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# Synthesis and structural analysis of mono-oxo Re(V) complexes with phosphino-carboxylato ligands

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## Abstract

 $[^{n}Bu_{4}N][Re(O)Cl_{4}]$  or  $[Re(O)Cl_{2}(OEt)(PPh_{3})_{2}]$  react with PCOOH (2-(diphenylphosphanyl)benzoic acid) in different stoichiometries leading to the mono-substituted complexes  $[^{n}Bu_{4}N][Re(O)Cl_{3}(PCOO)]$  (2) and  $[Re(O)Cl_{2}(PCOO)(PPh_{3})]$  (5), respectively. In  $CH_{2}Cl_{2}$ -MeOH, 2 rearranges partially into the neutral  $[Re(O)Cl_{2}(PCOO)(MeOH)]$  (3). The mixed  $[Re(O)(OCH_{2}CH_{2}O)(PCOO)(MeOH)]$  (4) is obtained by reacting  $[^{n}Bu_{4}N][Re(O)Cl_{4}]$ , ethylene glycol and PCOOH. The  $[PCOO]^{-1}$ ligand is bidentate and the coordination geometry around rhenium is distorted octahedral, as shown by the X-ray structural analysis of 2 and 3. In these complexes the phosphorus and the oxygen atoms of the phosphino-carboxylato ligand occupy an equatorial and an axial position, respectively. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oxo complexes; Phosphino-carboxylato complexes; Rhenium complexes; Crystal structures

#### 1. Introduction

Previous investigations using some of the functionalized phosphines depicted in Scheme 1 have demonstrated the efficacy of such chelate ligands towards both reduction of the  $[M^{VII}O_4]^-$  salts (M = Tc, Re) and coordination to the metal centers, producing complexes of variable stoichiometry depending on the nature of the functional group introduced in the tertiary phosphine framework [1–8].

Besides tris-substituted  $[M^{III}(PX)_3]$  neutral compounds (A) [1,3], various partially reduced oxo-M<sup>V</sup> species have been prepared. When PNH<sub>2</sub> and POH ligands were utilized, the complexes were usually bissubstituted with general formulae  $[M^VO(PX)_2Y]$  (B) (Y = monodentate group such as halide) [2,5,7]. The two phosphines act as bidentate ligands and occupy asymmetric positions in a distorted octahedral environment with mutual *cis*-P,P and *cis*-X,X configurations (Scheme 2).

However, careful control of the ligand to metal ratio allowed the isolation of a mono-substituted compound  $[\text{ReOCl}_3(\text{PO})]^-$  (1), in which the phosphino-phenolato



Scheme 2.

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fragment spans an equatorial position (P) and the apical site (O) trans to the oxo group (Scheme 2), thereby producing a quasi-linear O=Re-O stick [7]. This geometry allows delocalization of the electron density of the oxo oxygen and the generation of a substitution-inert [Re(O)( $\eta^2$ -PO)] moiety. On the other hand, the halide groups in 1 are substitution-labile and they can be readily replaced by incoming ligands of superior denticity. Hence, a class of oxo-Re(V) mixed ligand complexes of general formula  $[Re(O)(\eta^2 -$ PO(SNS)] (SNS = tridentate aminedithiolato), have been synthesized [9,10]. Attempts to transfer this 'mixed-ligand' approach at 'non-carrier added' level utilizing the 99mTc isomer have met severe obstacles so far owing to the difficulty to isolate mono-substituted P, O species. In fact, the excess of ligand utilized during these nanomolar preparations always promotes the formation of bis-substituted 99mTcV and homoleptic trissubstituted 99mTcIII species [8]. On going from fivemembered chelate rings typical of the phosphino-phenolato fragment to six-membered chelate rings arising from the coordination of the phosphino-carboxylato ligand (PCOOH) we have observed an increasing tendency to form mono-substituted compounds. Aiming at the elucidation of this behavior we have investigated in detail the reactivity of labile oxo-rhenium(V) precursors with the potentially bidentate (2-diphenylphosphanyl)benzoic acid ligand (PCOOH). A series of mono-substituted oxo-rhenium(V) 2-5 have been prepared and characterized by means of the usual physicochemical techniques including X-ray crystal structure analysis of the representative anionic [Re(O)Cl<sub>3</sub>- $(PCOO)^{-}$  (2) and neutral [ReOCl<sub>2</sub>(PCOO)(MeOH)] (3) complexes.

