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# Bidentate phosphinophenol $R_2P$ -OH ligands. Oxo and imido Re(V) complexes of 2-diphenylphosphinomethyl-4-methylphenol (P-OH). Crystal structure of ReOCl(P-O)<sub>2</sub>

Fabienne Connac<sup>a</sup>, Yolande Lucchese<sup>a</sup>, Marie Gressier<sup>a</sup>, Michèle Dartiguenave<sup>a,\*</sup>, André L. Beauchamp<sup>b</sup>

<sup>a</sup> Laboratoire de Chimie Inorganique, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex, France <sup>b</sup> Département de Chimie, Université de Montréal, C.P. 6128, Succ. Centre-ville, Montréal, Que., Canada H3C 3J7

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#### Abstract

The PPh<sub>3</sub> ligands were displaced and ReOCl<sub>3</sub>(P–OH)<sub>2</sub> (1) was formed when ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> and 2 equiv. of the title ligand (P–OH) were refluxed in acetonitrile. In the presence of the proton quencher NEt<sub>3</sub>, ligand deprotonation took place and the bis-chelate complex ReOCl(P–O)<sub>2</sub> (2) was isolated. Under similar conditions, ReO(OEt)(P–O)<sub>2</sub> (3) was obtained from ReO(OEt)Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. NMR data are consistent with the *trans*-O–Re=O-*cis*-P,P 'twisted' octahedral geometry for these species. The corresponding phenylimido complex Re(NPh)Cl(P–O)<sub>2</sub> (4), similarly prepared from Re(NPh)Cl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>, adopts the *trans*-O–Re–NPh-*trans*-P,P arrangement. The structure of **2** was confirmed by X-ray diffraction. The methylene group in the side-arm imparts flexibility to the chelate ring and allows the bond angles to be closer to the ideal octahedral values than in the corresponding diphenylphosphinophenolato compound. The six-membered rings adopt a flattened boat conformation bringing the phenolate unit out of the coordination plane and making the overall van der Waals envelope substantially different from that of the diphenylphosphinophenol-based complex. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Rhenium complexes; Oxo complexes; Alkoxo complexes; Imido complexes

## 1. Introduction

As part of our continuous interest in developing Re(V) complexes for potential application for therapeutic radiopharmaceuticals based on <sup>188</sup>Re isotope and for modeling the technetium derivatives, we have studied the chelating properties of the bidentate phosphinophenol ligand: Ph<sub>2</sub>PCH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)OH, toward the oxo, phenylimido and nitrido Re(V) precursors: ReOCl<sub>3</sub>-(PPh<sub>3</sub>)<sub>2</sub>, Re(NPh)Cl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> and ReNCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. This ligand belongs to the group of functionalized phosphines that have been developed by substituting one phenyl group in PPh<sub>3</sub> by alkyl groups bearing acido [1,2], keto [3,4] or thiolato [5–8] functionalities. Other examples resulted from hydrogen substitution at the *ortho* position of one or more phenyl groups by hydroxo [9-12], silyloxo [13], amino [14,15] and thiolato [16] functions leading in some cases to polydentate ligands.

Our interest in the bidentate  $Ph_2PCH_2C_6H_3(CH_3)OH$ ligand lies on the presence of a phenol group bonded to the phosphorus atom through a  $CH_2$  linker. This has, as a consequence, to lengthen the carbon chain between the two donor atoms and to give a non-planar preorganization for the ligand. Thus, comparison of the reactivity of this ligand with our previous results on phosphinophenol will increase our knowledge on the influence of the steric and electronic effect of these ligands when they are coordinated to electrophilic Re(V) centers. Few transition metal complexes bearing this ligand have been reported [17]. On the other hand, several technetium [18,19] and rhenium [9–13] oxo complexes with chelating phosphinophenolato ligands

<sup>\*</sup> Corresponding author. Tel.: + 33-5-6155 6121; fax: + 33-5-6155 6118.

E-mail address: dartigue@iris.ups-tlse.fr (M. Dartiguenave)

 $[Ph_2PC_6H_4O]^-$  have been described but Re-imido compounds remain still scarce. We recently described *trans*-PP Re(NPh)X(P–O)<sub>2</sub> complexes (P–O<sup>-</sup> = diphenylphosphinophenolato and diisopropylphosphinophenolato) [12]. *Cis* and *trans*-PP Re-imido compounds were also reported with the tridentate  $[PhP(C_6H_4O)_2]^2$  ligand [9].

We describe here the reaction of  $Ph_2PCH_2$ -C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)OH on the rhenium-oxo, -imido and -nitruro precursors. As expected, a difference in the reactivity was observed when compared to diphenylphosphinophenol. While only one Re-oxo species was obtained in the first case, the reaction of Ph<sub>2</sub>PCH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)OH gave three Re-oxo species depending on the solvent. On the contrary, several phenylimido complexes were characterized with phosphinophenol while only one species was present here.

