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Polyhedron 19 (2000) 1111–1116

POLYHEDRON

Bidentate phosphinophenol ligand: synthesis and characterization of oxo and phenylimido rhenium(V) complexes of 2-diisopropylphosphinophenol

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Received 20 January 2000; accepted 8 March 2000

Abstract

Six-coordinate, monosubstituted and disubstituted phosphinophenol complexes $ReYX_2(PPh_3)(P\sim O)$ and $ReYX(P\sim O)_2$ (Y = O, NPh; X = Cl, Br, I) were obtained by reacting 2-diisopropylphosphinophenol (P ~ OH) with $ReOX_3(PPh_3)_2$ and $Re(NPh)X_3(PPh_3)_2$ in toluene. A mixture of the monosubstituted and disubstituted complexes $ReYX_2(PPh_3)(P\sim O)$ and $ReYX(P\sim O)_2$ was precipitated when the reactions were performed with a 2:1 ligand to metal ratio. Excess ligand (4 equiv.) was needed to obtain quantitatively the disubstituted complexes. ^1H and $^{31}P\{^1H\}$ NMR show that all monosubstituted and disubstituted complexes exist as single isomers with a *trans*-P,P 'twisted' octahedral geometry, the site *trans* to the multiple bond being filled by the oxygen donor of one P ~ O ligand. The compounds were also characterized by microanalysis, IR and mass spectrometry.

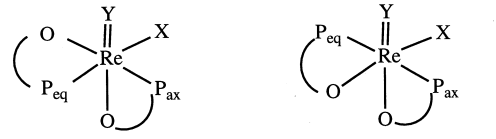
Keywords: Phosphinophenols; Rhenium

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 chelates for metallic radioisotopes to develop imaging (technetium) and therapeutic (rhenium) agents in nuclear medicine.

In the recent past, studies have been conducted on the reaction of $ReOCl_3(PPh_3)_2$, $Re(NPh)Cl_3(PPh_3)_2$ and $[TcO_4]^-$ with various diphenylphosphines functionalized with nucleophilic substituents such as $Ph_2P–Z–CO_2H$ (Z = CH_2, $CH_2–CH_2$, *o*-C_6H_4) [1,2], $Ph_2PCH{=}CPh(OH)$ [3], $Ph_2PC_6H_4OH$ [4–8], $Ph_2PCH_2C_6H_4OH$ [9] and $Ph_2PC_6H_4OSiMe_3$ [10], i.e. bidentate ligands with soft phosphorus(III) donor and hard carboxo, hydroxo or phenoxo groups. Although several configurations are possible for octahedral complexes bearing three different ligands, most of the previously reported oxo and imido complexes adopt the *cis*-P_{eq},P_{ax} 'twisted' octahedral arrangement A with an O=Re–O linkage (Scheme 1), while the *trans*-P_{eq},P_{ax} arrangement B with a PhN=Re–O linkage was observed for Re-imido species. Thus these ligands favour the formation of a single isomer, which is essential for radiopharmaceutical applications.

In contrast to the relatively abundant literature on the reactions of $Ph_2PC_6H_4OH$ ligands on rhenium precursors [4–8], to our knowledge the reactivity of dialkylphosphinophenols has not yet been investigated. This may be due in part to the increased reductive character of the alkylphosphines which are known to stabilize Re(III) complexes. In order to determine the influence of an alkyl substituent on the phosphinophenol reactivity, we have studied the reaction of 2-(diisopropylphosphino)phenol (P ~ OH) on $ReOX_3$-



A (cis-P,P « twisted ») **B** (trans-P,P « twisted »)

Scheme 1.

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0277-5387/00/$ - see front matter
PII S0277-5387(00)00360-0

$(PPh_3)_2$ and $Re(NPh)X_3(PPh_3)_2$ (X = Cl, Br, I) by comparison with $Ph_2P\sim OH$. Isopropyl substituents increase the steric hindrance of the phosphine (cone angle of 137° for $^iPr_2P\sim OH$ compared to 127° for $Ph_2P\sim OH$) [11] and its basicity ($pKa(PPh_3) = 2.73$; $pKa(P^iPr_3) = 9.30$)) [12]. We observe the formation of Re(V) complexes without reduction of the metal centre whose structures are controlled by the steric hindrance of the ligand.

