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Synthesis, characterization and molecular structure of oxo and phenylimido rhenium(V) complexes of 1-phenyl-2-(diisopropylphosphino)-ethanone

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Abstract

New rhenium-oxo and phenylimido complexes were synthetized and isolated by reaction of 1-phenyl-2-(diisopropylphosphino)ethanone on $ReOX_3(PPh_3)_2$ (X = Cl, Br, I), $ReO(OEt)Cl_2(PPh_3)_2$ and $Re(NPh)Cl_3(PPh_3)_2$ in basic media (NEt_3). In these complexes the ligand bonds mainly as monoanionic enolato chelating agent. The reactions are solvent dependent. The disubstituted $ReOX(P–O)_2$ compounds (**1**–**7**) adopt a 'twisted' octahedral structure with a mixture of *cis*-PP and *trans*-PP configurations in toluene, thus indicating that in this case the stability gap between the two diastereoisomers is small. In ethanol, only the 'twisted' *cis*-PP conformers $ReOCl(P–O)_2$(**1**) and $ReO(OEt)(P–O)_2$ (**7**) were observed. The ethoxo-oxo complex $ReO(OEt)(P–O)_2$ (**7**) resulting from the stereoselective substitution of the halide by the ethoxo group is the unique species isolated when X = Br and I. The reaction with $Re(NPh)Cl_3(PPh_3)_2$ was less selective and, in ethanol, excess of ligand was needed to get *trans*-PP-$Re(NPh)Cl(P–O)_2$ (**8**) as unique species. A mixture of (**8**), of the monosubstituted $Re(NPh)Cl_2(PPh_3)(P–O)$ (**9**) and of $Re(NPh)Cl_2(P–C=O)(P–O)$ (**10**) was observed in toluene with and without base. All these data emphasize the influence of the basicity and steric hindrance of the phosphinoenolato ligand on the rhenium complexes formation.

Keywords: Synthesis; Oxo-rhenium(V) complexes; Phenylimido rhenium(V) complexes; 1-Phenyl-2-(diisopropylphosphino)-ethanone

1. Introduction

Because of their chemical and structural diversity and their good coordinative properties, functionalized phosphines have attracted considerable attention in strategies aimed at developing new technetium complexes as imaging agents in nuclear medicine. The recent availability of rhenium 188, obtained from $^{188}W/^{188}Re$ generator boosted the use of this radioelement as radiotherapeutic anti cancer agent [1–4]. As a consequence, development of suitable rhenium complexes remains an important goal.

In the recent past, many studies on Re(V) complexes have been devoted on ligand exchange reactions between $ReOCl_3(PPh_3)_2$, $Re(NPh)Cl_3(PPh_3)_2$ and various diphenylphosphines functionalized with nucleophilic substituents such as phenol or ketone i.e. bidentate ligands with soft phosphorus(III) donor and hard phenolato or enolato groups [5–12]. All the complexes were characterized by the O=Re–O linkage (in all the Re-oxo species) and PhN=Re–O one (in all the Re-phenylimido compound). This has for consequence to stabilize 'twisted' octahedral complexes with either *cis*-PP (**A**) or *trans*-PP (**B**) conformation. In both cases the enolato ligands are located in two perpendicular planes (Scheme 1). Thus these ligands, besides having strong coordinative properties, favor the formation of single isomer, which is essential for radiopharmaceutical applications.

In this work, we report on the characterization of the oxo and imido complexes resulting from the reaction of the 1-phenyl-2-(diisopropylphosphino)ethanone $^{i}Pr_2P$-$CH_2C(=O)Ph$ on $ReOX_3(PPh_3)_2$ and $Re(NPh)Cl_3(PPh_3)_2$ and compare the data with those obtained with the related diphenylphosphinoketone, the main

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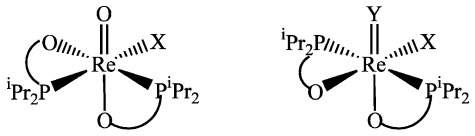


cis - P,P **(A)** *trans* - P,P **(B)**

Y = O, NPh

Scheme 1.

differences between these two ligands being the steric hindrance (~156° for the 1-phenyl-2-(diisopropylphosphino)ethanone compared to ~136° for the 1-phenyl-2-(diphenylphosphino)ethanone [13]) and the basicity ($pK_a = 2.73$ for PPh_3 and 9.30 for $P^{i}Pr_3$) of the phosphines [14]. It is of interest also to compare these results to those obtained with the related phosphinophenol $R_2PC_6H_4OH$ (R = iPr and Ph) where the steric hindrance of the phosphine played the major role.