# 2. Experimental

# 2.1. General

chemicals were of reagent grade. All 2-(Diphenylphosphanyl)benzoic acid and the complexes  $[^{n}Bu_{4}N][Re(O)Cl_{4}]$  and  $[Re(O)Cl_{2}(EtO)(PPh_{3})_{2}]$  were prepared as reported in the literature [11-13]. The reactions were run in air unless otherwise indicated. <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Varian Unity 300 MHz spectrometer; <sup>1</sup>H chemical shifts were referenced with the residual solvent resonance relative to tetramethylsilane and the <sup>31</sup>P chemical shifts were measured with external 85% H<sub>3</sub>PO<sub>4</sub> solution as reference. Chemical shifts are given in ppm. The NMR samples were prepared in CDCl<sub>3</sub>. Infrared (IR) spectra were recorded in the range 4000-400 cm<sup>-1</sup> on a Perkin-Elmer 577 spectrometer using KBr pellets. Elemental analyses were performed on a Fisons EA1108 elemental analyzer.

#### 2.2. Preparation of the rhenium complexes

#### 2.2.1. $[^{n}Bu_{4}N][Re(O)Cl_{3}(PCOO)]$ (2)

Solid PCOOH (0.050 g, 0.16 mmol) was added under stirring at room temperature (r.t.) to a pale-green solution of [<sup>n</sup>Bu<sub>4</sub>N][Re(O)Cl<sub>4</sub>] (0.081 g, 0.14 mmol) in EtOH (20 cm<sup>3</sup>). The mixture turned blue and after 15 min deposited a turquoise solid, which was filtered off, washed with ethanol (1 cm<sup>3</sup>), ether (10 cm<sup>3</sup>) and dried under vacuum. The product is soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, Me<sub>2</sub>CO, insoluble in alcohols and Et<sub>2</sub>O. Green crystals, suitable for X-ray diffraction analysis were obtained by recrystallization from dichloromethanemethanol. Yield 0.110 g (93%). Anal. Calc. for C<sub>35</sub>H<sub>50</sub>Cl<sub>3</sub>NO<sub>3</sub>PRe: C, 49.1; H, 5.9; N, 1.4. Found: C, 49.6; H, 5.9; N, 1.5%. IR (cm<sup>-1</sup>): 2962, 2874, v(C-H<sub>aliphatic</sub>); 1651, v(C=O); 983, v(Re=O). <sup>1</sup>H NMR  $(CDCl_3)$ :  $\delta$  0.87 (t, 12H), 1.26 (q, 8H), 1.56 (m, 8H) and 3.16 (m, 8H)  $[CH_3-CH_2-CH_2-CH_2]_4-N$ ; 6.92 (m, 1H), 7.36–7.66 (12H) 8.19 (m, 1H),  $[(C_6H_5)_2-P C_6H_4$ -COO]. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  - 22.8 (s).

# 2.2.2. [Re(O)Cl<sub>2</sub>(PCOO)(MeOH)] (3)

During recrystallization of complex 2, a small amount of light blue crystals corresponding to complex 3 were obtained. The complex was only characterized by X-ray diffraction analysis.

## 2.2.3. [Re(O)(eg)(PCOO)(MeOH)] (4)

To a MeOH (20 cm<sup>3</sup>) solution of [<sup>n</sup>Bu<sub>4</sub>N][Re(O)Cl<sub>4</sub>] (0.140 g, 0.24 mmol) are added ethylene glycol (eg) (0.054 cm<sup>3</sup>, 0.96 mmol) and 1 M sodium acetate in MeOH (0.96 cm<sup>3</sup>, 0.96 mmol). Solid PCOOH (0.073 g, 0.24 mmol) is added to the brown colored solution, which quickly turns violet. After stirring for 1 h, during which the color remained unchanged, the mixture was taken to dryness under a gentle stream of nitrogen. To the resulting violet oil, water is added  $(4 \times 3 \text{ cm}^3)$ aliquots), and the resulting precipitate is dried under P<sub>2</sub>O<sub>5</sub>. The compound is soluble in MeOH, EtOH, MeCN, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, insoluble in Et<sub>2</sub>O and hydrocarbons. Recrystallization by slow evaporation in MeOH gave, after 1 day, a violet crystalline powder. Yield 0.130 g (89%). Anal. Found: C, 44.3; H, 3.8. Calc. for  $C_{22}H_{22}O_6PRe: C, 44.1; H, 3.7\%$ . IR (cm<sup>-1</sup>): 2914, 2818, v(C-H<sub>aliphatic</sub>); 1634, v(C=O); 946, v(Re=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.69 (s, 3H; CH<sub>3</sub>OH), 4.43 (m, 2H) and 4.85 (m, 2H) [O-CH<sub>2</sub>-CH<sub>2</sub>-O], 7.31-7.75 (14 H)  $[(C_6H_5)_2 - P - C_6H_4 - COO]$ . <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$ -1.3 (s).