# 2. Experimental

## 2.1. General

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. ReOCl<sub>3</sub>- $(PPh_3)_2$  [20],  $Re(NPh)Cl_3(PPh_3)_2$  [21],  $ReNCl_2(PPh_3)_2$ [22] and 2-(diphenylphosphinomethyl)-4-methylphenol (P-OH) [23] were prepared as described in the literature. The preparation of ReO(OEt)Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> was adapted from the literature [24] by using NH<sub>4</sub>ReO<sub>4</sub> as starting material. Infrared (IR) spectra (4000-400 cm<sup>-1</sup>) were recorded as KBr pellets on a Vector 22 Bruker spectrometer. <sup>1</sup>H NMR spectra were obtained at room temperature (r.t.) in CD<sub>2</sub>Cl<sub>2</sub> on Bruker AMX 400 and WM 250 instruments. The residual solvent signal ( $\delta = 5.30$  ppm) was used as internal standard and the chemical shifts are reported with respect to  $Me_4Si$ . For the  ${}^{31}P{}^{1}H$  NMR spectra, the AC 200, AMX 300 and ARX 400 instruments were used and the external standard was H<sub>3</sub>PO<sub>4</sub> (82% D<sub>2</sub>O,  $\delta = 0.0$  ppm). Mass spectra were measured with a NERMAG R10-10 spectrometer. Elemental analyses were carried out at the Laboratoire de Chimie de Coordination du CNRS, Toulouse, and at the Service Central de Microanalyses du CNRS, Lyon, France.

## 2.2. Preparative work

## 2.2.1. $[ReOCl_3(P-OH)_2]$ (1)

ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> (421 mg, 0.50 mmol) was added to a solution of P–OH (310 mg, 1.00 mmol) in CH<sub>3</sub>CN (50 ml). After refluxing for 3 h, the brown solution was cooled, the brown precipitate was filtered off, and dried in vacuo. Yield: 441 mg (83%). The brown solid is insoluble in all common solvents. *Anal.* Calc. for  $C_{40}H_{38}Cl_3O_3P_2Re: C, 52.15; H, 4.16; P, 6.72; Re, 20.21.$ 

Found: C, 52.13; H, 3.95; P, 6.85; Re, 20.48.%. IR (cm<sup>-1</sup>, KBr): 960,  $\nu$ (Re=O); 3374,  $\nu$ (O-H); 1258,  $\nu$ (C-OH).

## 2.2.2. $[ReOCl(P-O)_2]$ (2)

Solid P-OH (310 mg, 1.00 mmol) and ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> (421 mg, 0.50 mmol) were suspended in CH<sub>3</sub>CN (50 ml). NEt<sub>3</sub> (0.17 ml, 1.20 mmol) was added and the reaction mixture was refluxed for 3 h. After cooling, the brown solution was evaporated in vacuo until a green precipitate appeared. The solid was filtered off and recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O yielded 397 mg (93%) of **2**. Anal. Calc. for  $C_{40}ClH_{36}O_{3}P_{2}Re$ , 0.5 CH<sub>2</sub>Cl<sub>2</sub>: C, 54.61; H, 4.19; P, 6.95; Cl, 7.96; Re, 20.9. Found: C, 53.58; H, 4.36; P, 6.63; Cl, 8.60; Re, 20.14%. IR  $(cm^{-1}, KBr)$ : 960, v(Re=O); 1251, v(C=ORe). MS  $(DCI/NH_3)$ :  $m/z = 849 [M + H]^+$ . <sup>1</sup>H NMR  $(CD_2Cl_2)$ ppm): 2.16 (s, 3H, CH<sub>3</sub>), 2.25 (s, 3H, CH<sub>3</sub>), 2.34 (dd, 1H, PC $H_A$ H<sub>B</sub>Ph, <sup>2</sup> $J_{PH}$  = 12.4 Hz, <sup>2</sup> $J_{HH}$  = 14.8 Hz), 3.69 (t, 1H, PCH<sub>A</sub>H<sub>B</sub>Ph,  ${}^{2}J_{PH} = 14.7$  Hz,  ${}^{2}J_{HH} = 14.8$  Hz), 3.86 (t, 1H, PCH<sub>A</sub>H<sub>B</sub>Ph,  ${}^{2}J_{PH} = 13.3$  Hz,  ${}^{2}J_{HH} = 13.1$  Hz), 4.23 (dd, 1H, PCH<sub>A</sub>H<sub>B</sub>Ph,  ${}^{2}J_{PH} = 10.8$  Hz,  ${}^{2}J_{HH} =$ 13.1 Hz), 6.30-7.37 (m, 28H, aryl). <sup>31</sup>P{<sup>1</sup>H} (CD<sub>2</sub>Cl<sub>2</sub>, ppm): 10.0 (s), -20.4 (s).

