DALTON
FULL PAPER

Synthesis and characterization of novel phosphinoketone and phosphinoenolato rhenium(V) nitrido complexes. Crystal structure of $ReNCl_2\{^iPr_2PCH_2C(Ph){=}O\}_2$

Xavier Couillens,[a] **Marie Gressier,**[a] **Michèle Dartiguenave,***[a] **Sébastien Fortin**[b] **and André L. Beauchamp**[b]

[a] *Laboratoire de Chimie Inorganique, UA 870, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France. E-mail: dartigue@chimie.ups-tlse.fr*
[b] *Département de Chimie, Université de Montréal, C. P. 6128, Succ. Centre-ville, Montréal, QC, H3C 3J7, Canada*

Received 14th February 2002, Accepted 24th May 2002
First published as an Advance Article on the web 10th July 2002

Refluxing $ReNCl_2(PPh_3)_2$ with phosphinoketone ligands (P~C=O) of the type $R_2PCH(R')C(R'')$=O (R = phenyl, isopropyl; R′ = H, methyl; R″ = phenyl, *tert*-butyl) in toluene or ethanol yields selectively the octahedral nitridorhenium(V) complexes $ReN(PR_3)(P{\sim}O)_2$, where the P atoms of two deprotonated $P{\sim}O^-$ ligands occupy *cis* positions and an oxygen donor lies *trans* to the Re≡N bond. The sixth coordination site is filled by a monodentate phosphine, either PPh_3 or non-deprotonated P~C=O, depending on the metal-to-ligand ratio. When $^iPr_2PCH_2C(Ph)$=O is refluxed for 1 h (2/1 L/Re ratio), $ReNCl_2\{^iPr_2PCH_2C(Ph){=}O\}_2$ (**1**) precipitates as the only species. X-Ray diffraction shows that the Re(V) centre of **1** is six-coordinated with a distorted octahedral geometry, being bonded to the nitrido N atom, two *trans* chlorides, two *trans* P atoms and the oxygen of one of the phosphinoketones lying *trans* to the N^{3-} ligand. The short Re≡N bond (1.629(4) Å) and the long *trans* Re–O bond (2.466(5) Å) reflect the large *trans* influence of the nitrido ligand. The mono- and bi-dentate phosphinoketones in this compound are involved in an intramolecular interchange process.

Introduction

Rhenium(V) complexes are of interest because of the potential use of ^{186}Re in nuclear medicine and the chemical similarity of Re/Tc, largely used for the design of ^{99m}Tc radiopharmaceuticals.[1,2] As a consequence, an extensive literature on technetium(V) and rhenium(V) complexes with a variety of ligands is devoted to developing the "best" species, that is, the one combining the highest thermodynamic stability with the optimum kinetic inertness for medical applications.

Bidentate phosphinophenols (P~OH) have been observed to give stable neutral chiral Re-oxo and Re-imido complexes[3–9] which are of particular interest because both in the solid state and in solution, their linear O=Re–O or PhN=Re–O entities lead to stereochemical purity. The phosphinoenolato ligands studied in this paper belong to the same category of soft–hard P,O-donor chelating agents. They are readily generated *in situ* by α-deprotonation of the phosphinoketones with a base and we previously found that they lead to stable Re(V) oxo and phenylimido derivatives.[10,11] Although the $[Re{\equiv}N]^{2+}$ core is isoelectronic with $[ReO]^{3+}$ and $[ReNPh]^{3+}$, Re≡N complexes are not as common as their oxo counterparts. This has been ascribed mainly to the increased π-donor ability (greater *trans* influence) and steric hindrance of the nitrido ligand, but the reactions still remain poorly understood. For example, molecular $ReN(PPh_3)(P{\sim}O)_2$ species have been reported to form with diphenylphosphinophenolato ligands,[3] while no nitrido compounds could be obtained with 2-(diisopropylphosphino)phenol (different phosphine substituent) or 2-(diphenylphosphinomethyl)-4-methylphenol (formation of puckered six-membered metallacycles).

In a preliminary study, we noticed that 1-phenyl-2-(diphenylphosphino)ethanone behaved similarly toward the Re-oxo or -nitrido cores, giving molecular $ReOCl(P{\sim}O)_2$ and $ReN(PPh_3)(P{\sim}O)_2$ complexes, respectively.[10] In order to get more information on these nitrido compounds, we decided to investigate more thoroughly the reaction of phosphinoketones on $ReNCl_2(PPh_3)_2$.