2. Experimental

2.1. Reagents and physical measurements

All reactions were carried out in a nitrogen atmosphere using standard Schlenk techniques. Ether and toluene were dried over sodium benzophenone ketyl and distilled prior to use. Ethanol and acetonitrile were distilled on molecular sieves (3 Å). $ReOX_3(PPh_3)_2$ [13,14], $Re(NPh)X_3(PPh_3)_2$ [15], and 2-diisopropylphosphinophenol [16] were prepared by literature methods.

Infrared spectra (4000–200 cm^{-1}) were recorded as CsI pellets on a Bruker Vector 22 spectrometer. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded at room temperature in CD_2Cl_2, $CDCl_3$ or C_6D_6 on Bruker ARX 400 and AMX 300 WB spectrometers, using $SiMe_4$ as internal reference (^1H, ^{13}C) and H_3PO_4 (82%/D_2O) as external reference (^{31}P). All chemical shifts are reported in ppm. Desorption chemical ionization using NH_3 (DCI/NH_3) was recorded on a NERMAG R 1010 mass spectrometer. Elemental analyses were run at the Laboratoire de Chimie de Coordination du CNRS, Toulouse, France.

2.2. Synthetic work

$ReOCl_2(PPh_3)(P\sim O)$ (**1**) and $ReOCl(P\sim O)_2$ (**2**). The two complexes were obtained from the reaction of $P\sim OH$ (0.373 g, 1.77 mmol) and $ReOCl_3(PPh_3)_2$ (0.739 g, 0.89 mmol) in refluxing toluene under N_2 for 35 h. Concentration of the solution in vacuo produced a green solid. Work-up with diethyl ether and cooling of the solution gave a mixture of **1** and **2**. Purification by column chromatography using silica as support gave **1** with chloroform and **2** with diethyl ether as eluents. Recrystallization from diethyl ether at −20°C gave **1** (yield 10%) and **2** (yield 43%) as green crystals.

1. *Anal*. Calc. for $C_{30}H_{33}Cl_2O_2P_2Re$: C, 48.39; H, 4.47. Found: C, 47.82; H, 4.78%. IR (CsI): 970 cm^{-1}, ν(Re=O). MS (DCI/NH_3): *m/z* 745 $[M+H]^+$, 709 $[M-HCl+H]^+$. $^{31}P\{^1H\}$ NMR (C_6D_6, 161.98 Hz, ppm): 7.1; 24.7 (dd, $^2J_{PP} = 262$ Hz). ^1H NMR (C_6D_6, 400.14 MHz, ppm): 1.36 (dd, 6H, CH_3, $^3J_{HH} = 7$ Hz, $^3J_{HP} = 15$ Hz); 1.50 (dd, 6H, CH_3, $^3J_{HH} = 7$ Hz, $^3J_{HP} = 17$ Hz); 3.33 (d of septets, 2H, CH, $^3J_{HH} = 7$ Hz, $^2J_{HP} = 2$ Hz); 6.22 (dd, 1H, Ph, $^3J_{HH} = 7$ Hz, $^4J_{HP} = 4$ Hz); 6.56 (dd, 1H, Ph, $^3J_{HH} = 7$ Hz); 6.93 (dd, 2H, Ph, $^3J_{HH} = 7$ Hz); 7.03 (m, 9H, Ph); 8.04 (ddd, 6H, Ph, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 1$ Hz, $^3J_{HP} = 11$ Hz).

2. *Anal*. Calc. for $C_{24}H_{36}ClO_3P_2Re$: C, 43.93; H, 5.53; Cl, 5.40; P, 9.44; Re, 28.38. Found: C, 48.85; H, 5.56; Cl, 6.55; P, 9.19; Re, 26.13%. IR (CsI): 962 cm^{-1}, ν(Re=O). MS (DCI/NH_3): *m/z* 621 $[M-HCl+H]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz, ppm): 34.0; 41.6 (dd, $^2J_{PP} = 213$ Hz). ^1H NMR ($CDCl_3$, 400.14 MHz, ppm): 1.4 (dd, 12H, CH_3, $^3J_{HH} = 7$ Hz, $^3J_{HP} = 17$ Hz); 1.7 (dd, 12H, CH_3, $^3J_{HH} = 7$ Hz, $^3J_{HP} = 17$ Hz); 2.8 (d of septets, 1H, CH, $^3J_{HH} = 7$ Hz, $^2J_{HP} = 1$ Hz); 3.0 (d of septets, 2H, CH, $^3J_{HH} = 7$ Hz, $^2J_{HP} = 1$ Hz); 3.4 (d of septets, 1H, CH, $^3J_{HH} = 7$ Hz, $^2J_{HP} = 1$ Hz); 6.3–7.5 (m, 8H, Ph).