2. Experimental

2.1. Reactants and physical measurements

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. $ReOX_3(PPh_3)_2$ [15], $ReO(OEt)X_2(PPh_3)_2$ [16], $Re(NPh)Cl_3(PPh_3)_2$ [17] and 1-phenyl-2-(diisopropylphosphino)ethanone (P–C=O) [18] were prepared as described in the literature. IR spectra (4000–400 cm^{-1}) were recorded as KBr pellets on a Vector 22 Bruker spectrophotometer. ^1H NMR spectra were obtained at room temperature on Bruker AMX 400 and WM 250 instruments. The residual solvent signals ($\delta = 5.20$ ppm for CD_2Cl_2 and 7.30 for $CDCl_3$) were used as internal standards and the chemical shifts are reported with respect to Me_4Si. For the $^{31}P\{^1H\}$ NMR spectra, the AC 200, AMX 300 and ARX 400 instruments were used and the external standard was H_3PO_4 (82% D_2O, $\delta = 0.0$ ppm). Mass spectra were measured with a NERMAG R10-10 spectrometer. Elemental analyses were carried out at the Laboratoire de Contrôle de l'Ecole Nationale Supérieure de Chimie de Toulouse.

2.2. Synthetic work

2.2.1. Synthesis of cis-PP-ReOCl(P–O)$_2$ (1)

A mixture of 0.423 g (0.51 mmol) of $ReOCl_3(PPh_3)_2$, 0.24 g (1.02 mmol) of P–C=O and 0.102 g (1.01 mmol) of NEt_3 was refluxed in 20 ml of $C_6H_5CH_3$ for 4 h. Cooling the solution to room temperature (r.t.) produced the precipitation of $(HNEt_3)Cl$ as a white solid that was eliminated by filtration. The resulting green solution was concentrated to one-half. Addition of C_5H_{12} gave a green solid which was filtered, washed with, C_5H_{12} and dried in vacuo (yield: 27%). *Anal.* Calc. (found) for $C_{28}H_{40}ClO_3P_2Re$: C, 47.48 (47.37); H, 5.69 (5.34)%. IR (KBr, cm^{-1}): 974 (ν(Re=O)); 1543 (ν(C=C–O). MS DCI/NH_3 *m/z* (%): 726 (37) $[M+NH_4]^+$; 709 (100) $[M+H]^+$; 690 (21) $[M-HCl+NH_4]^+$; 673 (5) $[M-HCl+H]^+$. ^1H NMR ($CDCl_3$, 400.13 MHz; ppm): 1.02 (dd, $^3J_{HP} = 16$, $^3J_{HH} = 7$ Hz, 3H, CH_3); 1.13 (dd, $^3J_{HP} = 17$, $^3J_{HH} = 7$ Hz, 3H, CH_3); 1.17 (dd, $^3J_{HP} = 16$, $^3J_{HH} = 7$ Hz, 3H, CH_3); 1.33 (dd, $^3J_{HP} = 14$, $^3J_{HH} = 7$ Hz, 3H, CH_3); 1.43 (dd, $^3J_{HP} = 16$, $^3J_{HH} = 7$ Hz, 3H, CH_3); 1.51 (dd, $^3J_{HP} = 13$, $^3J_{HH} = 7$ Hz, 3H, CH_3); 1.62 (dd, $^3J_{HP} = 16.5$, $^3J_{HH} = 7$ Hz, 3H, CH_3); 1.64 (dd, $^3J_{HP} = 15$, $^3J_{HH} = 7$ Hz, 3H, CH_3); 2.24 (dhep, $^2J_{HP} = 12$, $^3J_{HH} = 7$ Hz, 1H, CH–CH_3); 2.36 (oct, $^2J_{HP} = {}^3J_{HH} = 7$ Hz, 1H, CH–CH_3); 2.68 (dhep, $^2J_{HP} = 9$, $^3J_{HH} = 7$ Hz, 1H, CH–CH_3); 3.25 (dhep, $^2J_{HP} = 12$, $^3J_{HH} = 7$ Hz, 1H, CH–CH_3); 5.51 (d, $^2J_{HP} = 5.0$ Hz, 1H, CH); 5.77 (d, $^2J_{HP} = 5.0$ Hz, 1H, CH); 7.11–8.13 (m, 10H, aromatics).

2.2.2. Synthesis of trans-PP-ReOCl(P–O)$_2$ (2)

Same method as above for **1**. The solution remaining after filtration of **1** at r.t. was concentrated in vacuo. The residue was dissolved in Et_2O (10 ml). Addition of C_5H_{12} gave **2** as a pure microcrystalline green solid which was filtrated and dried in vacuo (yield: 21%). *Anal.* Calc. (Found) for $C_{28}H_{40}ClO_3P_2Re$: C, 47.48 (48.33); H, 5.69 (5.80)%. IR (KBr, cm^{-1}): 969 (ν(Re=O)), 1537 (ν(C=C–O)). MS DCI/NH_3 *m/z* (%): 726 (3) $[M+NH_4]^+$; 709 (100) $[M+H]^+$; 690 (3) $[M-HCl+NH_4]^+$; 673 (11) $[M-HCl+H]^+$. ^1H NMR ($CDCl_3$, 400.13 MHz, ppm): 1.23 (dd, $^3J_{HP} = 15.5$, $^3J_{HH} = 7$ Hz, 3H, CH_3); 1.43–1.63 (m, 21H, 7 CH_3); 2.54 (dhep, $^2J_{HP} = 11$, $^3J_{HH} = 7$ Hz, 1H, CH–CH_3); 2.77 (dhep, $^2J_{HP} = 11$, $^3J_{HH} = 7$ Hz, 1H, CH–CH_3); 2.92 (dhep, $^2J_{HP} = 11$, $^3J_{HH} = 7$ Hz, 1H, CH–CH_3); 3.32 (dhep, $^2J_{HP} = 11$, $^3J_{HH} = 7$ Hz, 1H, CH–CH_3); 4.58 (dd, $^2J_{HP} = 3$, $^4J_{HP} = 1.3$ Hz, 1H, CH); 4.94 (dd, $^2J_{HP} = 5.9$, $^4J_{HP} = 1.4$ Hz, 1H, CH); 7.13–7.84 (m, 10H, aromatics).

