfluorinated analog; Re–$P_{average}$ is 2.476(1) Å in **1** and 2.453(2) Å in the dppe analog, indicating the weaker donor capability of the fluorinated phosphine ligand and a stronger interaction between the rhenium center and the oxo ligand. The angle formed by the oxo, rhenium and trans chloro ligand (O–Re–Cl_{trans}) varies from 161.63(13)° to 169.05(8)° for **1–5**, which is in the range found for other fac-cis complexes of this type. A comparison of the degree of bending along the O–Re–Cl_{trans} axis for similar complexes using the Cambridge Crystallographic Database (CCD)[47] shows that complex **1** has the most pronounced bend (deviation from 180°) of the 12 known examples. For comparison, the degree of bending for the dppe analog is 163.02°.[45,46]

The structure of compound **2** (Fig. 4) comprises an eight-membered ring system [P1–Re–P2 angle 98.83(7)°], where the tricyclic backbone connecting the two phosphorus atoms in xantphos is displaced away from the rhenium-oxo group. This distortion away from the equatorial plane is also apparent in square-planar palladium or rhodium complexes with this large-bite-angle ligand.[30,48] A consequence of the displacement of the tricyclic backbone away from the Re═O hemisphere is that the phenyl groups at the two phosphorus atoms are arranged with near C_s symmetry as a result. Fig. 5 shows the more typical phenyl array expected for tetraaryl-substituted diphosphines. Coordination of the endocyclic ether oxygen of the xantphos backbone to a metal center (P–O–P *vs.* P–P coordination) has been reported in a number of complexes.[48–50] However, in complex **2** the ether group is clearly remote from the rhenium center and it seems unlikely that there is any significant interaction between the rhenium atom and the endocyclic ether oxygen. In addition, the P1–Re–P2 angle in **2** [98.83(7)°] is smaller than the P1–M–P2 angle observed for P–O–P coordinated complexes (average 163.5°).[48–50] For P–P coordinated systems, the P1–M–P2 angle ranges from 103.50(6)° (M = Pt; four coordinate complex)[51] to 152.61(5)° (M = Pd; four coordinate complex).[49] The rigid nature of the xantphos backbone gives rise to the nonequivalency observed for the methyl groups in the proton NMR of this compound as discussed above. The Re═O and Re–$P_{average}$ distances are typical for this type of Re(v) complex at 1.718(6) and 2.572(2) Å, respectively.

Solutions of compounds **3** and **4** exhibit nonequivalent phosphorus atoms in their ^{31}P NMR spectra, indicating the

Table 3 Selected bond distances (Å) and angles (°) for complexes **1–5**

	1	2	3	4	5
Re(1)–O(1)	1.665(4)	1.718(6)	1.744(2)	1.813(4)	1.688(3)
Re(1)–P(1)	2.470(1)	2.574(2)	2.4854(9)	2.478(2)	2.5111(12)
Re(1)–P(2)	2.483(1)	2.570(2)	2.4803(9)	2.476(2)	2.5424(13)
Re(1)–Cl(1)	2.437(2)	2.401(2)	2.3749(9)	2.348(2)	2.3799(13)
Re(1)–Cl(2)	2.3454(13)	2.375(2)	2.3749(9)	2.359(2)	2.3589(12)
Re(1)–Cl(3)	2.353(1)	2.343(2)	2.3847(9)	2.371(2)	2.3817(11)
P(1)–Re(1)–P(2)	83.93(5)	98.83(7)	92.19(3)	94.69(6)	102.93(4)
P(1)–Re(1)–O(1)	86.59(13)	89.6(2)	87.16(8)	83.59(13)	85.26(11)
P(2)–Re(1)–O(1)	92.44(12)	86.3(2)	90.97(8)	89.29(13)	86.76(11)
P(1)–Re(1)–Cl(1)	78.31(5)	81.18(7)	87.73(3)	87.57(6)	88.78(4)
O(1)–Re(1)–Cl(1)	161.63(13)	167.8(2)	169.05(8)	165.4(1)	164.86(11)
Cl(1)–Re(1)–Cl(2)	88.25(5)	92.75(8)	86.82(3)	87.54(7)	91.40(5)
Cl(1)–Re(1)–Cl(3)	90.16(5)	88.10(8)	89.90(3)	92.32(6)	90.34(5)
Cl(2)–Re(1)–Cl(3)	86.59(5)	82.86(8)	86.38(3)	85.36(7)	84.66(4)
Cl(1)–Re(1)–P(2)	75.76(5)	87.19(8)	79.55(3)	79.90(6)	81.02(4)
Cl(3)–Re(1)–O(1)	104.41(13)	101.8(2)	96.06(8)	97.88(13)	98.34(11)