## 2.2.4. [Re(O)Cl<sub>2</sub>(PCOO)(PPh<sub>3</sub>)] (5)

To a suspension of  $[Re(O)Cl_2(EtO)(PPh_3)_2]$  (0.102 g, 0.12 mmol) in EtOH (15 cm<sup>3</sup>) solid PCOOH (0.037 g, 0.12 mmol) is added. The mixture is refluxed for 2 h during which the color of the suspended solid changes

Table 1 Crystallographic data for **2** and **3** 

	2	3
Empirical formula	C <sub>35</sub> H <sub>50</sub> Cl <sub>3</sub> NO <sub>3</sub> - PRe·CH <sub>3</sub> OH	C <sub>20</sub> H <sub>18</sub> Cl <sub>2</sub> O <sub>4</sub> PRe· 0.5CH <sub>3</sub> OH
Formula weight	888.32	626.43
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\overline{1}$
Unit cell dimensions		
a (Å)	9.727(1)	9.835(2)
b (Å)	26.741(3)	11.840(2)
c (Å)	17.784(2)	19.540(3)
α (°)		83.25(1)
β (°)	97.829(9)	82.81(1)
γ (°)		81.18(2)
$V(Å^3)$	4582.8(8)	2219.5(7)
Z	4	4
$D_{\rm calc} ({\rm g \ cm^{-3}})$	1.288	1.875
Crystal size (mm)	$0.52 \times 0.20 \times 0.16$	$0.45 \times 0.23 \times 0.18$
$\mu ({\rm mm}^{-1})$	2.893	5.814
2θ Range (°)	3.0-52.0	3.0-56.0
No. of measured reflections	7372	10 930
No. of independent	6936 (0.0692)	10622 (0.0337)
reflections $(R_{int})$		
No. of observed $[I > 2\sigma(I)]$	3683	7378
No. of parameters	405	526
<sup>a</sup> R <sub>1</sub>	0.0762	0.0560
$^{\mathrm{b}}WR_{2}$	0.1567	0.1153
Goodness-of-fit	1.065	1.055
$a R = \Sigma   F   -  F   / \Sigma  F $		

$K_1 = \Delta   r_0   -  r_c  /\Delta  r_0 .$	
<sup>b</sup> $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(w(F_o^2)^2)]^{1/2};$	$w = 1/[\sigma^2(F_o^2) + (aP)^2 +$
$bP$ ], where $P = (F_0^2 + 2F_c^2)/3$ .	

Table 2 Selected bond lengths (Å) and angles (°) for **2** 

Re–O(1)	1.64(1)	Re–Cl(1)	2.377(4)
Re-O(2)	2.03(1)	Re–Cl(2)	2.364(5)
Re–P	2.421(4)	Re–Cl(3)	2.379(5)
O(2)–C(1)	1.32(2)	C(1)–O(3)	1.21(2)
O(1)-Re-O(2)	167.0(5)	O(2)–Re–P	75.8(3)
O(1)-Re- $Cl(1)$	94.9(4)	Cl(1)-Re-Cl(2)	167.4(2)
O(1)-ReCl(2)	96.7(4)	Cl(1)-Re- $Cl(3)$	85.6(2)
O(1)-Re- $Cl(3)$	103.7(4)	Cl(1)–Re–P	89.9(1)
O(1)–Re–P	91.2(4)	Cl(2)–Re–Cl(3)	86.8(2)
O(2)–Re–Cl(1)	86.4(3)	Cl(2)–Re–P	94.8(2)
O(2)-Re-Cl(2)	83.4(3)	Cl(3)–Re–P	164.7(2)
O(2)–Re–Cl(3)	89.4(3)		

from green-brown to light-green. The precipitate is filtered off and washed with EtOH (4 × 1 cm<sup>3</sup> aliquots) and dried under vacuum. The product is soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, insoluble in MeOH, EtOH, MeCN, Et<sub>2</sub>O and hydrocarbons. Yield 0.096 g (95%). *Anal.* Found: C, 53.2; H, 3.4. Calc. for C<sub>37</sub>H<sub>29</sub>O<sub>3</sub>P<sub>2</sub>Cl<sub>2</sub>Re: C, 52.9; H, 3.5%. IR (cm<sup>-1</sup>): 1667,  $\nu$ (C=O); 977,  $\nu$ (Re=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.15-8.26 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>-P-C<sub>6</sub>H<sub>4</sub>-COO]. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  2.2 (d) and -17.6 (d), <sup>2</sup>J<sub>PP</sub> = 332 Hz.