In this paper, we report on the reaction of four phosphinoketones $R_2PCH(R')C(R'')$=O where various combinations of R (= Ph, ^{i}Pr), R′ (= H, Me) and R″ (= Ph, ^{t}Bu) introduce differences in the phosphine basicity and the keto group environment. Surprisingly, although the reaction of diphenylphosphinoketones gave mainly Re-nitrido complexes bearing ligands in the phosphinoenolato form, the diisopropyl derivative allowed us to isolate, as an intermediate, a Re(V)-nitrido complex in which the phosphinoketone is coordinated as a monodentate phosphine. To our knowledge, this $ReNCl_2(P{\sim}C{=}O)_2$ compound is the first Re(V) species including a hemilabile phosphinoketone ligand,[12] the only previous example in rhenium chemistry being the Re(I) complex $Re(CO)_3Br(PR_2{\sim}C{=}O)$.[13]

Experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. $ReNCl_2(PPh_3)_2$,[14] 1-phenyl-2-(diisopropylphosphino)ethanone ($P^1{\sim}C{=}O$),[15] 1-phenyl-2-(diphenylphosphino)ethanone ($P^2{\sim}C{=}O$),[16] 1-*tert*-butyl-2-(diphenylphosphino)ethanone ($P^3{\sim}C{=}O$),[17] 1-phenyl-2-(diphenylphosphino)propanone ($P^4{\sim}C{=}O$),[17] and $ReN(PPh_3)(P^2{\sim}O)_2$[10] (**4**) were prepared as described in the literature. Infrared spectra (4000–400 cm^{-1}) were recorded as KBr pellets on a Vector 22 Bruker spectrophotometer. ^{1}H NMR spectra were obtained at room temperature on Bruker AMX 400 and WM 250 instruments. The residual solvent signals (δ = 5.20 ppm for CD_2Cl_2 and 7.30 ppm for $CDCl_3$) were used as internal standards

DOI: 10.1039/b201632j

and the chemical shifts are reported with respect to Me_4Si. For the $^{31}P\{^1H\}$ NMR spectra, 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 R1010 spectrometer. Elemental analyses were carried out at the Laboratoire de Contrôle de l'Ecole Nationale Supérieure de Chimie de Toulouse.

Syntheses

$ReNCl_2(P^1{\sim}C{=}O)_2$ (1). To an orange suspension of 0.197 g (0.25 mmol) of $ReNCl_2(PPh_3)_2$ in 20 mL of toluene were added 0.29 g (1.24 mmol) of $P^1{\sim}C{=}O$ and 0.124 g (1.22 mmol) of NEt_3. The mixture was refluxed for 1 h until complete reaction of $ReNCl_2(PPh_3)_2$. Elimination of toluene *in vacuo* gave a brown–red solid, which was dissolved in ether (20 mL). The solution was filtered off and the solvent evaporated *in vacuo* to give red air-stable crystals of the 1/2 diethyl ether solvate. Yield: 66%. Anal. calc. for $C_{30}H_{47}Cl_2NO_{2.5}P_2Re$: C, 46.15; H, 6.07; N, 1.78. Found: C, 46.16; H, 6.22; N, 1.75%. IR (KBr, cm^{-1}): 1637, 1678 ν(C=O). MS FAB$^+$ (*m*/*z* (%)): 743.3 (75) $[M]^+$; 708.3 (78) $[M - HCl]^+$; 672.3 (73) $[M - 2HCl]^+$.

$ReN(PPh_3)(P^3{\sim}O)_2$ (5). The same method was used as described above for **1**, but the reaction was performed in ethanol and the solution was refluxed for 4 h: 0.504 g (0.65 mmol) of $ReNCl_2(PPh_3)_2$, 0.360 g (1.30 mmol) of $P^3{\sim}C{=}O$, 1.121 g (1.20 mmol) of NEt_3, 50 mL of ethanol. A red solid precipitated from the solution cooled to 0 °C. Yield: 30%. Anal. calc. for $C_{54}H_{55}NO_2P_3Re$: C, 63.02; H, 5.39; N, 1.36. Found: C, 62.73; H, 5.44; N, 1.32%. IR (KBr, cm^{-1}): 1520–1535 ν(C$\cdots$C$\cdots$O). MS DCI/NH_3 (*m*/*z* (%)): 1032 (2) $[M + H]^+$; 785 (100) $[M - PPh_3 + NH_4]^+$; 768 (19) $[M - PPh_3 + H]^+$.

$ReN(PPh_3)(P^4{\sim}O)_2$ (6). $ReNCl_2(PPh_3)_2$ (0.318 g, 0.40 mmol), $P^4{\sim}C{=}O$ (0.280 g, 0.88 mmol) and NEt_3 (0.089 g, 0.88 mmol) were refluxed in 40 mL of ethanol for 15 h. Filtration of the solution and addition of pentane (20 mL) at RT gave a yellow solid, which was filtered off, washed with ethanol and ether, and dried under reduced pressure. Yield: 58%. Anal. calc. for $C_{60}H_{51}NO_2P_3Re$: C, 65.62; H, 4.68; N, 1.28. Found: C, 64.78; H, 4.52; N, 1.22%. IR (KBr, cm^{-1}): 1524–1558 ν(C$\cdots$C$\cdots$O). MS electrospray (*m*/*z*): 1098 $[M + H]^+$; 836 $[M - PPh_3 + H]^+$.