## 2.2.3. $[ReO(OEt)Cl_2(P-O)_2]$ (3)

To a suspension of 500 mg (0.59 mmol) of ReO(OEt)Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in 40 ml of EtOH were added 361 mg (1.18 mmol) of P-OH and 0.2 ml of NEt<sub>3</sub>. The mixture was refluxed for 3 h, then cooled to r.t. A green precipitate was filtered off, washed with Et<sub>2</sub>O, then dried in vacuo. Yield: 322 mg (63%). Anal. Calc. for C<sub>42</sub>H<sub>41</sub>O<sub>4</sub>P<sub>2</sub>Re: C, 58.73; H, 4.81. Found: C, 58.22; H, 4.47%. IR (cm<sup>-1</sup>, KBr): 952, v(Re=O), 1247 and 1271, v(C-ORe). MS (FAB > 0 MNBA): m/z = 858 [M]<sup>+</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm): 1.05 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>O,  ${}^{3}J_{\rm HH} = 6.9$  Hz), 2.12 (s, 3H, CH<sub>3</sub>Ph), 2.21 (s, 3H, CH<sub>3</sub>Ph), 2.21 (dd, 1H, PC $H_AH_BPh$ ,  ${}^2J_{PH} = 6.6$  Hz,  ${}^{2}J_{\rm HH} = 14.2$  Hz), 3.28 (t, 1H, PCH<sub>A</sub>H<sub>B</sub>Ph,  ${}^{2}J_{\rm PH} = 12.6$ Hz,  ${}^{2}J_{HH} = 14.2$  Hz), 3.6 (t, 1H, PC $H_{A}H_{B}Ph$ ,  ${}^{2}J_{PH} =$ 13.4 Hz,  ${}^{2}J_{\rm HH} = 13.1$  Hz), 4.21 (dd, 1H, PCH<sub>A</sub>H<sub>B</sub>Ph,  ${}^{2}J_{\rm PH} = 9.7$  Hz,  ${}^{2}J_{\rm HH} = 13.1$  Hz), 5.03 (m, 1H,  $CH_3CH_CH_DO$ ,  ${}^2J_{HH} = 12.2$  Hz,  ${}^3J_{HH} = 6.9$  Hz,  ${}^4J_{HPe} =$ 3.5 Hz), 5.56 (m, 1H, CH<sub>3</sub>CH<sub>C</sub> $H_DO$ , <sup>2</sup> $J_{HH} = 12.2$  Hz,  ${}^{3}J_{\rm HH} = 6.9$  Hz,  ${}^{4}J_{\rm HPe} = 0.5$  Hz), 6.18 - 7.57 (m, 28H, aryl). <sup>31</sup>P{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>)  $\delta$  (ppm): -8.3 (s), 2.3 (s).

## 2.2.4. $[Re(NPh)Cl(P-O)_2]$ (4)

A mixture of 840 mg (0.93 mmol) of Re(NPh)Cl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>, 570 mg (1.86 mmol) of (P–OH) and 0.31 ml (2.20 mmol) of NEt<sub>3</sub> in 100 ml of EtOH was refluxed for 3 h. The brown solid was filtered, washed with EtOH, and dried in vacuo. Yield: 550 mg (65%). *Anal.* Calc. for C<sub>46</sub>ClH<sub>41</sub>NO<sub>2</sub>P<sub>2</sub>Re: C, 59.84; H, 4.44; N, 1.52. Found: C, 59.26; H, 4.31; N, 1.60%. IR (cm<sup>-1</sup>, KBr): 1107,  $\nu$ (Re=NPh); 1252 and 1266,  $\nu$ (C–

ORe). MS (FAB > 0 MNBA): m/z = 923 [M]<sup>+</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm): 2.17 (s, 3H, CH<sub>3</sub>), 2.22 (s, 3H, CH<sub>3</sub>), 3.84 (dd, 1H, PCH<sub>A</sub>H<sub>B</sub>Ph, <sup>2</sup>J<sub>PH</sub> = 7.3 Hz, <sup>2</sup>J<sub>HH</sub> = 13.3 Hz), 3.87 (dd, 1H, PCH<sub>A</sub>H<sub>B</sub>Ph, <sup>2</sup>J<sub>PH</sub> = 5.8 Hz, <sup>2</sup>J<sub>HH</sub> = 13.3 Hz), 4.01 (dt, 1H, PCH<sub>A</sub>H<sub>B</sub>Ph, <sup>2</sup>J<sub>PH</sub> = 7.8 Hz, <sup>2</sup>J<sub>HH</sub> = 13.5 Hz), 4.16 (dd, 1H, PCH<sub>A</sub>H<sub>B</sub>Ph, <sup>2</sup>J<sub>PH</sub> = 4.8 Hz, <sup>2</sup>J<sub>HH</sub> = 13.5 Hz), 6.70–7.70 (m, 28H, aryl). <sup>31</sup>P{<sup>1</sup>H} (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm): 12.5 (d, <sup>2</sup>J<sub>PP</sub> = 306 Hz), -0.9 (d, <sup>2</sup>J<sub>PP</sub> = 306 Hz). The same compound is obtained in CH<sub>3</sub>CN or toluene.