## 2.3. X-ray structural determination

A green crystal of 2 and a blue crystal of 3 were mounted in thin-walled glass capillaries. The crystals were mounted in nujol and fixed inside the capillaries in solvent atmosphere to avoid loss of crystallinity, mainly for 2. The relevant crystal data and structural parameters of the two complexes are summarized in Tables 1-3. Data were collected at r.t. on an Enraf-Nonius CAD4-diffractometer with graphite-monochromatized Mo K $\alpha$  radiation, using a  $\omega$ -2 $\theta$  scan mode. Unit cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections with  $15.8 < 2\theta <$ 23.8° for **2** and  $15.0 < 2\theta < 19.2°$  for **3**. Data were corrected [14] for Lorentz and polarization effects, for linear decay (for 2) and for absorption by empirical corrections based on  $\Psi$  scans. The heavy atom positions were located by Patterson methods using SHELXS-86 [15]. The remaining atoms were located by sucessive difference Fourier maps and refined by least-squares refinements on  $F^2$  using SHELXL-93 [16]. One methanol and an half-methanol disordered molecules of crystallization were also located in the Fourier difference map for 2 and 3, respectively. All the non-hydrogen atoms (except the solvent methanol atoms in 3) were refined with anisotropic thermal motion parameters and the contribution of the hydrogen atoms were included in calculated positions (except those of the solvent in 2 and of the OH groups in the methanol molecules in 3).

Table 3 Selected bond lengths (Å) and angles (°) for  ${\bf 3}$ 

Molecule 1		Molecule 2	
Re(1)-O(1)	1.670(6)	Re(2)–O(1A)	1.654(7)
Re(1)-O(2)	2.035(6)	Re(2)–O(2A)	2.048(6)
Re(1)-O(4)	2.098(7)	Re(2)–O(4A)	2.088(6)
Re(1)-Cl(1)	2.381(3)	Re(2)–Cl(3)	2.363(3)
Re(1)-Cl(2)	2.348(3)	Re(2)–Cl(4)	2.364(3)
Re(1) - P(1)	2.400(2)	Re(2)–P(2)	2.403(2)
O(2)–C(2)	1.31(1)	O(2A)–C(2A)	1.28(1)
C(2)–O(3)	1.24(1)	C(2A)–O(3A)	1.23(1)
O(1)-Re(1)-O(2)	168.2(3)	O(1A)-Re(2)-O(2A)	168.0(3)
O(1)-Re(1)-O(4)	102.5(3)	O(1A)-Re(2)-O(4A)	104.9(3)
O(1)-Re(1)-Cl(1)	94.8(3)	O(1A)-Re(2)-Cl(3)	97.2(3)
O(1)-Re(1)-Cl(2)	98.2(3)	O(1A)-Re(2)-Cl(4)	97.0(3)
O(1) - Re(1) - P(1)	91.1(3)	O(1A) - Re(2) - P(2)	91.6(3)
O(2)-Re(1)-O(4)	89.2(3)	O(2A)-Re(2)-O(4A)	87.0(3)
O(2) - Re(1) - Cl(1)	84.4(2)	O(2A)-Re(2)-Cl(3)	84.7(2)
O(2) - Re(1) - Cl(2)	83.9(2)	O(2A)-Re(2)-Cl(4)	82.8(2)
O(2) - Re(1) - P(1)	77.2(2)	O(2A) - Re(2) - P(2)	76.7(2)
O(4) - Re(1) - Cl(1)	89.8(2)	O(4A)-Re(2)-Cl(3)	87.6(2)
O(4) - Re(1) - Cl(2)	82.1(2)	O(4A)-Re(2)-Cl(4)	82.1(3)
O(4) - Re(1) - P(1)	166.3(2)	O(4A)-Re(2)-P(2)	163.3(3)
Cl(1)-Re(1)-Cl(2)	165.9(1)	Cl(3)-Re(2)-Cl(4)	164.2(1)
Cl(1)-Re(1)-P(1)	90.58(9)	Cl(3)-Re(2)-P(2)	87.57(9)
Cl(2)-Re(1)-P(1)	94.55(9)	Cl(4)-Re(2)-P(2)	98.92(9)



Scheme 3. (i) EtOH, r.t.; (ii) NaOAc, MeOH, ethylene glycol, r.t.; (iii) CH<sub>2</sub>Cl<sub>2</sub>-MeOH.