$ReN(P^3{\sim}C{=}O)(P^3O)_2$ (7). $ReNCl_2(PPh_3)_2$ (0.208 g, 0.25 mmol), $P^3{\sim}C{=}O$ (0.21 g, 0.76 mmol) and NEt_3 (0.080 g, 0.80 mmol) were refluxed for 6 h in 20 mL of ethanol. Evaporation of the solvent *in vacuo* gave a light-yellow solid, which was dissolved in diethyl ether. The solution was filtered to eliminate the ammonium salt. Concentration of the solution gave a yellow product which was recrystallized from ether–pentane (1/1). Cooling the solution to −20 °C afforded a yellow microcrystalline solid. Yield: 61%. Anal. calc. for $C_{54}H_{61}NO_3P_3Re$: C, 61.70; H, 5.81; N, 1.33. Found: C, 61.82; H, 5.82; N, 1.27%. IR (KBr, cm^{-1}): 1706 ν(C=O); 1520–1535 ν(C$\cdots$C$\cdots$O). MS DCI/NH_3 (*m*/*z* (%)): 1052 (9) $[M + H]^+$; 785 (100) $[M - (P_3{\sim}C{=}O) + NH_4]^+$; 768 (37) $[M - (P_3{\sim}C{=}O) + H]^+$.

Crystallographic measurements and structure determination for 1

A red crystal of **1** was glued to a glass fiber and transferred rapidly under cold nitrogen to an Enraf-Nonius CAD-4 system equipped with a low-temperature gas-stream cryostat for data collection at 233 K. A preliminary search from an axial photograph yielded a reduced triclinic cell,[18] which actually corresponded to a primitive monoclinic cell. Laue symmetry and systematic absences were eventually checked from the full data set. Space group $P2_1/n$ was uniquely defined from the systematic absences. A whole sphere of data was collected, corrected for absorption,[19] and averaged to provide the basic two-octant set. Crystal data are provided in Table 1.

Table 1 Crystallographic data

Empirical formula	$C_{28}H_{42}Cl_2NO_2P_2Re\cdot 1/2C_4H_{10}O$
Formula weight	788.77
a/Å	18.786(10)
b/Å	9.637(6)
c/Å	19.444(17)
β/°	101.27(6)
V/Å^3	3452(4)
Z	4
Space group	$P2_1/n$ (no. 14)
T/K	233
λ/Å	1.54056 (CuKα)
Crystal size/mm	0.53 × 0.11 × 0.05
μ/mm^{-1}	9.398
$R1^a$ $(I > 2\sigma(I))$	0.0294
$wR2^b$ $(I > 2\sigma(I))$	0.0770
S^c	1.021

[a] $R1 = \Sigma(||F_o| - |F_c||/\Sigma(|F_o|)$; [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; [c] $S = [\Sigma[w(F_o^2 - F_c^2)^2]/(N_{\mathrm{reflns}} - N_{\mathrm{params}})]^{1/2}$.

The structure was solved by the heavy-atom method. The Re atom was located from a Patterson synthesis using SHELXS96[20] and the remaining non-hydrogen atoms from ΔF syntheses using SHELXL96.[21] The non-hydrogen atoms were refined anisotropically. Hydrogens were constrained to the parent site using a riding model and the default C–H distances (0.93–0.98 Å) of SHELXL96. Their isotropic thermal parameters were adjusted to 50% (methyl) or 20% (others) above the U_{eq} value of the supporting atom.

Diethyl ether solvent molecules were found to be disordered over two equally populated symmetry-equivalent orientations about the inversion centres at (1/2, 1/2, 0) and (0, 0, 1/2). The amount and the identity of the solvent (V_s = 213 Å^3 and 35 electrons per site) were confirmed from the SQUEEZE routine of the PLATON software.[22] The solvent was refined isotropically using SAME/SADI restraints to help convergence and its hydrogens were neglected. In the final ΔF map, two peaks of 1.1–1.3 e Å^3 were found within 1.1 Å of the rhenium atom, whereas the general background was below 0.60 e Å^3.

CCDC reference number 179587.

See http://www.rsc.org/suppdata/dt/b2/b201632j/ for crystallographic data in CIF or other electronic format.

Results and discussion

Reaction with $^iPr_2PCH_2C(Ph){=}O$ ($P^1{\sim}C{=}O$)

Refluxing $Re^VNCl_2(PPh_3)_2$ and a five-fold excess of $^iPr_2PCH_2C(Ph){=}O$ in toluene for 1 h, with or without NEt_3 base, produces immediately a brown solution from which a red–brown solid precipitates. Its microanalysis and mass spectrum correspond to $ReNCl_2(P^1{\sim}C{=}O)_2$ (**1**).

A triplet at 4.07 ppm in the ^1H NMR spectrum (Table 2), turning into a singlet after ^{31}P decoupling, results from the equivalent methylene protons coupled with the two P atoms ($^2J_{HP} = {}^4J_{HP}$ = 3.9 Hz), which must therefore be *trans* to one another.[23] Similarly, a triplet of heptets due to the four ^iPr methyne protons becomes a simple heptet in the decoupled spectrum. Thus, the room-temperature ^1H NMR data are consistent with a *trans*-P,P octahedral structure resulting from stereoselective substitution of the two PPh_3 by two equivalent $^iPr_2PCH_2C(Ph){=}O$ ligands behaving as monodentate phosphines.