$ReOBr_2(PPh_3)(P\sim O)$ (**3**) and $ReOBr(P\sim O)_2$ (**4**). The same method was used as for **1** and **2**, starting from 0.380 g (1.8 mmol) of $P\sim OH$ and 0.873 g (0.9 mmol) of $ReOBr_3(PPh_3)_2$, stirred in 30 ml of refluxing toluene under N_2 for 46 h.

3. Green solid, yield 9%. *Anal*. Calc. for $C_{30}H_{33}Br_2O_2P_2Re$: C, 43.23; H, 3.99. Found: C, 44.27; H, 3.58%. IR (CsI): 969 cm^{-1}, ν(Re=O). MS (DCI/NH_3): *m/z* 835 $[M+H]^+$, 755 $[M-HBr+H]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz, ppm): 8.0; 26.1 (dd, $^2J_{PP} = 260$ Hz). ^1H NMR ($CDCl_3$, 400.14 MHz, ppm): 1.55 (dd, 6H, CH_3, $^3J_{HH} = 7$ Hz, $^3J_{HP} = 16$ Hz); 1.64 (dd, 6H, CH_3, $^3J_{HH} = 7$ Hz, $^3J_{HP} = 16$ Hz); 3.62 (d of septets, 2H, CH, $^3J_{HH} = 7$ Hz, $^2J_{HP} = 2$ Hz); 5.9–7.8 (m, 19H, Ph). $\Lambda(CH_3CN)$: 30.3 Ω^{-1} cm^2 M^{-1} (molecular).

4. Green solid, yield 50%. *Anal*. Calc. for $C_{24}H_{36}BrO_3P_2Re$: C, 41.15; H, 5.18. Found: C, 41.40; H, 4.92%. IR (CsI): 964 cm^{-1}, ν(Re=O). MS (DCI/NH_3): *m/z* 701 $[M+H]^+$, 621 $[M-HBr+H]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz, ppm): 34.1, 41.7 (dd, $^2J_{PP} = 212$ Hz). ^1H NMR ($CDCl_3$, 400.14 MHz, ppm): 1.1–1.7 (dd, 24H, CH_3, $^3J_{HH} = 7$ Hz, $^3J_{HP} = 16$ Hz); 2.8–3.1 (m, 4H, CH); 6.3–7.5 (m, 8H, Ph). $\Lambda(CH_3CN)$: 15.1 Ω^{-1} cm^2 M^{-1} (molecular).

$ReOI_2(PPh_3)(P\sim O)$ (**5**) and $ReOI(P\sim O)_2$ (**6**). The same method was used as for **1** and **2**, starting from the reaction of 0.45 g (2.14 mmol) of $P\sim OH$ and 1.185 g (1.07 mol) of $ReOI_3(PPh_3)_2$ in refluxing toluene under N_2 for 46 h. Concentration of the solution gave an oily solid. Work-up with diethyl ether and cooling the solution gave a mixture of **5** (yield 27%) and **6** (yield 9%) as a dark brown solid, which was filtered off and dried in vacuo. Purification by column chromatography as for the Cl and Br analogues gave **5** and **6** as pure compounds.

5. Brown solid, yield 27%. *Anal*. Calc. for $C_{30}H_{33}I_2O_2P_2Re$: C, 38.85; H, 3.59; I, 27.36. Found: C, 38.07; H, 3.28; I, 26.94%. ^{31}P NMR ($CDCl_3$, 161.98 MHz, ppm): 6.9; 17.4 (dd, $^2J_{PP} = 257$ Hz). MS (DCI/NH_3): *m/z* 929 $[M+H]^+$.

6. Brown solid, yield 9%. *Anal*. Calc. for $C_{24}H_{36}IO_3P_2Re$: C, 38.56; H, 4.85; I, 16.97. Found: C, 38.17; H, 4.60; I, 16.12%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz, ppm): 33.1;

42.4 (dd, $^2J_{PP}$ = 210 Hz). MS (DCI/NH_3): *m/z* 749 $[M+H]^+$.