The final difference-Fourier synthesis was featureless for **2**, and revealed residual electron densities between 2.57 and -2.05 e Å<sup>-3</sup> for **3**, near the heavy atoms. Atomic scattering factors and anomalous dispersion terms were taken as in Ref. [16]. The drawings were made with ORTEPII [17] and all the calculations were performed on a DEC  $\alpha$  3000 computer.

#### 3. Results and discussion

#### 3.1. Synthesis

The new mono-anionic trichlorooxorhenium(V) complex 2 was obtained in high yield by reaction of [<sup>n</sup>Bu<sub>4</sub>N][Re(O)Cl<sub>4</sub>] with (2-diphenylphosphanyl) benzoic acid (PCOOH) in ethanol at r.t. The same mono-substituted complex 2 is obtained by using a threefold molar excess of PCOOH ligand and/or refluxing the reaction mixture for hours. This compound is soluble in chlorinated solvents and insoluble in alcohols. Complex 2 was recrystallized from a mixture of CH<sub>2</sub>Cl<sub>2</sub>-MeOH, yielding green crystals suitable for X-ray crystallographic analysis. During recrystallization of 2 some blue crystals appeared, which were identified by X-ray as the neutral mono-oxo complex 3 (Scheme 3). The formation of 3 results from the replacement of a chloride atom by a methanol molecule, with formation of [<sup>n</sup>Bu<sub>4</sub>N]Cl. The 'mixed ligand' oxocomplex 4 is obtained in high yield by reacting [<sup>n</sup>Bu<sub>4</sub>N][Re(O)Cl<sub>4</sub>] with PCOOH and ethylene glycol (1:1:4 molar ratio) in the presence of a base (NaOAc) (Scheme 3). Complex 4 is a violet crystalline solid soluble in chlorinated solvents and in alcohols but insoluble in diethyl ether and hydrocarbons.

The neutral mono-oxo complex **5** was obtained as a light-green solid in high yield by refluxing  $[Re(O)Cl_2(EtO)(PPh_3)_2]$  with PCOOH in EtOH, at a 1:1 molar ratio (Scheme 4). Complex **5** is soluble in chlorinated solvents and insoluble in alcohols, acetonitrile,

diethyl ether and hydrocarbons. Complexes 2-5 are air and moisture stable.

#### 3.2. Characterization

The characterization of **2**, **4** and **5** has been done by elemental analysis, IR, <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy, and by X-ray crystallographic analysis in the case of **2**. Complex **3** was only characterized by X-ray diffraction analysis.

The IR spectra of compounds 2, 4 and 5 display the characteristic bands of PCOOH, namely the C-H and C-C out-of-plane bending vibrations in mono-substituted benzene rings (in the 690-750 cm<sup>-1</sup> region) and the v(C=O) stretching vibrations of the carboxylato group (2, 1651 cm<sup>-1</sup>; 4, 1634 cm<sup>-1</sup>; 5, 1667 cm<sup>-1</sup>). The v(C=O) vibrations are significantly shifted and lower in energy, with respect to the free ligand (1690  $cm^{-1}$ ), indicating co-ordination of the chelate. The values found for v(C=O) in 2, 4 and 5 compare well with the value found for the same vibration in the complex [Re(O)( $\eta^3$ -PNO)( $\eta^2$ -PCOO)] and [Tc( $\eta^2$ - $PCOO_{3}$  [3,19]. The IR spectra of 2, 4 and 5 exhibit also characteristic v(Re=O) stretching bands at 983, 946 and 977  $\text{cm}^{-1}$ , respectively, which are in the range reported for similar mono-oxorhenium complexes  $(945-1067 \text{ cm}^{-1})$  [18].

The <sup>31</sup>P NMR spectra of complexes **2** and **4** show one singlet at  $\delta$  – 22.8 and – 1.3, respectively. The <sup>31</sup>P NMR spectrum of **5** presents two doublets at  $\delta$  2.2 and – 17.6 ppm, with a <sup>2</sup>J<sub>PP</sub> coupling constant of 332 Hz, which indicates the magnetic unequivalence of the two



Scheme 4. (i) EtOH, reflux.





Fig. 1. An ORTEP view of the anionic complex 2, with thermal ellipsoids drawn at the 35% probability level. Hydrogen atoms are omitted for clarity.