At room temperature, the $^{31}P\{^1H\}$ NMR spectrum of **1** displays only one singlet at 34 ppm, indicating that the two P atoms are equivalent on the NMR time scale, in agreement with the ^1H NMR data. On cooling the sample to 181 K (Fig. 1), this resonance broadens, coalescence occurs at 223 K, and then a doublet of doublets (AB spin system) appears at 33 and 41 ppm. The $^2J_{PP}$ value of 197 Hz is consistent with two

Table 2 $^{31}P\{^1H\}$ and ^1H NMR spectral data of the $[Re{\equiv}N]^{2+}$ complexes

Complex	^{31}P/ppm (*J*/Hz)	^1H/ppm (*J*/Hz)
$ReNCl_2(P^1{\sim}C{=}O)_2$ (**1**)	[b]34.0	[b]1.40 (q, $^3J_{HH} = {}^3J_{HP} = {}^5J_{HP} = 7.2$, 12H, C$H_3$) 1.45 (q, $^3J_{HH} = {}^3J_{HP} = {}^5J_{HP} = 7.2$; 12H, C$H_3$) 3.06 (t hep, $^3J_{HH} = 7.2$, $^2J_{HP} = {}^4J_{HP} = 3.4$, 4H, PC$H$) 4.07 (t, $^2J_{HP} = {}^4J_{HP} = 3.9$, 4H, PC$H_2$) 7.48–8.03 (m, 10H, aromatic)
$ReN(PPh_3)(P^1{\sim}O)_2$ (**2**)	[a]20.9 (br) 23.7 (d, $^2J_{PP} = 204$) 46.0 (d, $^2J_{PP} = 204$)	
$ReN(P^1{\sim}C{=}O)(P^1{\sim}O)_2$ (**3**)	[a]21.0 (br) 28.4 (dd, $^2J_{PP} = 207$, $^2J_{PP} = 7$, PPh_3) 44.1 (dd, 207, 10)	
$ReN(PPh_3)(P^2{\sim}O)_2$ (**4**)[10]	[b]12.3 (dd, $^2J_{PP} = 13$, $^2J_{PP} = 10$) 27.2 (dd, $^2J_{PP} = 210$, $^2J_{PP} = 13$, PPh_3) 35.5 (dd, $^2J_{PP} = 210$, $^2J_{PP} = 10$)	[b]4.89 (d, $^2J_{HP} = 3.0$, 1H, CH) 4.95 (d, $^2J_{HP} = 2{,}0$ Hz, 1H, CH) 6.28–8.14 (m, 45 H, aromatic)
$ReN(PPh_3)(P^3{\sim}O)_2$ (**5**)	[a]11.6 (br) 21.6 (dd, $^2J_{PP} = 218$, $^2J_{PP} = 11$, PPh_3) 31.3 (dd, $^2J_{PP} = 218$, $^2J_{PP} = 11$)	[a]0.31 (s, 9H, CH_3) 0.89 (s, 9H, CH_3) 4.20 (d, $^2J_{HP} = 3.2$, 1H, CH) 4.52 (d, $^2J_{HP} = 4.2$, 1H, CH) 6.77–7.62 (m, 35 H, aromatic)
$ReN(PPh_3)(P^4{\sim}O)_2$ (**6**)	[a]26.5 (dd, $^2J_{PP} = 218$, $^2J_{PP} = 11$; PPh_3) 29.7 (br) 47.3 (dd, $^2J_{PP} = 218$, $^2J_{PP} = 11$)	[b]1.45 (d, $^3J_{HP} = 9$, 3H, CH_3) 1.59 (d, $^3J_{HP} = 9$; 3H, CH_3) 6.61–8.20 (m, 45 H, aromatic)
$ReN(P^3{\sim}C{=}O)(P^3{\sim}O)_2$ (**7**)	[a]12.3 (br) 16.3 (dd, $^2J_{PP} = 220$, $^2J_{PP} = 11$; $P_3{\sim}C{=}O$) 32.8 (dd, $^2J_{PP} = 220$, $^2J_{PP} = 11$)	[a]0.63 (s, 9H, CH_3); 0.71 (s, 9H, CH_3); 1.19 (s, 9H, CH_3) 2.39 (dd, $^2J_{HH} = 16.8$, $^2J_{HP} = 9.8$, 1H, CH) 3.66 (dd, $^2J_{HH} = 16.8$, $^2J_{HP} = 2.8$, 1H, CH) 4.53 (d, $^2J_{HP} = 2.9$, 1H, CH) 4.69 (d, $^2J_{HP} = 4.0$, 1H, CH) 6.9–8.3 (m, 30 H, aromatic)

[a] $CDCl_3$; [b] CD_2Cl_2.