## 2.3. X-ray crystallography

Due to the presence of solvent of crystallization  $(CH_2Cl_2)$ , the crystals precipitated from a 1/1 mixture of  $CH_2Cl_2$ /ether were not used for X-ray determination. However, suitable green crystals of **2** were obtained by slow evaporation of an ethanol solution. A specimen was glued to a glass fiber and the data were collected on an Enraf–Nonius CAD-4 diffractometer [25] over the whole sphere ( $2\theta_{max} = 140^\circ$ ), corrected for absorption (NRCVAX package [26], Gaussian integration based on crystal faces), and averaged. Crystal data and conditions for data collection are summarized in Table 1.

The Re atom was located by the direct methods of SHELXS-86 [27]. The remaining non-hydrogen atoms were located from  $\Delta F$  syntheses calculated with SHELXL-93 [28]. Hydrogen atoms were placed at idealized positions and refined as riding atoms with C–H distances of 0.97 (methylene), 0.96 (methyl) or 0.93 Å

| Table 1 |      |     |       |           |     |
|---------|------|-----|-------|-----------|-----|
| Crystal | data | for | ReOCl | $(P-O)_2$ | (2) |

| Formula                                     | $C_{40}H_{36}ClO_3P_2Re\cdot C_2H_5OH$ |
|---|--|
| Formula weight                              | 894.36                                 |
| Space group                                 | $P\overline{1}$                        |
| Unit cell dimensions                        |  |
| a (Å)                                       | 11.858(4)                              |
| b (Å)                                       | 12.908(7)                              |
| <i>c</i> (Å)                                | 14.175(6)                              |
| α (°)                                       | 76.78(4)                               |
| β (°)                                       | 86.54(3)                               |
| γ (°)                                       | 65.24(4)                               |
| $V(Å^3)$                                    | 1917(2)                                |
| Z   | 2                                      |
| <i>T</i> (K)                                | 293(2)                                 |
| $D_{\rm calc}$ (g cm <sup>-3</sup> )        | 1.550                                  |
| Radiation                                   | Cu Ka                                  |
| $\lambda$ (Å)                               | 1.54056                                |
| $\mu ({\rm mm}^{-1})$                       | 7.75                                   |
| No. reflections measured                    | 14318                                  |
| No. independent reflections                 | 7284                                   |
| No. observed reflections $[I > 2\sigma(I)]$ | 5674                                   |
| R <sup>a</sup>                              | 0.0479                                 |
| $wR_2^{a}$                                  | 0.0919                                 |
| S   | 0.99                                   |
|   |  |

<sup>a</sup>  $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ,  $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma (wF_o^2)^2]^{1/2}$ ,  $S = [\Sigma w (F_o^2 - F_c^2)^2 / (\text{no. of reflections} - \text{no. of parameters})]^{1/2}$ .

(others). Their isotropic displacement factors  $U_{\rm iso}$  were adjusted 50% (methyl) or 20% (others) above the value of the bonded carbon atom. All non-hydrogen atoms were refined anisotropically. Residuals originating from a disordered lattice ethanol molecule were observed in the  $\Delta F$  map phased on this model. They were assembled into two individuals and refined isotropically, constraints being applied on the C–C and C–O distances during the refinement. Occupancies converged to 0.80 and 0.20. The general background in the final  $\Delta F$  map was within  $\pm 0.12$  e Å<sup>-3</sup>, with highest peaks (1.3 e Å<sup>-3</sup>) and deepest valley (-1.4 e Å<sup>-3</sup>) near the Re atom.

#### 3. Results

#### 3.1. Reactivity

2-diphenylphosphinomethyl-4-The reaction of methylphenol (P-OH) on the oxo precursor  $ReOCl_3(PPh_3)_2$  is complex. Various species were observed depending on the temperature, the solvent used, and whether the proton quencher NEt<sub>3</sub> was present or not (Scheme 1). In contrast to the similar reactions with diphenylphosphinophenol [11], bidentate coordination of P-OH did not take place in the absence of NEt<sub>3</sub>. Thus, refluxing a 2/1 ratio of P–OH and ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> in toluene for 3 h resulted in the substitution of both PPh<sub>3</sub> ligands by two monodentate P-coordinated P-OH units. The same reaction conducted in acetonitrile gave the same brown insoluble material ReOCl<sub>3</sub>(P-OH)<sub>2</sub>.