Re(NPh)Cl_2(PPh_3)(P∼O) (**7**) and Re(NPh)Cl(P∼O)$_2$ (**8**). The same method was used as for **1** and **2**, starting from the reaction of P∼OH (0.47 g, 2.24 mmol) and Re(NPh)Cl_3(PPh_3)$_2$ (1.02 g, 1.12 mmol) in refluxing toluene (40 ml) under N_2 for 37 h.

7. Beige solid, yield 45%. *Anal*. Calc. for $C_{36}H_{38}Cl_2NOP_2Re$: C, 52.75; H, 4.67; N, 1.71. Found: C, 51.91; H, 4.73; N, 1.78%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 161.98 MHz, ppm): −5.2; 27.7 (dd, $^2J_{PP}$ = 260 Hz). MS (DCI/NH_3): *m/z* 820 $[M+H]^+$.

8. Beige solid, yield 10%. *Anal*. Calc. for $C_{30}H_{41}ClNO_2P_2Re$: C, 49.27; H, 5.65; N, 1.92. Found: C, 48.95; H, 5.90; N, 1.72%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 161.98 MHz, ppm): 30.7; 33.3 (dd, $^2J_{PP}$ = 224 Hz). MS (DCI/NH_3): *m/z* 732 $[M+H]^+$.

Re(NPh)Br_2(PPh_3)(P∼O) (**9**) and Re(NPh)Br(P∼O)$_2$ (**10**). The same method was used as for **7** and **8**, starting from 0.55 g (2.6 mmol) of P∼OH and 1.362 g (1.3 mmol) of Re(NPh)Br_3(PPh_3)$_2$ in 35 ml of toluene. **9** yield 56%, and **10** yield 14%.

9. *Anal*. Calc. for $C_{36}H_{38}Cl_2NOP_2Re$: C, 47.59; H, 4.22; N, 1.54. Found: C, 46.95; H, 4.08; N, 1.42%. MS (DCI/NH_3): *m/z* 910 $[M+H]^+$. $^{31}P\{^1H\}$ NMR (C_6D_6, 161.98 MHz, ppm): −6.3; 24.1 (dd, $^2J_{PP}$ = 246 Hz).

10 was obtained in 30% yield by refluxing a mixture of 0.355 g (1.7 mmol) of P∼OH and 0.44 g (0.42 mmol) of Re(NPh)Br_3(PPh_3)$_2$ in 20 ml of toluene for 46 h. Concentration of the solution gave a brown precipitate, which was recrystallized from diethyl ether (20 ml). Cooling the solution at −20°C gave **10** as a brown solid which was filtered off, washed with diethyl ether and dried in vacuo. *Anal*. Calc. for $C_{30}H_{41}BrNO_2P_2Re$: C, 46.45; H, 5.33; N, 1.81. Found: C, 46.50; H, 4.77; N, 1.64%. IR (CsI): 1026 cm^{-1}, ν(Re=O). MS (DCI/NH_3): *m/z* 776 $[M+H]^+$. $^{31}P\{^1H\}$ NMR (C_6D_6, 161.98 MHz, ppm): 30.8; 33.1 (dd, $^2J_{PP}$ = 222 Hz). ^1H NMR (C_6D_6, 400.14 MHz, ppm): 0.7–1.6 (dd, 24H, CH_3, $^3J_{HH}$ = 7 Hz, $^3J_{HP}$ = 15 Hz); 2.5–3.4 (d of septets, 4H, CH, $^3J_{HH}$ = 7 Hz, $^2J_{HP}$ = 1 Hz); 6.6–7.8 (m, 13H, Ph).

Re(NPh)I_2(PPh_3)(P∼O) (**11**) and Re(NPh)I(P∼O)$_2$ (**12**). The complexes were synthesized as for **9** and **10**, with Re(NPh)I_3(PPh_3)$_2$ (1.237 g, 1.05 mmol) and P∼OH (0.44 g, 2.09 mmol) in toluene (35 ml) for 47 h. Work-up with ether and purification by column chromatography with $CHCl_3$ and ether as eluents and recrystallization from diethyl ether at −20°C gave **11** (yield 54%) and **12** (yield 13%) as brown microcrystalline compounds.