2.2.3. Synthesis of trans-PP-ReOBr(P–O)$_2$ (4)

Same method as above for **1** with 0.450 g (0.40 mmol) of $ReOBr_3(PPh_3)_2$, 0.33 g (1.39 mmol) of P–C=O, 0.130 g (1.43 mmol) of NEt_3 refluxed in 20 ml of $C_6H_5CH_3$ for 4 h. Filtration of the solution to eliminate $(HNEt_3)Cl$, concentration by one-half, addition of C_5H_{12} (20 ml) and cooling to −20 °C gave a green micro crystalline solid which was filtrated, washed with C_5H_{12} and dried under reduced pressure. Recrystallisation from $C_6H_5CH_3/C_5H_{12}$ (1/1) gave **4** as a pure complex (yield: 37%). *Anal.* Calc. (Found) for $C_{28}H_{40}BrO_3P_2Re$: C, 44.69 (45.37); H, 5.36 (5.46)%. IR (KBr, cm^{-1}): 969 (ν(Re=O)), 1537 (ν(C=C–O)). MS DCI/NH_3 *m/z* (%): 753 (100) $[M+H]^+$; 690 (1) $[M-HBr+NH_4]^+$; 673 (4) $[M-HBr+H]^+$. ^1H NMR ($CDCl_3$, 400.13 MHz, ppm): 1.25 (dd, $^3J_{HP} = 15.5$, $^3J_{HH} = 7$ Hz, 3H, CH_3); 1.43–1.66

(m, 21H, 7 CH_3); 2.54 (dhep, $^2J_{HP}=11$, $^3J_{HH}=7$ Hz, 1H, CH–CH_3); 2.82 (dhep, $^2J_{HP}=11$, $^3J_{HH}=7$ Hz, 1H, CH–CH_3); 2.96 (dhep, $^2J_{HP}=11$, $^3J_{HH}=7$ Hz, 1H, CH–CH_3); 3.48 (dhep, $^2J_{HP}=11$, $^3J_{HH}=7$ Hz, 1H, CH–CH_3); 4.60 (dd, $^2J_{HP}=3$, $^4J_{HP}=1.2$ Hz, 1H, CH); 4.99 (dd, $^2J_{HP}=6$, $^4J_{HP}=1.3$ Hz, 1H, CH); 7.11–7.80 (m, 10H, aromatics).

2.2.4. Synthesis of cis-PP-ReOI(P–O)$_2$ (5)

$ReOI_3(PPh_3)_2$ (0.366 g, 0.33 mmol), P–C=O (0.25 g, 1.06 mmol), NEt_3 (0.109 g, 1.08 mmol) were refluxed in 20 ml of $C_6H_5CH_3$ for 4 h. Concentration of the solution in vacuo gave a green solid which dissolved in Et_2O. After elimination of $(HNEt_3)Cl$ by filtration, the green solution was concentrated to one-half and cooled to −20 °C until precipitation of **5** as a green microcrystalline compound (yield: 13%). *Anal.* Calc. (Found) for $C_{28}H_{40}IO_3P_2Re$: C, 42.05 (44.73); H, 5.04 (5.20)%. IR (KBr, cm^{-1}): 964 (ν(Re=O)), 1543(ν(C=C–O)). MS DCI/NH_3 *m/z* (%): 818 (4) $[M+NH_4]^+$; 801 (100) $[M+H]^+$; 673 (10) $[M-HI+NH_4]^+$. ^{1}H NMR ($CDCl_3$, 400.13 MHz; ppm): 0.96 (dd, $^3J_{HP}=16$, $^3J_{HH}=7$ Hz, 3H, CH_3); 1.11 (dd, $^3J_{HP}=17$, $^3J_{HH}=7$ Hz, 3H, CH_3); 1.19 (dd, $^3J_{HP}=16$, $^3J_{HH}=7$ Hz, 3H, CH_3); 1.32 (dd, $^3J_{HP}=14$, $^3J_{HH}=7$ Hz, 3H, CH_3); 1.44 (dd, $^3J_{HP}=16$, $^3J_{HH}=7$ Hz, 3H, CH_3); 1.51 (dd, $^3J_{HP}=13$, $^3J_{HH}=7$ Hz, 3H, CH_3); 1.62 (dd, $^3J_{HP}=16.5$, $^3J_{HH}=7$ Hz, 3H, CH_3); 1.64 (dd, $^3J_{HP}=15$, $^3J_{HH}=7$ Hz, 3H, CH_3); 2.20 (dhep, $^2J_{HP}=12$, $^3J_{HH}=7$ Hz, 1H, CH–CH_3); 2.39 (oct, $^2J_{HP}=^3J_{HH}=7$ Hz, 1H, CH–CH_3); 2.68 (oct, $^2J_{HP}=^3J_{HH}=7$ Hz, 1H, CH–CH_3); 3.54 (dhep, $^2J_{HP}=12$, $^3J_{HH}=7$ Hz, 1H, CH–CH_3); 4.38 (d, $^2J_{HP}=5.7$ Hz, 1H, CH); 5.65 (d, $^2J_{HP}=5.7$ Hz, 1H, CH); 7.11–8.15 (m, 10H, aromatics).