An approximatively 1/1 mixture of the twisted *trans* and cis-PP ReOCl(P-O)<sub>2</sub> species was obtained starting from a heated mixture of P-OH, NEt<sub>3</sub> and  $\text{ReOCl}_3(\text{PPh}_3)_2$  in the 2/2/1 molar ratio or by reaction of 2 moles of NEt<sub>3</sub> on ReOCl<sub>3</sub>(P-OH)<sub>2</sub>, in toluene. They were unambiguously characterized by two AB spectra: a doublet of doublets at -13.1 and 18.2 ppm  $(^{2}J_{PP} = 308 \text{ Hz})$  for the *trans*-PP complex and a broad doublet at -20.4 and 10.8 ppm ( $^{2}J_{PP} \sim 0$  Hz) for the cis-PP complex. Recrystallization of this mixture in  $CH_2Cl_2$ /ether (1/1) gives quantitatively the *cis*-isomer, as a green precipitate which crystallizes with CH<sub>2</sub>Cl<sub>2</sub>. Complex 2 was also the unique species obtained in 92%yield when the reaction was performed in acetonitrile (Scheme 1). When the reaction was run in EtOH, an equimolar mixture of cis-PP ReOCl(P-O)<sub>2</sub> (2) and of cis-PP oxo-ethoxo ReO(OEt)(P-O)<sub>2</sub> (3) was obtained, 3 showing the ethanolysis of the Cl ligand.

Attempts to isolate the 1:1 complex  $\text{ReOCl}_2$ -(P–O)(PPh<sub>3</sub>) by refluxing 1 equiv. of P–OH with  $\text{ReOCl}_3(\text{PPh}_3)_2$  in EtOH for 3 h failed, the disubstituted oxo-ethoxo compound  $\text{ReO}(\text{OEt})(\text{P-O})_2$  (3) being invariably formed [23]. The reduction of  $\text{NH}_4\text{ReO}_4$  with 3 equiv. of HCl and 3 equiv. of the phosphine in glacial  $\operatorname{ReOCl}_{3}(\operatorname{PPh}_{3})_{2} + 2 \operatorname{P-OH} \xrightarrow[-2 \ PPh_{3}]{} \operatorname{ReOCl}_{3}(\operatorname{P-OH})_{2}$ 













acetic acid, which is the method used to prepare  $\text{ReOCl}_3(\text{PPh}_3)_2$ , was no more successful since no clean reaction was observed.

In contrast to the complicated reactivity found for the oxo system, the corresponding phenylimido starting material  $\text{Re}(\text{NPh})\text{Cl}_3(\text{PPh}_3)_2$  reacted selectively: the *trans*-PP isomer  $\text{Re}(\text{NPh})\text{Cl}(\text{P-O})_2$  (4) was isolated quantitatively in the three solvents (ethanol, acetonitrile and toluene) (Scheme 2).

No reaction occurred when P–OH was reacted with ReNCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in a 2/1 ratio, in presence of NEt<sub>3</sub>. In toluene, the starting complex was recovered intact as indicated by <sup>31</sup>P NMR but decomposition occurred in CH<sub>3</sub>CN since free PPh<sub>3</sub> and OP–OH were observed. Such a result was also obtained with other ligands such as phosphinophenol, NH(PPh<sub>2</sub>)<sub>2</sub> and NH(XPPh<sub>2</sub>)<sub>2</sub> which all gave oxo and imido Re complexes but no nitrido species [12,29,30].

## 3.2. Spectroscopic characterization

The brown compound obtained in absence of NEt<sub>3</sub> shows a very poor solubility in all common solvents. It is formulated as ReOCl<sub>3</sub>(P–OH)<sub>2</sub> on the basis of the elemental analysis. The IR spectrum confirms that the phenol group is not deprotonated, since it includes a v(O-H) vibration at 3374 cm<sup>-1</sup>, whereas the v(C-OH) band at 1258 cm<sup>-1</sup> is not appreciably displaced with respect to the free ligand (1260 cm<sup>-1</sup>).

The formulae of the oxo bis-chelate complexes Re-OCl(P–O)<sub>2</sub> (**2**) and ReO(OEt)(P–O)<sub>2</sub> (**3**) deduced from microanalyses are confirmed by the mass spectra, where the parent-ion peaks are found at m/z = 849 ([M + H]<sup>+</sup>, DCI/NH<sub>3</sub>) for **2** and 858 ([M]<sup>+</sup>, FAB<sup>+</sup>) for **3**. Typical strong Re=O stretching vibrations are observed at 960 and 952 cm<sup>-1</sup>, respectively, in the IR spectra, in the normal range for these linkages [31]. The v(C–ORe)

vibration characteristic of ligand complexation appears as a broad band at 1251 cm<sup>-1</sup> for **2** and as resolved peaks at 1247 cm<sup>-1</sup> and 1271 cm<sup>-1</sup> for **3**.

The conformation of complexes 2 and 3 were unambiguously deduced from the  ${}^{31}P{}^{1}H$ ) NMR spectra. A structure with the 2 equiv. *trans* (P–O) ligands located in the equatorial plane, perpendicular to the Re=O bond [10] was ruled out in both cases by the  ${}^{31}P{}^{1}H$ } NMR data. They show two signals, at 10.0 and – 20.4 ppm for 2 and at 2.3 and – 8.3 ppm for 3 which indicate the inequivalence of the two P–O. These peaks exhibit no splitting, but they likely correspond to close doublets with a  $J_{PP}$  coupling constant too small to be measured, and thus indicate a *cis*-PP configuration (Scheme 3). The upfield resonances at – 20.4 for 2 and