11. *Anal*. Calc. for $C_{36}H_{38}I_2NOP_2Re$: C, 43.12; H, 3.82; N, 1.40; I, 25.31. Found: C, 41.80; H, 3.75; N, 1.35; I, 25.05%. MS (DCI/NH_3): *m/z* 1004 $[M+H]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz, ppm): −6.3; 24.1 (dd, $^2J_{PP}$ = 246 Hz).

12. *Anal*. Calc. for $C_{30}H_{41}INO_2P_2Re$: C, 43.80; H, 5.02; N, 1.70; I, 15.43. Found: C, 41.92; H, 4.93; N, 1.65; I, 15.28%. MS (DCI/NH_3): *m/z* 824 $[M+H]^+$; 696 $[M-HI+H]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.98 MHz, ppm): 31.8; 33.3 (dd, $^2J_{PP}$ = 217 Hz).

3. Results and discussion

3.1. Synthesis

$^iPr_2PC_6H_4OH$ (P∼OH) reacts readily, in refluxing toluene, on ReOX_3(PPh_3)$_2$ and Re(NPh)X_3(PPh_3)$_2$ but the reactions are sensitive to the ligand:metal ratio and care must be taken to use carefully dried and degassed solvents to prevent phosphine oxidation.

A 4:1 ligand to metal ratio gives quantitatively the disubstituted ReYX(P∼O)$_2$ complexes (Y = O, NPh; X = Cl, Br, I). However, when the reaction is performed in a stoichiometric ratio (L:M = 2:1), a mixture of monosubstituted and disubstituted ReYX_2(PPh_3)(P∼O) and ReYX(P∼O)$_2$ complexes is obtained; the ratio ReYX(P∼O)$_2$/ReYX_2(PPh_3)(P∼O) decreases as the size of the halide increases. Such a mixture of complexes was not observed with diphenylphosphinophenol whose reactions were stoichiometric, indicating that the basicity of the phosphine is not the main factor governing the reaction.

In an effort to follow the reaction, to detect intermediate compounds and to confirm that chelation of the phosphine ligand occurs with the concomitant release of both PPh_3 and Cl, we monitored the reaction of P∼OH with ReOCl_3(PPh_3)$_2$ by ^{31}P NMR (Fig. 1). The spectrum after 5 h reveals the presence of all of the expected species. Besides free PPh_3 (singlet at −4 ppm), the major species is ReOCl_2(PPh_3)(P∼O) (**1**) (pair of doublets at 7 and 25 ppm, $^2J_{PP}$ = 262 Hz), followed by ReOCl(P∼O)$_2$ (**2**) (pair of doublets at 34 and 42 ppm, $^2J_{PP}$ = 213 Hz) (vide infra). A third pair of doublets at 20.5 and 31 ppm ($^2J_{PP}$ = 220 Hz) could be assigned to the *trans*-P,P-*trans*-O,O complex ReOCl_2(P∼OH)(P∼O) containing a unidentate P∼OH ligand. The remaining signals, a pair of unresolved peaks at 21.2 and 23.2 ppm and a singlet at 27.2 ppm, which disappear quickly, could correspond to the thermodynamically unstable *cis*-P,P ReOCl(P∼O)$_2$ and the *trans*-P,P ReOCl_3(P∼OH)$_2$ species, respectively. After an extra 10 h under reflux, the spectrum shows free PPh_3, ReOCl_2(PPh_3)(P∼O) (**1**), ReOCl(P∼O)$_2$ (**2**) and ReOCl_2(P∼OH)(P∼O). 20 h later, the spectrum has become remarkably simple: besides free PPh_3, only ReOCl_2(PPh_3)(P∼O) (minor component) and ReOCl(P∼O)$_2$ (major component) are observed. Thus, ReOCl(P∼O)$_2$ is the thermodynamic product, since no further changes occur as heating is continued. Interestingly, under the same experimental conditions, using $Ph_2PC_6H_4OH$ as ligand produced quantitatively ReOCl(P∼O)$_2$.