2.2.5. Synthesis of cis-PP-ReO(OEt)(P–O)$_2$ (7)

$ReO(OEt)Cl_2(PPh_3)_2$ (0.241 g, 0.29 mmol), P–C=O (0.27 g, 1.14 mmol) and NEt_3 (0.116 g, 1.15 mmol) were refluxed in 20 ml of EtOH for 1 h. The resulting brown solution was evaporated under reduced pressure until precipitation of a brown solid. Filtration then dissolution of the solid in 20 ml of Et_2O precipitated $(HNEt_3)Cl$ as a white solid which was eliminated. The remaining solution was evaporated under reduced pressure giving a brown solid that was recrystallized from MeCN (10 ml) at −20 °C for 1 day. (Yield: 32%.) *Anal.* Calc. (Found) for $C_{30}H_{45}O_4P_2Re$: C, 50.19 (50.77); H, 6.27 (6.15)%. IR (KBr, cm^{-1}): 956 (ν(Re=O)); 1534, 1550 (ν(C=C–O)). MS DCI/NH_3 *m/z* (%): 719 (10) $[M+H]^+$; 690 (100) $[M-EtOH+NH_4]^+$; 673 (20) $[M-EtOH+H]^+$. ^{1}H NMR ($CDCl_3$, 400.13 MHz; ppm): 1.07 (dd, $^3J_{HH}=7$, $^3J_{HP}=2.5$ Hz, 3H, CH_3); 1.11 (dd, $^3J_{HH}=7$, $^3J_{HP}=3.5$ Hz, 3H, CH_3); 1.18 (dd, $^3J_{HP}=16$, $^3J_{HH}=7$ Hz, 3H, CH_3); 1.22 (dd, $^3J_{HP}=14.5$, $^3J_{HH}=7$ Hz, 3H, CH_3); 1.27 (t, $^3J_{HH}=7$ Hz, 3H, O–CH_2–CH_3); 1.37 (dd, $^3J_{HP}=16$, $^3J_{HH}=7$ Hz, 3H, CH_3); 1.45 (dd, $^3J_{HP}=13$, $^3J_{HH}=7$ Hz, 3H, CH_3); 1.48 (dd, $^3J_{HP}=15.5$, $^3J_{HH}=7$ Hz, 3H, CH_3); 1.55 (dd, $^3J_{HP}=15$, $^3J_{HH}=7$ Hz, 3H, CH_3); 2.00 (dhep, $^2J_{HP}=7.5$, $^3J_{HH}=7$ Hz, 1H, CH–CH_3); 2.12 (dhep, $^2J_{HP}=11.5$, $^3J_{HH}=7$ Hz, 1H, CH–CH_3); 2.77 (dhep, $^2J_{HP}=9.5$, $^3J_{HH}=7$ Hz, 1H, CH–CH_3); 2.88 (dhep, $^2J_{HP}=12.5$, $^3J_{HH}=7$ Hz, 1H, CH–CH_3); 4.90 (d, $^2J_{HP}=2.2$ Hz, 1H, CH); 5.19 (d, $^2J_{HP}=4.7$ Hz, 1H, CH); 5.35 (ABH_3P, $^2J_{AB}=10.8$, $^3J_{AH}=6.9$, $^4J_{AP}=2.0$ Hz, ^{1}H, OCH_2); 5.43 (ABH_3P, $^2J_{BA}=10.8$, $^3J_{BH}=6.9$, $^4J_{BP}=3.8$ Hz, ^{1}H, OCH_2); 7.10–8.10 (m, 10H, aromatics).