Table 2

Selected distances (Å) and angles (°) in  $\text{ReOCl}(\text{P-O})_2$  complexes with 2-(diphenylphosphinomethyl)phenol (2) and 2-(diphenylphosphino)phenol (5)

|                | 2         | 5         |
|----------------|-----------|-----------|
| Bond distances |           |           |
| Re–P2          | 2.480(3)  | 2.451(2)  |
| Re–P1          | 2.446(3)  | 2.443(2)  |
| Re–O3          | 1.654(7)  | 1.686(4)  |
| Re–O2          | 1.945(7)  | 2.003(4)  |
| Re-O1          | 2.015(7)  | 1.987(4)  |
| Re-Cl          | 2.404(3)  | 2.394(2)  |
| Bond angles    |           |           |
| P1–Re–Cl       | 161.81(9) | 163.57(7) |
| P2-Re-O1       | 172.0(2)  | 162.7(1)  |
| O2–Re–O3       | 168.2(3)  | 164.3(2)  |
| P1-Re-P2       | 93.90(9)  | 99.96(6)  |
| P1-Re-O1       | 87.5(2)   | 80.9(1)   |
| P1-Re-O2       | 79.6(2)   | 79.8(1)   |
| P1-Re-O3       | 100.8(2)  | 93.7(2)   |
| P2-Re-Cl       | 95.15(9)  | 90.01(6)  |
| P2–Re–O2       | 81.7(2)   | 77.7(1)   |
| P2–Re–O3       | 86.4(2)   | 89.4(2)   |
| O1–Re–Cl       | 81.5(2)   | 85.7(1)   |
| O1–Re–O2       | 90.8(3)   | 85.5(2)   |
| O1–Re–O3       | 101.0(3)  | 107.8(2)  |
| O2–Re–Cl       | 86.1(2)   | 89.7(1)   |
| O3–Re–Cl       | 95.5(2)   | 99.5(2)   |
| C12–O1–Re      | 127.4(6)  | 124.8(4)  |
| C22–O2–Re      | 137.9(6)  | 127.2(4)  |

-8.3 ppm for **3** are assigned to the P<sub>ax</sub> atom of the axial ligand, i.e. the ligand located in a plane containing the Re=O bond. The more strongly bonded P<sub>eq</sub> atom of the equatorial ligand, located in the plane perpendicular to the Re=O bond, gives the downfield resonances at 10.0 and 2.3 ppm, respectively. Such differences between P<sub>ax</sub> and P<sub>eq</sub> has been already observed in rhenium-phosphinophenol complexes and attributed to difference in the bonding [9,10,12].

Inequivalence of the two P-O ligands is also evidenced from the <sup>1</sup>H NMR spectra. Besides the aromatic protons displaying multiplets in the 6.2-7.6 ppm region, two singlets are found for the inequivalent ring methyl groups, at 2.16 and 2.25 ppm for 2, and at 2.12 and 2.21 ppm for 3. Complex 2 exhibits a complex pattern of four multiplets between 2.2 and 4.3 ppm for the methylene protons in the metallacycles (3.4 ppm in the free ligand). A similar pattern is found in the 2.2–4.2 ppm range for 3. They were assigned unambiguously by selective irradiation of each of the P atoms. This pattern originates from the inequivalence of the two methylene protons  $(H_A \text{ and } H_B)$  in each of the non-equivalent ligands, as indicated in Scheme 3. Each multiplet should actually be a doublet of doublet, since the doublet due to H<sub>A</sub>-H<sub>B</sub> coupling is further split by H-P coupling. However, in some cases, a pseudo-triplet is observed, because one of the  $J_{H-P}$ constant is close to  $J_{H_A-H_{B^*}}$  The low field multiplets at 3.86 and 4.23 ppm becomes two doublets upon decoupling the low field phosphorus atom (Peq at 10.0 ppm) indicating that the protons belong to the equatorial P-O<sup>-</sup> ligand. Similar decoupling of the upfield phosphorus atom  $P_{ax}$  (at -20.4 ppm) transforms the multiplets at 2.34 and 3.69 ppm into two doublets showing that this proton belongs to the CH<sub>2</sub> group of the axial ligand. Similar patterns were found after selective phosphorus decoupling of 3. In both complexes, the protons belonging to the methylene group of the equatorial ligand are more downfield shifted than the protons of the axial one: 3.86 and 4.23 ppm compared to 2.34 and 3.69 ppm for  $H_A$  and  $H_B$  in  $\boldsymbol{2}$  and 3.60 and 4.21 compared to 2.21 and 3.28 ppm for  $H_A$  and  $H_B$  in 3. This agrees with the better donor capacity of the equatorial phosphine compared to the axial one.