The corresponding bromo and iodo complexes give the same final products when the reaction is run under identical conditions, starting from ReOBr_3(PPh_3)$_2$ and ReOI_3(PPh_3)$_2$, respectively. ReOBr_2(PPh_3)(P∼O) (**3**) and ReOBr(P∼O)$_2$ (**4**) form in roughly equal amounts, whereas

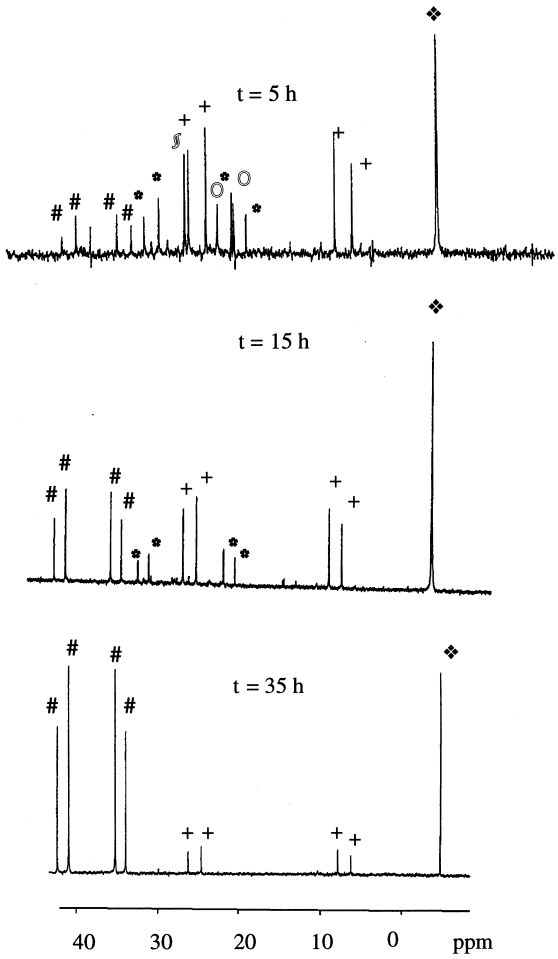


Fig. 1. Monitoring by $^{31}P\{^{1}H\}$ NMR of the reaction of P∼OH on $ReOCl_3(PPh_3)_2$ (2:1 ratio) in refluxing toluene. Spectra at $t = 5$ h (top) (Bruker AMX 300WB), 15 h (middle) and 35 h (bottom) (Bruker ARX 400). (♦) free PPh_3; +, *trans*-P,P $ReOCl_2(PPh_3)(P{\sim}O)$ (**1**); (#) *trans*-P,P $ReOCl(P{\sim}O)_2$ (**2**); (*), *trans*-P,P $ReOCl_2(P{\sim}OH)(P{\sim}O)$; (○) *cis*-P,P $ReOCl(P{\sim}O)_2$; (Ⓢ), *trans*-P,P $ReOCl_3(P{\sim}OH)_2$).

$ReOI_2(PPh_3)(P{\sim}O)$ (**5**) is predominant over $ReOI(P{\sim}O)_2$ (**6**) (∼4:1 ratio). This can be ascribed to the increasing size of the halogen.

The reaction of P∼OH with $Re(NPh)X_3(PPh_3)_2$ follows a similar pattern: a 2:1 ratio leads to a mixture of the monosubstituted and disubstituted species, whereas a 4:1 ratio is needed to obtain $Re(NPh)X(P{\sim}O)_2$.

In all cases, the monosubstituted and disubstituted complexes are successfully separated by column chromatography on silica, using $CHCl_3$ as eluent in one case and ether in the other, and recrystallized from ether.

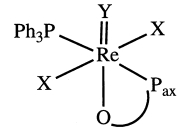
3.2. Characterization of the compounds

3.2.1. Rhenium(V) oxo complexes

Mass spectrometry confirms the mononuclear formulation based on elemental analysis: the DCI/NH_3 spectra all exhibit the $[M+H]^+$ parent peak. In several cases, $[M-HX+H]^+$ peaks due to halide loss are also observed, suggesting that the bidentate P∼O ligand is more tightly bound than the monodentate halide. Besides the main ligand vibrations, all complexes exhibit a Re=O stretching band in the 953–970 cm^{-1} range, typical of multiply bonded Re=O complexes [17].