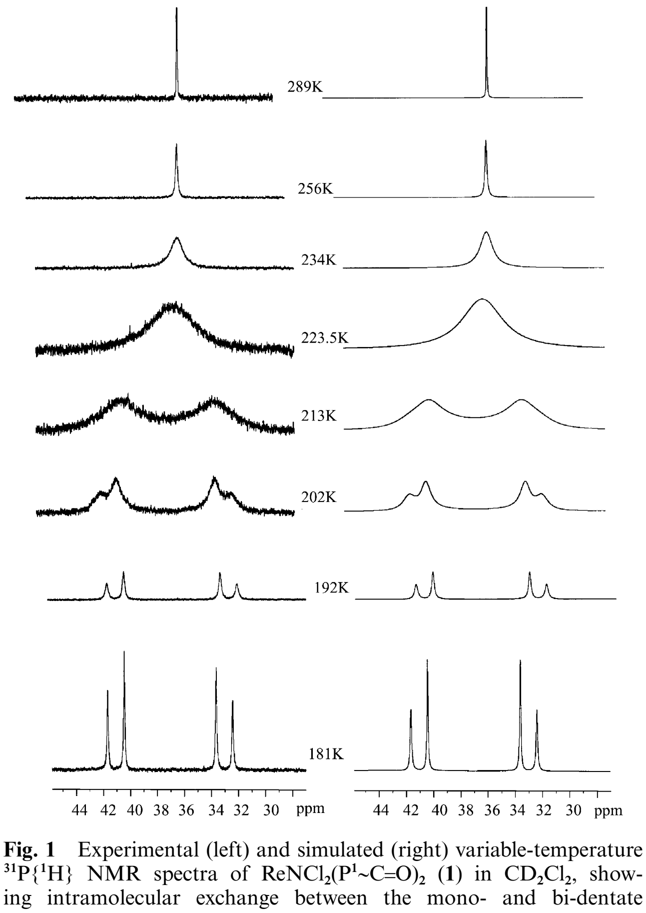
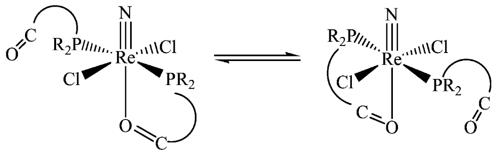


Fig. 1 Experimental (left) and simulated (right) variable-temperature $^{31}P\{^1H\}$ NMR spectra of $ReNCl_2(P^1{\sim}C{=}O)_2$ (**1**) in CD_2Cl_2, showing intramolecular exchange between the mono- and bi-dentate phosphinoketones.

mutually *trans* P atoms in a penta- or hexa-coordinate Re(v) complex.[8,11] The $\Delta G^*_{223\ K}$ value of 41 kJ mol^{-1} lies within the range observed for fast intramolecular exchange between two inequivalent neutral oxygen-donor groups competing for a common coordination site in octahedral complexes (Scheme 1).[24–26]

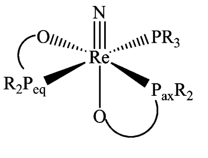


Scheme 1

Inequivalence of the two ligands in the solid state is evidenced from IR spectroscopy, where two *ν*(CO) frequencies at 1678 and 1637 cm^{-1} are found for the uncoordinated and the pseudo-coordinated keto groups, respectively (1672 cm^{-1} in the free ligand). A definite proof is provided by the X-ray diffraction study (see below).

By increasing the refluxing time to 4 h, the coordinated ligands deprotonate, giving the bis(enolato) complexes $ReN(PPh_3)(P^1{\sim}O)_2$ (**2**) or $ReN(P^1{\sim}C{=}O)(P^1{\sim}O)_2$ (**3**) depending on the ligand-to-metal ratio. A large ligand excess (L/Re ≈ 5) gives **3** as the only species. We notice, in these cases, the presence the phosphonium cation $[HP^1{\sim}C{=}O]^+$ signal in the $^{31}P\{^1H\}$ NMR spectra (δ = 54 ppm), which indicates that the basic $P^1{\sim}C{=}O$ ligand competes with NEt_3 for proton scavenging.

The characteristic ABX patterns observed in the $^{31}P\{^1H\}$ spectra of **2** and **3** (Table 1) are consistent with the ligands in the enolato form giving "twisted" *cis*-P,P octahedral Re(v) complexes[10] (Scheme 2). The downfield signal (46.0 ppm for **2**, 44.1 ppm for **3**) is assigned to the enolate ligand perpendicular to the Re≡N bond (P_{eq}), whereas the other enolate in a plane parallel to the Re≡N bond (P_{ax}) gives the 21 ppm signal. The small $^2J_{PP}$ values (≈0) indicate that these two P atoms occupy *cis*



Scheme 2

positions. Therefore, the monodentate phosphines (PPh_3 in **2**, $^iPr_2PCH_2C(Ph){=}O$ in **3**) are located *trans* to P_{eq}.

Thus, the first step of the reaction involves stereoselective phosphine substitution. Activation of one keto oxygen then takes place, followed, in basic media, by intramolecular deprotonation of the keto function to give complexes **2** and **3**. It occurs with stereochemical rearrangement of the Re-P bonds, the two P atoms being located *trans* to each other in **1** and *cis* in **2**,**3**. This is related to the electronic properties of the electrophilic d^2 rhenium centre, which takes optimum advantage of its bonding capability with $P{\sim}O^-$ ligands when these ligands adopt the "twisted" *cis*-P,P configuration.[11]

Reactions with $Ph_2PCH_2C(Ph){=}O$ ($P^2{\sim}C{=}O$), $Ph_2PCH_2C(^tBu){=}O$ ($P^3{\sim}C{=}O$) and $Ph_2PCH(Me)C(Ph){=}O$ ($P^4{\sim}C{=}O$)