Interestingly, the <sup>1</sup>H NMR data for 3 confirms the stereochemistry of the molecule and the chemical shift values attributed to the  $P_{ax}$  and  $P_{eq}$  atoms because of the presence of the equatorial ethoxy group which contains inequivalent  $H_C$  and  $H_D$  methylene protons. The methyl group resonates as a triplet at 1.05 ppm ( ${}^{3}J_{\rm HH} = 6.9$  Hz). Assignment for the inequivalent methylene hydrogens was confirmed by selective irradiation of the methyl group and of the two phosphorus atoms. The methylene multiplets occur at 5.03 ( $H_C$ ) and 5.56 ( $H_D$ ) ppm, respectively, as two doublets of quadruplet for each proton. They result from a  $H_C-H_D$  cou-



Fig. 1. <sup>1</sup>H NMR spectrum of the methylene protons ( $H_{\rm C}$  and  $H_{\rm D}$ ) of the ethanolato ligand in (3) ( $CD_2Cl_2$ , 400.137 MHz, RT): (1) <sup>31</sup>P<sub>BB</sub> decoupling, (2) <sup>31</sup>P<sub>ax</sub> decoupling, (3) <sup>31</sup>P<sub>eq</sub> decoupling, (4) no <sup>31</sup>P decoupling.



Fig. 2. ORTEP drawing of the  $\text{ReOCl}(\text{P-O})_2$  molecule (2). Ellipsoids correspond to 40% probability. Hydrogens are omitted for clarity.

pling  $({}^{2}J_{\rm HH} = 12.2 \text{ Hz})$  and further couplings with the terminal methyl group  $({}^{3}J_{\rm HH} = 6.9 \text{ Hz})$  and the *trans*-Pe atom  $({}^{4}J_{\rm PH_{C}} = 3.5 \text{ Hz}; J_{\rm PH_{D}} = 0.5 \text{ Hz})$ . This is shown unambiguously by the selective decoupling of the phosphorus atoms  $P_{\rm ax}$  and  $P_{\rm eq}$  (Fig. 1).

The microanalysis and the FAB mass spectrum  $([M]^+$  at 923) are consistent with the Re(NPh)Cl(P–O)<sub>2</sub> formula proposed for 4. The IR spectrum exhibits the Re=NPh stretching vibrations at 1107 cm<sup>-1</sup>, in the typical range for this type of linkage [31]. The v(C–

ORe) vibration appears as two bands at 1252 and 1266  $cm^{-1}$ , in agreement with the presence of two inequivalent ligands coordinated via the phenolate oxygen. The  ${}^{31}P{}^{1}H$  NMR spectrum shows doublets at 12.5 and -0.9 ppm with a  ${}^{2}J_{P-P}$  coupling constant of 306 Hz. A trans-PP structure with a phenolate oxygen trans to the Re=NPh bond (Scheme 2) can be reasonably proposed, considering that the trans O=Re-O unit is known to be very stable and that the crystal structures of all related phenylimido compounds reported so far show this arrangement [12]. The <sup>1</sup>H NMR spectra are also consistent with the presence of inequivalent P-O ligands. However, the proton at 4.01 ppm, attributed to the CH<sub>2</sub> group of the equatorial ligand appears as a doublet of triplets, this indicating a long range phosphorus coupling with the trans-P<sub>ax</sub> atom  $(J_{H_{C}P_{eq}-Re-P_{ax}} = 4.2)$ Hz), which is often observed in transition metal phosphine complexes [32].

## 3.3. X-ray diffraction study

Single-crystal X-ray work on  $\text{ReOCl}(\text{P-O})_2$  (2) confirms the structure deduced from spectroscopic data. As shown in Fig. 2, the two deprotonated P–O ligands act as chelating agents. The phenolate oxygen of one ligand lies *trans* to the Re=O bond, making this chelate ring roughly coplanar with the Re=O bond. The other chelate ring is roughly perpendicular to this direction and its P donor is *cis* with respect to the first P atom. The sixth position is occupied by a chlorine atom. Thus, this complex adopts the *trans*-O–Re=O *cis*-P,P 'twisted' arrangement reported for related compounds with diphenylphosphinophenol.

The distances and angles around the Re center are listed and compared with those of the corresponding diphenylphosphinophenol complex 5 in Table 2. Greater flexibility introduced by the methylene group between the aromatic ring and the PPh2 unit contributes to making the trans angles (mean 167.3°) closer to 180° than in 5 (mean 163.3°). Also, the bite angles in 2 are closer to 90° (P1-Re-O1 = 87.5(2) and P2-Re- $O2 = 81.7(2)^{\circ}$  versus 80.9(1) and 77.8(1)°, respectively, in 5), whereas the repulsion between the bulky  $PPh_2$ groups is reduced  $(P1-Re-P2 = 93.90(9)^{\circ})$  versus 99.96(6)° in 5). In compounds containing an Re=O group, the *cis* ligands are usually displaced away from the multiple bond. The Re atom indeed lies at 0.23 Å from the O-P-P-Cl mean plane, on the Re=O side. However, the ligands do not experience this repulsive effect to the same extent: the O=Re-L angles are large for P1 (100.8(2)°) and O1 (101.0(3)°), but close to 90° for P2 (86.4(2)°) and Cl (95.5(2)°).