2.2.6. Synthesis of trans-PP-Re(NPh)Cl(P–O)$_2$ (8)

$Re(NPh)Cl_3(PPh_3)_2$ (0.269 g, 0.30 mmol), P–C=O (0.28 g, 1.19 mmol) and NEt_3 (0.124 g, 1.22 mmol) were refluxed in 20 ml of EtOH for 4 h. The resulting green solution was evaporated to dryness giving a green solid. This solid was redissolved in 20 ml of ether to eliminate $(HNEt_3)Cl$. The resulting green solution was concentrated to one half then cooled to −20 °C for 1 day giving a green microcrystalline solid. (Yield: 20%). *Anal.* Calc. (Found) for $C_{34}H_{45}ClNO_2P_2Re$: C, 52.13 (52.36); H, 5.75 (5.87); N, 1.79 (1.69)%. IR (KBr, cm^{-1}): 1537 (ν(C=C–O)). MS DCI/NH_3 *m/z* (%): 784 (100) $[M+H]^+$; 748 (7) $[M-HCl+H]^+$. ^{1}H NMR ($CDCl_3$, 300.13 MHz; ppm): 0.96 (dd, $^3J_{HP}=15.5$, $^3J_{HH}=7$ Hz, 3H, CH_3); 1.18–1.49 (m, 18H, 6 CH_3); 1.60 (dd, $^3J_{HP}=15.5$, $^3J_{HH}=7$ Hz, 3H, CH_3); 2.45 (dhep, $^2J_{HP}=11$, $^3J_{HH}=7$ Hz, 1H, CH–CH_3); 2.86 (dhep, $^2J_{HP}=10$, $^3J_{HH}=7$ Hz, 1H, CH–CH_3); 3.32 (dhep, $^2J_{HP}=10$, $^3J_{HH}=7$ Hz, 1H, CH–CH_3); 3.68 (dhep, $^2J_{HP}=10$, $^3J_{HH}=7$ Hz, 1H, CH–CH_3); 4.61 (dd, $^2J_{HP}=2.2$, $^4J_{HP}=1.2$ Hz, 1H, CH); 4.85 (dd, $^2J_{HP}=3.9$, $^4J_{HP}=1.3$ Hz, 1H, CH); 7.15–7.87 (m, 15H, aromatics).

2.2.7. Synthesis of trans-PP-Re(NPh)Cl$_2$(P–O)(P–C(=O)Ph) (10)

$Re(NPh)Cl_3(PPh_3)_2$ (0.192 g, 0.21 mmol), P–C=O (0.20 g, 0.85 mmol) and NEt_3 (0.086 g, 0.86 mmol) were refluxed in 20 ml of $C_6H_5CH_3$ for 4 h. The resulting green solution was concentrated to one-half. Addition of C_5H_{12} (20 ml) and cooling to −20 °C for 12 h produced a green microcrystalline solid (yield: 30%). *Anal.* Calc. (Found) for $C_{34}H_{46}Cl_2NO_2P_2Re$: C, 49.81 (49.49); H, 5.65 (5.91); N, 1.71 (1.88). IR (KBr, cm^{-1}): 1668 (ν(C=O)), 1542(ν(C=C–O)). MS DCI/NH_3 *m/z* (%): 820 (44) $[M+H]^+$; 784 (100) $[M-HCl+H]^+$. ^{1}H NMR ($CDCl_3$, 400.13 MHz, ppm): 1.13 (dd, $^3J_{HP}=16.5$, $^3J_{HH}=7$ Hz, 6H, 2 CH_3); 1.26 (dd, $^3J_{HP}=16$, $^3J_{HH}=7$ Hz, 6H, 2 CH_3); 1.29 (dd, $^3J_{HP}=14.5$, $^3J_{HH}=7$ Hz, 6H, 2 CH_3); 1.39 (dd, $^3J_{HP}=14$, $^3J_{HH}=7$ Hz, 6H, 2 CH_3); 3.25 (oct, $^2J_{HP}=^3J_{HH}=7$, $^4J_{HP}=1.3$ Hz, 1H, CH–CH_3); 3.29 (oct, $^2J_{HP}=^3J_{HH}=7$, $^4J_{HP}=1.3$ Hz, 2H, 2 CH–CH_3); 3.34 (oct, $^2J_{HP}=^3J_{HH}=7$, $^4J_{HP}=1.3$ Hz, 1H, CH–CH_3); 4.26 (d, $^2J_{HP}=9$ Hz, 2H, CH_2–P); 5.04 (dd,

$^2J_{HP} = 4.1$, $^4J_{HP} = 1.6$ Hz, 1H, C*H*); 7.22–8.01 (m, 15H, aromatics).

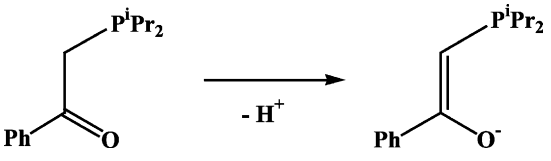
3. Results and discussion

3.1. Re(V) oxo complexes

Treating $ReOX_3(PPh_3)_2$ (X = Cl, Br, I) and $ReO(OEt)Cl_2(PPh_3)_2$ with 2 equiv. of $^iPr_2PCH_2C(=O)Ph$ in presence of 2 equiv. of NEt_3 as base, under reflux, produced quantitatively the diamagnetic pseudo-octahedral complexes ReOX(P–O)$_2$ (X = Cl, X = Br, X = I, X = OEt). Thus as expected the ligand reacts in its enol form, as an uninegative bidentate chelate (Scheme 2).