Refluxing $ReNCl_2(PPh_3)_2$ with $P^2{\sim}C{=}O$, $P^3{\sim}C{=}O$ or $P^4{\sim}C{=}O$ (1/2 ratio) in basic (NEt_3) ethanol gives $ReN(PPh_3)(P{\sim}O)_2$ (**4**, **5**, **6**) as single species. The $^{31}P\{^1H\}$ NMR spectra display the characteristic ABX pattern of twisted *cis*-P,P octahedral Re(V) complexes, PPh_3 sitting *trans* to P_{eq}, as observed in the previously reported crystal structure of **4**.[10] The enolato entity gives rise to the typical IR ν(C$\overset{\cdots}{-}$C$\overset{\cdots}{-}$O) stretch in the 1520–1540 cm^{-1} range, whereas the inequivalence of the enolato ligands is detected from the two individual doublets for the ethylene protons (in **4** and **5**) or methyl substituents (in **6**).

In all complexes, PPh_3 is replaced by a $P{\sim}C{=}O$ ligand when the reaction is performed with excess ligand, thereby indicating the lability of this coordination site. As an example, $ReN(P^3{\sim}C{=}O)(P^3{\sim}O)_2$ (**7**) was isolated as a yellow solid by using three equivalents of ligand. The presence of both monodentate phosphinoketone and bidentate phosphinoenolato is confirmed by the IR spectrum, which shows bands for ν(C=O) at 1706 cm^{-1} and for ν(C$\overset{\cdots}{-}$C$\overset{\cdots}{-}$O) in the 1520–1535 cm^{-1} range. In addition, the ^1H NMR spectrum includes three signals (1/1/1 ratio) for the ^tBu methyl protons, doublets at 4.53 and 4.69 ppm for the two inequivalent ethylene hydrogens of the enolato groups, respectively, and two signals for the diastereotopic methylene protons of the phosphinoketone. The ^{31}P NMR spectrum exhibits the expected ABX spin system, the main difference with respect to complex **5** being the doublet of doublets for the monodentate phosphine ligand, which shifts from 21.6 ppm in **5** (PPh_3) to 16.3 ppm in **7** ($P^3{\sim}C{=}O$).

Complexes **4**–**7** are stable both in the solid state and in solution for extended periods of time.

Crystal structure of $ReNCl_2(P^1{\sim}C{=}O)_2$ (1)

The structure consists of discrete monomers (Fig. 2) separated by normal van der Waals contacts. The Re atom shows a highly distorted octahedral geometry, being bonded to one nitrido ligand, two *trans* chlorides, two *trans* phosphorus atoms from non-deprotonated phosphinoketones and the keto oxygen O1 of one of these ligands. Selected interatomic distances and bond angles are listed in Table 3.

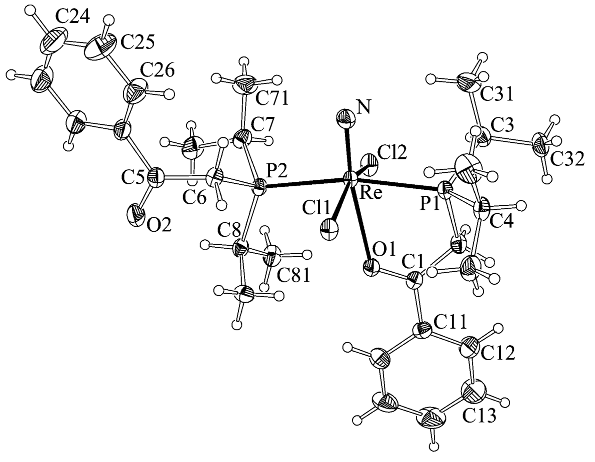


Fig. 2 ORTEP[35] drawing of **1**. Ellipsoids correspond to 40% probability.

Table 3 Selected bond lengths (Å) and angles (°)

Re–N	1.629(4)	O(1)–C(1)	1.226(5)
Re–Cl(1)	2.411(2)	C(1)–C(2)	1.509(6)
Re–Cl(2)	2.433(2)	C(2)–P(1)	1.840(5)
Re–P(1)	2.438(2)	O(2)–C(5)	1.206(6)
Re–P(2)	2.458(2)	C(5)–C(6)	1.506(6)
Re–O(1)	2.466(5)	C(6)–P(2)	1.839(5)
N–Re–Cl(1)	100.2(2)	O(1)–C(1)–C(2)	119.9(4)
N–Re–Cl(2)	101.5(2)	C(1)–C(2)–P(1)	111.8(3)
N–Re–P(1)	98.6(2)	C(2)–P(1)–Re	104.8(2)
N–Re–P(2)	95.4(2)	O(2)–C(5)–C(6)	121.0(5)
N–Re–O(1)	171.1(2)	C(5)–C(6)–P(2)	117.4(4)
O(1)–Re–Cl(1)	79.26(9)	C(6)–P(2)–Re	109.5(2)
O(1)–Re–Cl(2)	79.65(10)	C(3)–P(1)–Re	114.1(2)
O(1)–Re–P(1)	72.73(9)	C(4)–P(1)–Re	122.8(2)
O(1)–Re–P(2)	93.42(9)	C(2)–P(1)–C(3)	102.1(2)
Cl(1)–Re–Cl(2)	158.21(5)	C(2)–P(1)–C(4)	103.5(3)
Cl(1)–Re–P(1)	94.58(7)	C(3)–P(1)–C(4)	106.9(2)
Cl(1)–Re–P(2)	87.61(7)	C(7)–P(2)–Re	112.3(2)
Cl(2)–Re–P(1)	84.32(7)	C(8)–P(2)–Re	116.7(2)
Cl(2)–Re–P(2)	88.25(7)	C(6)–P(2)–C(7)	106.3(2)
P(1)–Re–P(2)	165.24(6)	C(6)–P(2)–C(8)	105.9(2)
Re–O(1)–C(1)	123.1(3)	C(7)–P(2)–C(8)	105.5(2)