The Re=O distance of 1.654(7) Å lies on the short side of the range observed for mono-oxo compounds [4,33,34]. In contrast with complex **5**, the Re–O2 bond *trans* to the Re=O group (1.945(7)Å) is shorter than the

equatorial Re-O1 bond, whose length (2.015(7) Å) can be regarded as normal. This is likely related with the opening of the Re-O2-C angle (137.9(6)°) compared with 127.4(6)° for Re-O1-C, since a very short Re-O distance of 1.915(3) Å has recently been reported for the ReOCl<sub>3</sub>(L)(PPh<sub>3</sub>) with 2-(diethylaminomethyl)-4methylphenol [34], where the monodentate phenolate group is almost end-on coordinated (Re-O-C = $166.0(3)^{\circ}$ ). This would be consistent with a change of the hybridization state of O2 toward sp, thereby increasing the  $\pi$  character and bond order of Re–O2. However, since short bonds (  $\sim 1.95$  Å) have also been reported for monodentate phenolate ligands coordinated with Re–O–C angles of ~126° [35], hybridization is probably not the only factor involved, intramolecular inter-ligand non-bonded contacts and distortion in the coordination polyhedron undoubtedly making contributions as well.

The two chelate rings have similar conformations, although the chiralities are opposite. Their conformation can be described as a very distorted boat, similar to those noted for  $Zn^{2+}$  and  $Cu^{2+}$  complexes of 2-(dialkylaminomethyl)phenols [36]. The pattern of torsion angles for an idealized boat conformation with all bond lengths identical and all bond angles equal to 109.5° would be  $60^{\circ}/0^{\circ}/-60^{\circ}/60^{\circ}/0^{\circ}/-60^{\circ}$  (or the opposite signs for the other chirality). The sets of values are  $-59^{\circ}/2^{\circ}/64^{\circ}/-64^{\circ}/23^{\circ}/34^{\circ}$  for ligand 1 and  $59^{\circ}/5^{\circ}/-53^{\circ}/50^{\circ}/-10^{\circ}/-45^{\circ}$  for ligand 2. The rather large deviations can be ascribed to the disparity in bond lengths around the ring and the presence of both sp<sup>2</sup> (aromatic ring) and sp<sup>3</sup> (side arm) hybridized atoms.

The molecules are packed individually in the unit cell without particular intermolecular interactions. The lattice includes one ethanol solvent molecule per complex, disordered over two differently populated orientations. In the most abundant orientation (80%), ethanol is weakly hydrogen-bonded to a Cl ligand (O4…Cl = 3.35(2) Å). In the other orientation, it forms a stronger O-H…O bond with the coordinated phenolate group O1 (O4…O1 = 2.92(3) Å).

## 4. Concluding remarks

 $Ph_2PCH_2C_6H_3(CH_3)OH$  readily reacts with  $ReOCl_3(PPh_3)_2$  and  $Re(NPh)Cl_3(PPh_3)_2$  by means of elimination of PPh<sub>3</sub> and chlorine but no reaction occurs with  $ReNCl_2(PPh_3)_2$ . Such a behavior was observed for the phosphinophenol ligands  $R_2PC_6H_4OH$ , but significative differences were observed.

Reaction with  $[Re=O]^{3+}$  gave in both cases twisted ReOCl(P–O)<sub>2</sub> complexes, but only the *cis*-PP octahedral stereochemistry was present for Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>OH while *cis*-PP and *trans*-PP isomers have been observed in solution for Ph<sub>2</sub>PCH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)OH. Moreover,

when the reaction was performed in ethanol, ethanolysis of the Re–Cl bond occurred for  $Ph_2PCH_2C_6H_3$ -(CH<sub>3</sub>)OH which was not observed for  $Ph_2PC_6H_4OH$ . Reaction of  $Ph_2PCH_2C_6H_3(CH_3)OH$  with the [Re=NPh]<sup>3+</sup> precursor gave only the *trans*-PP isomer while with  $Ph_2PC_6H_4OH$  both *cis*- and *trans*-PP isomers were characterized in solution. However, in the solid state, in both cases, only *cis*-PP isomers were isolated for the Re=O complexes and *trans*-PP isomers for the Re=NPh complexes. Comparison of the bond distances and angles of ReOCl(P–O)<sub>2</sub> indicates that the less strained configuration of  $Ph_2PCH_2C_6H_3(CH_3)OH$ decreases the complex rigidity.

The <sup>31</sup>P and <sup>1</sup>H NMR analysis agrees with the solid state structure already proposed for the Re-oxo and Re-imino complexes with  $[P-O]^-$  ligands. In all the cases, the P<sub>ax</sub> atoms are more shielded indicating that they donate less electrons to the rhenium center than the Pe atoms. This agrees with the Re–Pe bond being shorter than the Re–P<sub>ax</sub> one.

## 5. Supplementary material

Crystallographic data (lists of atomic positional and thermal parameters, observed and calculated structure factor amplitudes) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 138937. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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