Table 1
$^{31}P\{^{1}H\}$ NMR data

Complex	Solvent	δ (ppm)		J_{PP} (Hz)
$ReOCl_2(PPh_3)(P{\sim}O)$ (**1**)	C_6D_6	7.1, 24.7	dd	262
$ReOCl(P{\sim}O)_2$ (**2**)	$CDCl_3$	34.0, 41.6	dd	213
$ReOBr_2(PPh_3)(P{\sim}O)$ (**3**)	$CDCl_3$	8.0, 26.1	dd	260
$ReOBr(P{\sim}O)_2$ (**4**)	$CDCl_3$	34.1, 41.7	dd	212
$ReOI_2(PPh_3)(P{\sim}O)$ (**5**)	$CDCl_3$	6.9, 17.4	dd	257
$ReOI(P{\sim}O)_2$ (**6**)	$CDCl_3$	33.1, 42.4	dd	210
$Re(NPh)Cl_2(PPh_3)(P{\sim}O)$ (**7**)	CD_2Cl_2	−5.2, 27.7	dd	260
$Re(NPh)Cl(P{\sim}O)_2$ (**8**)	CD_2Cl_2	30.7, 33.3	dd	224
$Re(NPh)Br_2(PPh_3)(P{\sim}O)$ (**9**)	C_6D_6	−5.8, 26.3	dd	254
$Re(NPh)Br(P{\sim}O)_2$ (**10**)	C_6D_6	30.8, 33.1	dd	222
$Re(NPh)I_2(PPh_3)(P{\sim}O)$ (**11**)	$CDCl_3$	−6.3, 24.1	dd	246
$Re(NPh)I(P{\sim}O)_2$ (**12**)	$CDCl_3$	31.8, 33.3	dd	217



Scheme 2.

The ^{31}P NMR spectrum (in C_6D_6) of $ReOCl_2(PPh_3)(P{\sim}O)$ (**1**) consists of two doublets centred at 24.7 and 7.1 ppm, respectively, with a coupling constant of 262 Hz typical of a *trans*-P,P arrangement. In the structure proposed (Scheme 2), the very stable *trans*-[O=Re–O–] core is assumed to be retained. The downfield signal corresponds to the ring P_{ax} atom as confirmed by the exchange of PPh_3 with pyridine. When pyridine is added to a C_6D_6 solution of **1** in an NMR tube, the AB signal of **1** disappears within 2 h and the *trans*-P,P coupling is lost: new singlets appear at −4 ppm for free PPh_3 and at 19 ppm for a new pyridine complex. Thus, the doublet at 7.1 ppm for **1** corresponds to the labile PPh_3 ligand, which is stereoselectively substituted by pyridine. The upfield shift from 24.7 to 19 ppm experienced by the ring P atom is consistent with the substitution of PPh_3 by pyridine, a stronger σ donor and weaker π acceptor. The stereochemistry of **1** is confirmed by the ^{1}H NMR spectrum. The two pairs of CH_3 groups appear as doublets of doublets at 1.36 ppm ($^3J_{HH} = 7$ Hz, $^3J_{HP} = 15$ Hz) and 1.50 ppm ($^3J_{HH} = 7$ Hz, $^3J_{HP} = 17$ Hz) respectively, shifted slightly from the free ligand value. The two methine protons give a doublet of septets at 3.33 ppm ($^3J_{HH} = 7$ Hz, $^2J_{HP} = 2$ Hz). A

similar multiplet is present at 2.14 ppm ($^3J_{HH}=7$ Hz, $^2J_{HP}=2$ Hz) in the free ligand indicating that the signal has moved downfield on coordination, but that the magnetic equivalence of the two protons is not affected by the bonding to rhenium. This is consistent with the isomer containing the *trans*-[O=Re–O] core, since the other isomers would contain non-equivalent isopropyl groups and, as a consequence, probably give split methine signals. The aromatic protons give rise to five multiplets in the 6.2–8.0 ppm range.

The ^{31}P NMR spectrum of $ReOCl(P\sim O)_2$ (**2**) consists of a pair of doublets (AB spin system) with signals centred at 34.0 and 41.6 ppm, and a $^2J_{PP}$ value of 213 Hz, consistent with two equivalent P atoms occupying *trans* positions in a 'twisted' octahedron (B, Scheme 1). The structure is different to that obtained for diphenylphosphinophenol complexes where the ^{31}P NMR showed two non-equivalent P atoms occupying *cis* positions in a 'twisted' octahedron (A, Scheme 1), as observed in the crystal structure of $ReOCl(Ph_2P\sim O)_2$ [8]. The *trans*-P,P structure is consistent with the ^{1}H NMR data which show the inequivalence of all the protons of the two ligands. The two methyl signals of each ligand, corresponding to 12H, are observed as doublets of doublets centred at 1.4 and 1.7 ppm, respectively, with $^3J_{HP}=17$ Hz and $^3J_{HH}=7$ Hz shifted slightly downfield from the values of 0.9 and 1.1 ppm found in the free ligand. Doublets of septets at 2.8 (1H), 3.0 (2H) and 3.4 (1H) ppm, with coupling constants $^2J_{HP}=1$ Hz and $^3J_{HH}=7$ Hz, are due to the four non-equivalent methine hydrogens that have moved downfield upon coordination, but they are not individually affected by the low symmetry of the complex. Eight multiplets between 6.3 and 7.5 ppm originate from the aromatic protons.