The Re–N distance of 1.629(4) Å is the shortest ever reported for a six-coordinate nitrido complex (range 1.641–1.788 Å; mean 1.679 Å, 17 crystal structures).[27] Even when compared with five-coordinate compounds, this bond length lies on the low side of the observed range (1.602–1.663 Å, mean 1.640 Å, 12 structures). Therefore, not only does the rhenium–nitrogen bond show considerable triple-bond character,[28] but it seems not to be greatly affected electronically by the presence of the *trans* oxygen. There is evidence, however, that significant Re–O bonding takes place. The C1–O1 bond (1.226(5) Å) exhibits a significant lengthening compared with the C5–O2 bond (1.206(6) Å) in the free keto group of the other ligand. The Re–O1 bond (2.466(5) Å) is much longer than the one formed by the *trans* enolate oxygen in **4** (2.221(5) Å),[10] but still of reasonable length, considering that the Re≡N unit exerts a strong *trans* influence and that a carbonyl group is a much poorer donor than a formally anionic oxygen. In fact, bond lengths similar to ours have been observed in nitrido-Re(V) or -Tc(V) complexes for *trans* bonds with water (2.463 Å in $[ReN(CN)_4(H_2O)]^{2-}$,[29] 2.688(4) Å in $TcNL(H_2O)$, where L = 1,4,8,11-tetraazacyclotetradecane-5,7-dione,[30] 2.481(4) Å in $[TcN(pnao)(H_2O)](BPh_4)$, where $pnao^-$ = 3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioximate[31]) or the poorly-coordinating triflate oxygen in $ReNCl(PMe_2Ph)_3(O_3SF)$ (2.403 Å).[32] The Re–P2 distance (2.458(2) Å) for the monodentate phosphinoketone is greater than that of the chelated ligand (2.438(2) Å), but both do not differ greatly from those found for the related enolate chelates.[9,11] The Re–Cl distances are intermediate between those observed in the five-coordinate $ReNCl_2(PPh_3)_2$[33] and in the six-coordinate $ReNCl_2(PMe_2Ph)_3$ compounds.[34]

As commonly found in such systems, the Re≡N bond repels the adjacent ligands, so that the metal is displaced 0.38 Å from the Cl_2P_2 plane, on the nitrido side. The N–Re–(P,Cl) angles range from 95.4(2) to 101.5(2)°, whereas the O1–Re–Cl angles are reduced to ≈79.3°. The five-membered chelate ring imposes an O1–Re–P1 angle of 72.7(1)° and makes the N≡Re–O1 unit slightly non-linear (171.1(2)°). The small O1–Re–P1 angle is balanced by a large O1–Re–P2 angle of 93.4(1)° with the *trans* phosphine donor.

Thus, the main structural difference between **1** and the bis(enolato) complex $ReN(PPh_3)(P^2{\sim}O)_2$[10] lies in the N≡Re–O entity, which becomes definitely non-linear here, whereas the covalent Re-O1 bond in $ReN(PPh_3)(Ph_2P{\sim}O)_2$ leads to a decrease of the Re–O1 distance from 2.466(5) Å to 2.211(5) Å with a concomitant increase of the Re≡N bond length from 1.629(1) Å in **1** to 1.683(2) Å.

Concluding comments

The four phosphinoketone ligands studied here bind readily to the Re≡N-containing precursor regardless of the substituents present. Initial attack by the P atom of the non-deprotonated phosphinoketone leads to simple substitution of the PPh_3 ligands. This intermediate is isolated with the isopropyl-substituted phosphine, but the diphenylphosphino ligands give immediately the stable phosphinoenolato complexes as the single product. Interestingly, even though changing the substituents on the keto group had a determining effect on reactivity for the oxo and imido-rhenium systems, no appreciable influence is noted here and all ligands retain good coordinative ability towards the nitrido-rhenium precursor.

Acknowledgements

We are grateful to the French Ministère de l'Éducation Nationale, de la Recherche et de la Technologie and the Natural Sciences and Engineering Research Council of Canada for financial support.