Analysis of the clear green solutions obtained after refluxing for 4 h the mixture of reactants containing $ReOX_3(PPh_3)_2$ (X = Cl, Br, I) in toluene by ^{31}P NMR showed the singlet at about −5 ppm of free PPh_3 and two AX and AB spin systems with $^2J_{PP}$ coupling constants characteristic of the 'twisted' *cis*-PP and *trans*-PP pseudo octahedral complexes ReOX(P–O)$_2$ (Table 1, Scheme 3).

The *trans*-PP/*cis*-PP ratio increased from 1/1 when X = Cl to 5/1 when X = I that is with the size of the halide and no variation was observed with time. When the same reaction was performed with the analog but less hindered 1-phenyl-2-(diphenylphosphino)ketone $Ph_2PCH_2(C{=}O)Ph$, only the *cis*-PP isomer was obtained whatever the solvent was [12]. This is probably due to steric effects as was observed in square planar complexes of the type $MX_2(PR_3)_2$ (X = halides and PR_3 = tertiary phosphine) where the *trans*/*cis* ratio was favored by bulkier L and iodine over chloride [19]. However, it is likely that electronic effects resulting from differences in ionic radii, polarizabilities, π-donor availability and *trans*-influence of iodine compared to chlorine are significant factors but their relative importance remains a subject to be more investigated. However, the stability gap between the two isomers is small. Presence of the *trans* isomer in toluene is not surprising since it is well known that non polar solvent favors *trans*-isomerisation while increasing solvent polarity favors *cis* form [20]. This is consistent with the presence of the *cis*-PP isomer as the unique species when the reactions were performed in ethanol. When X = Cl, the complex was identified as *cis*-PP-ReOCl(P–O)$_2$ (**1**) while only *cis*-PP-ReO(OEt)(P–O)$_2$ (**7**) was obtained when X = Br or I. As



Scheme 2.

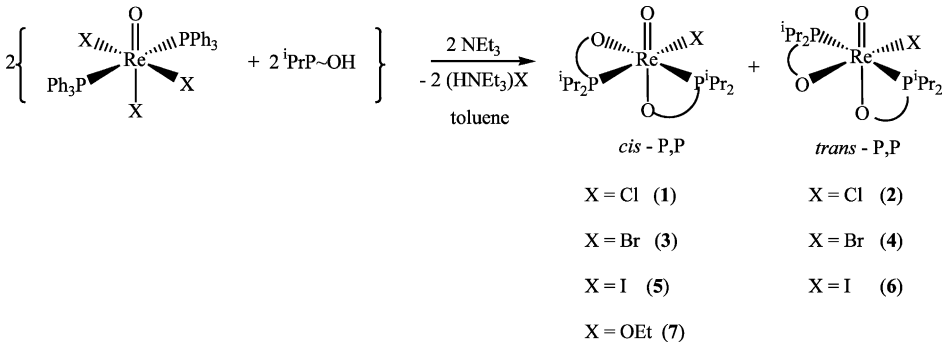
Table 1
$^{31}P\{^1H\}$ NMR and IR data for the complexes **1–10**

Compound	$^{31}P\{^1H\}$ ($CDCl_3$) [a]	ν(Re=O) cm^{-1}
cis-PP-ReOCl(P–O)$_2$ (**1**)	23.3 (d, $^2J_{PP}$ = 10 Hz) 37.4, (d, $^2J_{PP}$ = 10 Hz)	974
trans-PP-ReOCl(P–O)$_2$ (**2**)	43.1 (d, $^2J_{PP}$ = 194 Hz) 47.1 (d, $^2J_{PP}$ = 194 Hz)	969
cis-PP-ReOBr(P–O)$_2$ (**3**) [b]	21.8 (d, $^2J_{PP}$ = 9 Hz) 37.8 (d, $^2J_{PP}$ = 9 Hz)	
trans-PP-ReOBr(P–O)$_2$ (**4**)	42.1 (d, $^2J_{PP}$ = 194 Hz) 47.2 (d, $^2J_{PP}$ = 194 Hz)	969
cis-PP-ReOI(P–O)$_2$ (**5**)	21.7 (d, $^2J_{PP}$ = 6 Hz) 37.6 (d, $^2J_{PP}$ = 6 Hz)	964
trans-PP-ReOI(P–O)$_2$ (**6**) [b]	40.7 (d, $^2J_{PP}$ = 192 Hz) 48.2 (d, $^2J_{PP}$ = 192 Hz)	
cis-PP-ReO(OEt)(P–O)$_2$ (**7**)	22.1 (d, $^2J_{PP}$ = 8.5 Hz) 30.6 (d, $^2J_{PP}$ = 8.5 Hz)	956
trans-PP-Re(NPh)-Cl(P–O)$_2$ (**8**)	33.5 (d, $^2J_{PP}$ = 213 Hz) 39.4 (d, $^2J_{PP}$ = 213 Hz)	
trans-PP-Re(NPh)Cl$_2$-(PPh_3)(P–O) (**9**) [b]	−6.7 (d, $^2J_{PP}$ = 253 Hz) 33.8 (d, $^2J_{PP}$ = 253 Hz)	
trans-PP-Re(NPh)Cl$_2$-(P–C=O)(P–O) (**10**)	11.9 (dd, $^2J_{PP}$ = 234 Hz) 31.9 (dd, $^2J_{PP}$ = 234 Hz)	