O(3)

trans-positioned phosphorus atoms (Scheme 4) [20]. The resonances at -17.6 and 2.2 ppm were assigned to the phosphorus atom of the  $[\eta^2$ -PCOO]<sup>-</sup> ligand and of the PPh<sub>3</sub>, respectively, by comparison with the spectrum of 2. The <sup>31</sup>P signal of the phosphino-carboxylato in 2 and 5 is significantly high field shifted ( $\Delta = 18.8$ ppm, 2; 13.6 ppm, 5) compared with the value found for this resonance in the free PCOOH (-4.0 ppm). Contrasting behavior was shown by complex 4, which presents a <sup>31</sup>P resonance low field shifted ( $\Delta = 2.7$  ppm) relatively to the free phosphino-carboxylic ligand. These results seem to indicate that  $[\eta^2 - PCOO]^-$  is a better donor in 4 than in 2 and 5, where it seems to behave as a better acceptor. This trend agrees with the shift observed for the v(C=O) vibration which presents a higher decrease in energy for 4 ( $\Delta = 56 \text{ cm}^{-1}$ ) than for 2 ( $\Delta = 39$  cm<sup>-1</sup>) and 5 ( $\Delta = 23$  cm<sup>-1</sup>). The v(Re=O) stretching vibration in **4** is also significantly lower in energy than the values observed for 2 ( $\Delta = 37$ cm<sup>-1</sup>) and 5 ( $\Delta = 31$  cm<sup>-1</sup>), and the value found is typical of compounds with alkoxo groups coordinated trans to the oxo moiety [2]. All these data indicate that the acidity of the  $[Re=O]^{3+}$  moiety in 2 and 5 is higher than in 4 and also that in this complex there is a higher electron density along the Re=O axis. The spectroscopic data obtained for all the compounds as well as the X-ray structural analysis of 2 and 3 were the basis for the stereochemistry proposed for 4 and 5 and are depicted in Schemes 3 and 4.

It is interesting to note the different stereochemistry exhibited by 5-type complexes, depending on the nature of the anchor function inserted in the phosphine chelate. As sketched in Scheme 5, phenolato- and carboxylato-oxygen are located *trans* to the oxo group in complexes 5 and 6, whereas the phosphine-amido nitrogen prefers an equatorial site [21], *cis*-oriented with respect to the oxo group in complex 7. Also, the mutual phosphine phosphorus donors, which invariably occupy an equatorial site, show different orientations. As indicated by the magnitude of the  ${}^{2}J_{PP}$  coupling constant, the magnetically unequivalent P are *trans*-positioned only in the phosphino-carboxylato complex 5, whereas they assume a *cis*-orientation in phosphino-phenolato and phosphino-amido complexes 6 and 7.

While the coordination of the phosphine anchor groups appear to be governed primarily by electronic factors through the formation of strong [O=Re-O] (in 5 and 6) and [P-Re-N] (in 7) sticks, steric factors seem to play a determining role for the mutual phosphine phosphorus orientation. In fact, when five-membered chelate rings are involved in coordination (complexes 6 and 7), a *cis*-P configuration warrants an additional stabilization resulting from the  $\pi$ -stacking interaction of two facing phenyl rings [22]. Such stabilization is not active when the chelate ring increases from five- to six-membered, thereby favoring the more common *trans*-P configuration.

# 3.2.1. Crystal structures of $[^{n}Bu_{4}N][Re(O)Cl_{3}(\eta^{2}-PCOO)]$ (2) and $[Re(O)Cl_{5}(\eta^{2}-PCOO)(MeOH)]$ (3)

The structure of **2** consists of discrete monomeric  $[N(^{n}Bu)_{4}]$  cations and  $[Re(O)Cl_{3}(\eta^{2}-PCOO)]$  anions. Complex **3** crystallizes from a mixture of  $CH_{2}Cl_{2}$ –MeOH as monomers with two independent molecules in the asymmetric unit. ORTEP views of the anion of **2** and of molecule 1 of complex **3** are shown in Figs. 1 and 2, respectively.

Tables 2 and 3 present the selected bond distances and angles, respectively, for **2** and for molecules 1 and 2 of **3**. For both compounds the coordination geometry around the six-co-ordinate Re<sup>V</sup> atom is distorted octahedral. The axial positions in **2** and **3** are occupied by the oxo group and by one oxygen atom of the carboxylate group of the  $[\eta^2$ -PCOO]<sup>-</sup> ligand. The equatorial positions are defined by the phosphorus and the three chloride atoms in **2** and by the phosphorus, two chloride atoms and a methanol molecule in **3**.