References

1 J. R. Dilworth and S. Parrott, *Chem. Soc. Rev.*, 1998, **27**, 43.
2 K. Hashimoto and K. Yoshihara, *Top. Curr. Chem.*, 1996, **176**, 275.
3 H. Luo, I. Setyawati, S. J. Rettig and C. Orvig, *Inorg. Chem.*, 1995, **34**, 2287.
4 F. Loiseau, Y. Lucchese, M. Dartiguenave, F. Bélanger-Gariépy and A. L. Beauchamp, *Acta Crystallogr., Sect. C*, 1996, **52**, 1968.
5 C. Bolzati, F. Tisato, F. Refosco, G. Bandoli and A. Dolmella, *Inorg. Chem.*, 1996, **35**, 6221.
6 C. Bolzati, F. Tisato, F. Refosco and G. Bandoli, *Inorg. Chim. Acta*, 1996, **247**, 125.
7 C. Bolzati, F. Refosco, F. Tisato, G. Bandoli and A. Dolmella, *Inorg. Chim. Acta*, 1992, **201**, 7.
8 F. Loiseau, Y. Lucchese, M. Dartiguenave and Y. Coulais, *Polyhedron*, 2000, **19**, 1111.
9 F. Connac, Y. Lucchese, M. Gressier, M. Dartiguenave and A. L. Beauchamp, *Inorg. Chim. Acta*, 2000, **304**, 52.
10 F. Connac, Y. Lucchese, M. Dartiguenave and A. L. Beauchamp, *Inorg. Chem.*, 1997, **36**, 256.
11 X. Couillens, M. Gressier, R. Turpin, M. Dartiguenave, Y. Coulais and A. L. Beauchamp, *J. Chem. Soc., Dalton Trans.*, 2002, 914.
12 (*a*) A. Bader and E. Lindner, *Coord. Chem. Rev.*, 1991, **108**, 27; (*b*) E. Lindner, S. Meyer, P. Wegner, B. Kaile, A. Sickinger and B. Steger, *J. Organomet. Chem.*, 1987, **335**, 59; (*c*) R. W. Wegman, A. G. Abatjoglou and A. M. Harrison, *J. Chem. Soc., Chem. Commun.*, 1987, 1891.
13 P. Braunstein, L. Douce, F. Balegroune, D. Grandjean, D. Bayeul, Y. Dusausoy and P. Zanello, *New. J. Chem.*, 1992, **16**, 925.
14 P. Sullivan, J. Brewer and H. B. Gray, *Inorg. Synth.*, 1992, **29**, 146.
15 P. Braunstein, Y. Chauvin, J. Nähring, A. DeCian, J. Fischer, A. Tiripicchio and F. Ugozzoli, *Organometallics*, 1996, **15**, 5551.
16 S. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.*, 1986, **25**, 3765.
17 B. Demerseman, B. Guilbert, C. Renouard, M. Gonzalez, P. H. Dixneuf, D. Masi and C. Mealli, *Organometallics*, 1993, **12**, 3906.
18 Enraf-Nonius CAD-4 Software, Version 5, Enraf-Nonius, Delft, The Netherlands, 1989.
19 E. J. Gabe, Y. LePage, J. P. Charland, F. L. Lee and P. S. White, *J. Appl. Crystallogr.*, 1989, **22**, 384.
20 G. M. Sheldrick, SHELXS96, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1990.
21 G. M. Sheldrick, SHELXL96, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1996.
22 A. L. Spek, PLATON, Molecular Geometry Program, July 1995 version, University of Utrecht, Utrecht, The Netherlands, 1995.
23 D. A. Redfield and J. H. Nelson, *Inorg. Chem.*, 1973, **12**, 15; A. W. Verstuyft, D. A. Redfield, L. W. Cary and J. H. Nelson, *Inorg. Chem.*, 1977, **16**, 2776.
24 P. Braunstein, D. Matt, F. Mathey and D. Thavard, *J. Chem. Res. (S)*, 1978, 232.
25 N. W. Alcock, A. W. G. Platt and P. Pringle, *J. Chem. Soc., Dalton Trans.*, 1987, 2273.
26 E. Lindner and U. Schober, *Inorg. Chem.*, 1988, **27**, 212.
27 Cambridge Structural Database, Cambridge University, Cambridge, England, Oct. 2001 release.
28 W. A. Nugent and J. M. Mayer, *Metal-Ligand Multiple Bonds*, Wiley, New York, 1988.
29 J. F. Britten, C. J. L. Lock and Yi. Wei, *Acta Crystallogr., Sect. C*, 1993, **49**, 1277.
30 A. Marchi, R. Rossi, L. Magon, A. Duatti, U. Casellato, R. Graziani, M. Vidal and F. Riche, *J. Chem. Soc., Dalton Trans.*, 1990, 1935.
31 Y. Kani, T. Takayama, T. Sekine and H. Kudo, *J. Chem. Soc., Dalton Trans.*, 1999, 209.
32 U. Abram and I. Walker, *Acta Crystallogr., Sect. C*, 1995, **51**, 1250.
33 R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 1967, 204.
34 E. Forsellini, U. Casellato, R. Graziani and L. Magon, *Acta Crystallogr., Sect. B*, 1982, **38**, 3081.
35 M. N. Burnett and C. K. Johnson, ORTEP3, Report ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, 1996.