[a] In $CDCl_3$.
[b] Only observed in solution.

before, this probably results from the increased steric hindrance of Br and I and illustrates the competition between X^- and EtO^- for the sixth site of the octahedron which is the equatorial one. With $^iPr_2P$–O, the chloro complex is favored, which is the thermodynamic product and is also obtained by using $ReOCl_2(OEt)(PPh_3)_2$ as the rhenium precursor. In this case, monitoring by ^{31}P NMR the reaction of a fourfold excess of ligand in ethanol on $ReO(OEt)Cl_2(PPh_3)_2$ showed, after 1 h, a 3/1 mixture of the ethoxo and chloro derivatives. Heating 3 h more produced the total disappearance of ReO(OEt)(P–O)$_2$ and the formation of ReOCl(P–O)$_2$ as unique species. This is opposite to our precedent results on the diphenylphosphinoenolato complexes where the ethoxo derivative was the thermodynamic species and, thus, emphasis the importance of the balance between electronic and steric effects. The fact that, in ethanol, $^iPr_2P$–O favors the chloro species while Ph_2P–O stabilizes the ethoxo one indicates that here the electronic effect (basicity of the phosphine) is the main factor and influences the *trans* coordination (Cl is less nucleophilic than OEt).

cis-PP-ReOCl(P–O)$_2$ (**1**) and *trans*-PP-ReOCl(P–O)$_2$ (**2**) have been successfully isolated from toluene due to their differences in solubility after elimination of $(HNEt_3)Cl$ and concentration of the solution. Compound **1** was precipitated first at room temperature on addition of pentane. Compound **2** was obtained further by adding diethylether to the precedent filtrate. Improvements of the syntheses have been performed as



Scheme 3.

described in Section 2. Only the *trans*-PP-ReOBr(P–O)$_2$ (**4**) and *cis*-PP-ReOI(P–O)$_2$ (**5**) have been successfully isolated as green solids. The other complexes have only been characterized in solution by $^{31}P\{^1H\}$ NMR (Table 1). ReO(OEt)(P–O)$_2$ was isolated when the reaction was ruled out in ethanol. All the complexes are fairly stable in the solid state but may be stored under controlled atmosphere to prevent phosphine oxidation. Their elemental analyses confirm their proposed formula. Their stability is confirmed by their DCI/NH_3 mass spectra which always show the $[M+H]^+$ cation as the major species. Their spectrochemical features are as expected. The Re=O stretches lie in the narrow range of 956–974 cm^{-1} indicative of strong Re-oxo multiple bond. The lowest value of 956 cm^{-1} observed in **7** results from the increased basicity of the ethoxo ligand compared to Cl (974 cm^{-1} in **1**).

All the complexes show the doublet of doublet characteristic of an AX or AB pattern in their $^{31}P\{^1H\}$ NMR spectra (Table 1), consistent with two magnetically inequivalent phosphorus atoms and thus indicating for the complexes the *cis*-PP configuration **A** or the *trans*-PP configuration (**B**), depending on the coupling constants values (Scheme 1). The fact that the *cis* configuration is observed confirms that the electronic effect (basicity) of the ligand is more important than its steric hindrance. As already observed, the largest downfield shift is obtained with the equatorial phosphorus atom, which makes the strongest bond with the rhenium center.

The proton spectra present no unexpected feature, the signals of the four ^{i}Pr substituents being located between 1 and 1.5 ppm (CH_3), 2 and 3.5 ppm (CH) and those of the Ph substituent in the 7–9 ppm range. Two typical doublets in the 5 ppm range are characteristic of the two protons of the inequivalent enolato groups. In the *trans*-complexes they appear as doublet of doublet due to their coupling with the *trans*-phosphorus atom. In **7** each of the two stereotopic AB protons of the methylene group of the ethanolato ligand exhibits an ABH_3P type spectrum as expected from the location of OEt^- in the equatorial plane of the molecule in *trans* position to a phosphorus atom ($\delta P = 30.6$ ppm).