In 2 the distortion from the regular octahedral is mainly seen by the value found for the angles O(2)– Re–P (75.8(3)°) and O(1)–Re–O(2) (167.0(5)°). The Re atom in 2 is 0.27 Å deviated from the mean leastsquares equatorial plane, [P–Cl(1)–Cl(2)–Cl(3)], towards the axial O(1) atom. For molecules 1 and 2 of 3 the distortion from the regular octahedral geometry is comparable: O(2)–Re(1)–P(1) and O(2A)–Re(2)–P(2) angles of 77.2(2) and 76.7(2)°; the bent axial O(1)–

Re(1)-O(2) and O(1A)-Re(2)-O(2A) angles of 168.2(3) and 168.0(3)° for molecules 1 and 2, respectively; the Re(1) and the Re(2) atoms are, respectively, 0.26 and 0.30 Å out of the mean equatorial plane towards the axial O(1) and O(1A) atoms. The previously described [NBu<sub>4</sub>][ReOCl<sub>3</sub>(PO)], in which the phosphino-phenolato ligand also adopts a meridional configuration and forms a five-membered chelate ring, presents a distortion from the regular polyhedron comparable to what we observed for 2 and 3 (Re is 0.25 Å out of the mean equatorial plane; non-linear O<sub>oxo</sub>-Re-O axis, 163.6(3); O-Re-P, 76.1(2)) [7]. Apparently, the presence of six-membered chelate rings in 2 and 3 does not affect significantly the bond angles around the metal center as well as the displacement of the metal from the equatorial plane, showing wider Re-O-C and Re-P-C ring angles than in the above mentioned [ReOCl<sub>3</sub>(PO)] anion, much likely due the greater flexibility of the chelate rings. In 2 the  $PC_3O$  chelate ring show significant deviations from planarity (atomic deviations in the range -0.113 to 0.118 Å) as well as the corresponding RePC<sub>3</sub>O ring. For 3, the six-membered rings are non-planar in both molecules. The  $P(1)C_3O$ ring of one of the two independent molecules is planar (atomic deviations < 0.007 Å), which leads to a folding of the corresponding  $Re(1)PC_3O$  ring about the O(2)···P(1) axis of 39.9°. This difference between the two independent molecules is more likely a result of the packing of the molecules in the lattice. In the related  $[Re(O)Cl_3(PO)]^-$ , the ligand P-C-C-O is planar and the Re-P-C-C-O ring displays an envelope configuration.

A comparison of bond lengths and angles is difficult since only a few related compounds are available:  $[\text{Re}(O)\text{Cl}_3(\text{PO})]^-$ ,  $[\text{Re}(O)(\eta^3\text{-}\text{PNO})(\eta^2\text{-}\text{PCOO})]^-$  and the homoleptic  $[\text{Tc}(\eta^2\text{-}\text{PCOO})_3]$ , in which the metal is in a lower oxidation state [3,7,19].



Fig. 2. An ORTEP drawing of molecule 1 of complex **3**, with thermal ellipsoids at the 35% probability level. Hydrogen atoms are omitted for clarity.

The Re– $O_{oxo}$  bond distances in 2 (1.64(1) Å) and 3 (average, 1.662(6) Å) are comparable and are at the range (1.65–1.70 Å) so far observed for other six-coordinated oxocompounds [18]. However, the value found for the anionic compound 2 is at the lower end of this range, and is slightly shorter than the corresponding analogous 1.669(6) found the value А in  $[Re(O)Cl_3(PO)]^-$ [PO = (phosphino-phenolate]. This difference is certainly related to the nature of the phosphino-carboxylate ligand, that acting as a weaker donor, transfers less electron density to the metal than the phosphino-phenolate. The Re-Ocarboxylate bond distances in 2 (2.04(1) Å) and 3 (average, 2.042(6) Å) are comparable but are longer and shorter than the Re-O<sub>phenolate</sub> (2.016(6) Å) and Re-O<sub>carboxylate</sub> (2.100(4) Å) bond distances found in [Re(O)Cl<sub>3</sub>(PO)]<sup>-</sup> and  $[\text{Re}(O)(\eta^3-\text{PNO})(\eta^2-\text{PCOO})]^-$ , respectively [7,19]. These differences are due to the nature of the coordinating group and to the presence of co-ligands with different electronic and steric properties.