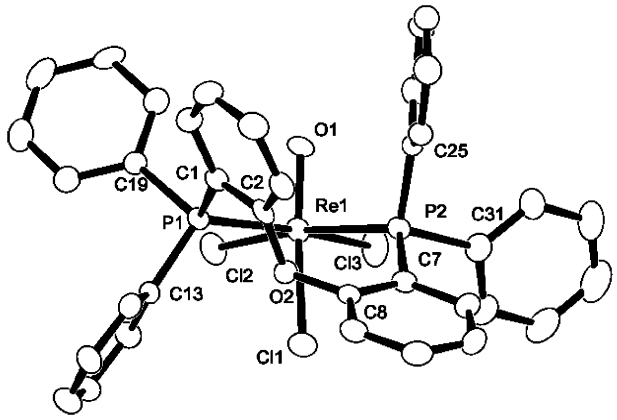


Fig. 7 Molecular structure of [$ReOCl_3$(DPEphos)] (**5**) showing the atom-numbering scheme. The molecule shown has a δ conformation of the ligand backbone.

presence of diastereotopic phosphorus atoms due in part to the nature of the diphosphine ligands. The structure of compound **3** (Fig. 5) shows the seven-membered ring formed by the coordination of the BINAP ligand to the rhenium center [P1–Re–P2 angle: 92.19(3)°; Re═O: 1.744(2) Å; Re–$P_{average}$: 2.4828(9) Å] and the steric demand of the rigid naphthyl backbone. Complex **4** (Fig. 6) has a similar configuration [P1–Re–P2 angle: 94.69(6)°; Re═O: 1.813(4) Å; Re–$P_{average}$: 2.477(2) Å]. The conformation of the PPh_2 groups is roughly C_2-symmetric due to the chirotropic ligand backbone. In contrast, in compound **2** the phenyl groups are arranged with near C_s symmetry as a result of the tricyclic backbone linking the phosphorus atoms.

The structure of compound **5** (Fig. 7), with an eight-membered chelate ring system [P1–Re–P2 angle: 102.93(4)°; Re═O: 1.688(3) Å; Re–$P_{average}$: 2.5268(13) Å] and a more flexible backbone compared to the closely related xantphos ligand, shows that the aryl groups along the backbone are not coplanar but rather are configured to exhibit the more typical configuration seen for chelating diphosphines (*cf.*, Fig. 5). Coordination of the DPEphos ligand to the metal gives rise to the largest bite angle in this series [102.93(4)° for **5** *vs.* 83.93(5)° for **1**; 98.83(7)° for **2**; 92.19(3)° for **3** and 94.69(6)° for **4**]. In a comparison between xantphos and DPEphos, it is clear that the additional linkage atom (C7) in the xantphos complex (Fig. 4) is critical in determining the coordination mode of this ligand and the orientation of the phenyl groups attached to the phosphorus atoms.

Conclusions

We have found that Re(v) complexes, supported by either small- or large-bite-angle chelating diphosphines, can be formed in good yield from [$ReOCl_3(AsPh_3)_2$]. These complexes exhibit a distorted octahedral geometry, similar to other cis-phosphine metal-oxo species. The presence of a rigid conformation of the ligand backbone can give rise to either chiral {[$ReOCl_3$(BINAP)] and [$ReOCl_3$(biphep)]} or achiral {[$ReOCl_3$(xantphos)]} complexes, while backbone flexibility allows for the interconversion of conformers in solution {[$ReOCl_3$(dppe-F_{20})] and [$ReOCl_3$(DPEphos)]}. The activity of these complexes in synthetic applications and oxygen transfer reactions is currently under investigation.

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