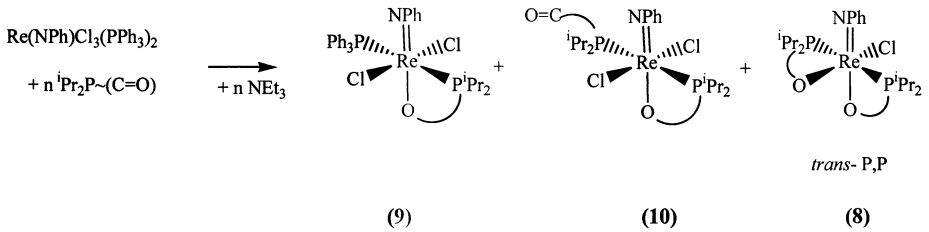
3.2. Re(V) imido complexes

The reaction of 1-phenyl-2-(diisopropylphosphino)ethanone with Re(NPh)$Cl_3(PPh_3)_2$ followed a similar pattern but the reaction was not stoichiometric and led to more species than were observed with Re-oxo compounds.

Monitoring by ^{31}P NMR, in refluxing toluene for 4 h, the reaction of Re(NPh)$Cl_3(PPh_3)_2$ with a twofold molar amount of ligand without base showed formation of two monosubstituted complexes: Re(NPh)$Cl_2(PPh_3)$(P–O) (**9**) as the major species and Re(NPh)Cl_2(P–C=O)(P–O) (**10**) as the minor one indicating monosubstitution plus phosphine exchange in the second case (Scheme 4).

Increasing the L/Re ratio to 4/1 gave (**10**) as the unique species. Addition of NEt_3 induced deprotonation of the ligand, but the process was not complete and a mixture of (**10**) and Re(NPh)Cl(P–O)$_2$ (**8**) in a 3/1 ratio was present. (**10**) was isolated by addition of pentane. However, obtainment of Re(NPh)Cl(P–O)$_2$ (**8**) as the unique species was possible in refluxing ethanol, by using 4 equiv. of ligand for 4 h. Surprisingly, no ethoxo complex formation was observed as was the case for Ph_2PCH_2(C=O)Ph where it was the only complex isolated [12]. This probably could be attributed to the difference in the basicity of the two ligands.

Both complexes (**8**) and (**10**) have been isolated. They present a *trans*-PP configuration as indicated by their ^{31}P NMR spectra which show AB pattern with large J_{PP} values (Table 1). Their elemental analyses and NMR spectra are as expected. The differences observed in their IR spectra (solid state) and ^1H NMR (solution) agree with their formulation as a bisubstituted complex (**8**) with two chelating anionic P–O ligands and a bisubstituted complex (**10**) with chelating P–O and modentate P–C(=O) ligands respectively. The IR spectrum of **8** shows only a broad band at 1537 cm^{-1} characteristic of the ν(C=C–O) vibration of the enolic ligands while in **10**, the enolato group presents its ν(C=C–O) at 1542



Scheme 4.

cm^{-1} while the ν(C=O) of the keto group vibrates at 1668 cm^{-1} (1672 cm^{-1} in the free ligand). Similar differences are also observed in the ^1H NMR spectra. The ethylenic protons of the two enolato chelates are present as doublet of doublet at 4.61 and 4.85 ppm because of the coupling with the nearby and *trans* phosphorus atoms. A similar patter is observed for the enolato proton in **10**, which shows the doublet of doublet of the ethylenic proton at 5.04 ppm while the 2 equiv. methylene protons of the phosphinoketone resonate at 4.26 ppm as a doublet because of their coupling with the nearby phosphorus atom.

The imido Re complexes present a *trans*-PP twisted octahedral structure which is the conformation the most currently observed with this rhenium core thus indicating that the presence of the phenyl imido susbtituent decreases significantly space in the rhenium coordination sphere.

In conclusion, new rhenium-oxo and -phenylimido complexes have been synthetized and isolated when 1-phenyl-2-(diisopropylphosphino)ethanone was used as ligand. The rhenium-oxo complexes are mainly *cis*-PP derivatives. The *trans*-PP stereoisomers were only observed in toluene as mixture of *cis*/*trans* species. In ethanol, only *cis*-PP isomers were obtained, *cis*-PP-ReOCl(P–O)$_2$ when X = Cl and *cis*-PP-ReO(OEt)(P–O)$_2$ when X = Br, I, OEt. Comparison with the related 1-phenyl-2-(diphenylphosphino)ethanone complexes emphasis in this case the importance of the phosphine basicity. This is different to the results obtained with phosphinophenols where the phosphine steric hindrance was the major factor. The reaction of 1-phenyl-2-(diisopropylphosphino)ethanone with the rhenium imido precursor afforded the *trans*-PP-Re(NPh)Cl(P–O)$_2$ as the unique species in ethanol while in toluene the reaction depends on the experimental conditions. As observed in all the complexes with phosphinophenolato and phosphinoenolato ligands, presence of the imido core favors the formation of the *trans* PP isomer. Thus, it may be concluded that 1-phenyl-2-(diisopropylphosphino)ethanone in basic ethanol is a good ligand for the synthesis of rhenium(V) complexes.

4. Supplementary material

The material is available from the authors on request.

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