The Re–P bond length in 2 (2.421(4) Å) compares value found in with the the anionic well  $[Re(O)Cl_3(PO)]^-$  (2.422(2) Å) but is longer than the Re-P bond length in 3 (average, 2.402(2) Å). The shorter distance in 3 is related to the lower *trans* effect of MeOH relatively to chloride. This effect compares with what was observed for the homoleptic  $[Tc(\eta^2 -$ PCOO)<sub>3</sub>], in which the Tc-P bond trans to oxygen atoms is shorter than the Tc-P bonds *trans* to other  $\pi$ accepting ligands [3]. The Re-Cl bond distances in 2 (average, 2.373(5) Å) and 3 (average, 2.364(3) Å) are comparable with those in the related  $[Re(O)Cl_3(PO)]^{-1}$ [average, 2.380(3) Å].

#### 4. Concluding remarks

In this work we have described novel and stable monosubstituted oxorhenium complexes 2-5, which are the only species formed even when an excess of the phosphino-carboxylato ligand (PCOOH) is used. The tendency to form this type of compound is different from what has been observed with the phosphino-phenolato and can be related to the presence of the sixmembered chelate ring, arising from the coordination of the phosphino-carboxylato ligand. These results are promising for further studies at the 'non-carrier added level', where an excess of ligand is normally used.

#### 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 155580 for complex **2** and 155581 for complex **3**. Copies of this information 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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#### References

- C. Bolzati, F. Refosco, F. Tisato, G. Bandoli, A. Dolmella, Inorg. Chim. Acta 201 (1992) 7.
- [2] F. Refosco, F. Tisato, G. Bandoli, C. Bolzati, A. Dolmella, A. Moresco, M. Nicolini, J. Chem. Soc., Dalton Trans. (1993) 605.
- [3] F. Refosco, F. Tisato, G. Bandoli, E. Deutsch, J. Chem. Soc., Dalton Trans. (1993) 2901.
- [4] F. Tisato, F. Refosco, G. Bandoli, C. Bolzati, A. Moresco, J. Chem. Soc., Dalton Trans. (1994) 1453.
- [5] C. Bolzati, F. Tisato, F. Refosco, G. Bandoli, Inorg. Chim. Acta 247 (1996) 125.

- [6] S. Catinella, F. Tisato, F. Refosco, C. Bolzati, P. Traldi, Rapid Commun. Mass Spectrom. 10 (1996) 1295.
- [7] C. Bolzati, F. Tisato, F. Refosco, G. Bandoli, A. Dolmella, Inorg. Chem. 35 (1996) 6221.
- [8] C. Bolzati, L. Uccelli, F. Refosco, F. Tisato, A. Duatti, M. Giganti, A. Piffanelli, Nucl. Med. Biol. 25 (1998) 71.
- [9] B. Nock, T. Maina, F. Tisato, M. Papadopoulos, C. Raptopoulou, A. Terzis, E. Chiotellis, Inorg. Chem. 38 (1999) 4197.
- [10] B. Nock, T. Maina, F. Tisato, M. Papadopoulos, C. Raptopoulou, A. Terzis, E. Chiotellis, Inorg. Chem. 39 (2000) 2178.
- [11] J.E. Hoots, T.B. Rauchfuss, D.A. Wrobleski, Inorg. Synth. 21 (1982) 175.
- [12] R. Alberto, R. Schibli, A. Egli, P. August Schubiger, W.A. Herrmann, G. Artus, U. Abram, T.A. Kaden, J. Organomet. Chem. 493 (1995) 119.
- [13] G. Rouschias, Chem. Rev. 74 (1974) 531.
- [14] C.K. Fair, Molen, Enraf-Nonius, Delft, The Netherlands, 1990.
- [15] G.M. Sheldrick, SHELXS-86: Program for the Solution of Crystal Structure, University of Göttingen, Germany, 1986.
- [16] G.M. Sheldrick, SHELXL-93: Program for the Refinement of Crystal Structure, University of Göttingen, Germany, 1993.
- [17] C.K. Johnson, ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- [18] W.A. Nugent, J.M. Mayer, Metal-Ligand Multiple Bonds, Wiley-Interscience, Wiley, New York, 1970.
- [19] J.D.G. Correia, Â. Domingos, A. Paulo, I. Santos, J. Chem. Soc., Dalton Trans. (2000) 2477.
- [20] R.G. Cavell, R.W. Hilts, H. Luo, R. McDonald, Inorg. Chem. 38 (1999) 897.
- [21] F. Refosco, F. Tisato, A. Moresco, G. Bandoli, J. Chem. Soc., Dalton Trans. (1995) 3475.
- [22] F. Tisato, F. Refosco, et al., manuscript in preparation.