3.2.2. Rhenium(V) imido complexes

The phenylimido complexes **7**–**12** are stable in the solid state and in organic solvents where they are soluble (DMSO, DMF, CH_2Cl_2, $CHCl_3$, THF). The formula proposed is based on microanalyses and mass spectra (DCI/NH_3), in which the parent $[M+H]^+$ peaks and $[M-HX+H]^+$ peaks corresponding to halide loss are observed. The Re=NPh stretch of phenylimido-Re(V) complexes, difficult to detect in the IR because of overlapping ligand vibrations, is only clearly identified at 1025 cm^{-1} for **9**, in agreement with the literature [17].

The trends observed above for the oxo systems apply to the imido complexes as well. The ^{31}P NMR spectra of the $Re(NPh)X(P\sim O)_2$ complexes (X=Cl, (**8**); X=Br, (**10**); X=I, (**12**)) in $CDCl_3$ all contain doublets at ~31 and ~33 ppm with J_{PP} coupling constants of ~220 Hz, consistent with *trans*-P,P 'twisted' octahedral species. The $Re(NPh)X_2(PPh_3)(P\sim O)$ compounds **7**, **9** and **11** also adopt a *trans*-P,P structure, since their ^{31}P NMR spectra show doublets around −6 and 26 ppm ($^2J_{PP}$ of 246–260 Hz). By analogy with $ReOCl_2(PPh_3)(P\sim O)$, the peak at ~26 ppm is assigned to the P~O ligand on the basis of PPh_3 exchange. When pyridine is added to a solution of $Re(NPh)Br_2(PPh_3)(P\sim O)$, the doublets at −6 and 26 ppm are replaced by two singlets, one at −4 ppm for free PPh_3 and the other at 22 ppm for the new pyridine complex.

4. Concluding remarks

All Re(V) complexes prepared in this study contain phosphinophenolato ligands in the bidentate anionic $P\sim O^-$ form, with one phenolato oxygen atom *trans* to the multiple bond. It has been shown previously that the disubstituted $ReOX(Ph_2P\sim O)_2$ complexes with a *cis*-P,P 'twisted' octahedral structure were the only products isolated when 2 equiv. of $Ph_2P\sim OH$ were reacted on $ReOCl_3(PPh_3)_2$ in refluxing toluene. However, under the same conditions, $^iPr_2P\sim OH$ leads to monosubstituted $ReOX_2(PPh_3)(P\sim O)$ complexes, along with $ReOX(P\sim O)_2$. Therefore chelation of one P~OH ligand takes place easily but binding the second ligand is more difficult, observations that suggest that although P~OH is a stronger σ donor, its reactivity is hampered by its greater steric demand. The fact that the *trans*-P,P 'twisted' octahedral structure is favoured for all $ReOX(P\sim O)_2$ complexes indicates that the electronic effect is not the factor determining the stereochemistry of the complexes and, as a consequence, that the steric effect is important. The reaction of the phenylimido precursor with P~OH does not follow the same trends as the oxo precursor since both ligands give *trans*-P,P isomers. A possible explanation is that the imido phenyl group increases steric hindrance as a whole even for $Ph_2P\sim OH$.

Thus, the thermodynamic stability and the structural variety of the Re(V) complexes with P~O ligands, together with their presence as a single isomer, suggest that it is worth pursuing the development of these molecules as candidates for eventual applications as radiopharmaceuticals.

Acknowledgements

This work was supported by The Ministère Français de l'Enseignement Supérieur, de la Recherche et de la Technologie and the Centre National de la Recherche Scientifique (MD) which are gratefully acknowledged.

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