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Reactions of Rhenium(V) Oxo and Nitrido Complexes with 1-Phenyl-2-(diphenylphosphino)ethanone (P⌒OH). Synthesis and Crystal Structure of ReOCl(P⌒O)$_2$ and ReN(PPh$_3$)(P⌒O)$_2$

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Introduction

Increasing interest has been devoted in the last decade to the behavior of chelating ligands combining soft (P) and hard (O, N) donors in the synthesis of metal complexes potentially active in catalytic processes.[2] Ligands of this type have also proved to be efficient chelating agents in stabilizing Re and Tc complexes of intermediate to high oxidation states, via the synergistic effect of the σ-bonding ability of phosphorus and the oxophilic character of the M(V) center.[3−6]

These features were recently illustrated with (2-hydroxyphenyl)diphenylphosphine, for which ReOClL$_2$ and ReN(PPh$_3$)L$_2$ complexes were prepared.[5] For the oxo compound, spectroscopic results indicated a *cis*-P,P configuration, which we have confirmed by an X-ray diffraction study.[6] In the case of ReN(PPh$_3$)L$_2$, a *mer*-P,P,P arrangement was proposed, with the P donors of the chelating ligands occupying mutually *trans* sites. However, this structure was not confirmed by crystallographic work, and the presence of chelate rings differently arranged in these two complexes remains unexplained. The only other pair of structurally characterized Re═O and Re≡N complexes, that is, the six-coordinated ReOCl$_3$(PPh$_3$)$_2$ and the five-coordinated ReNCl$_2$(PPh$_3$)$_2$ compounds,[7,8] do not cast more light on this question, since the phosphine is monodentate and the molecules have different coordination numbers.

As part of our ongoing studies on the ability of bidentate P⌒O ligands to form stable Re(V) complexes, we examined the reaction of the less sterically demanding bidentate ligand 1-phenyl-2-(diphenylphosphino)ethanone[9] (P⌒OH).[10] We wish to report here the synthesis of the novel complexes ReOCl(P⌒O)$_2$ (**1**) and ReN(PPh$_3$)(P⌒O)$_2$ (**2**), and their characterization by NMR and single-crystal X-ray diffraction.

Experimental Section

Reagents and Physical Measurements. All reactions were carried out in an atmosphere of nitrogen using standard Schlenk techniques. Ether, THF, and toluene were dried over sodium benzophenone ketyl and distilled prior to use. Ethanol was distilled on molecular sieves (3 Å). ReOCl$_3$(PPh$_3$)$_2$,[11] ReNCl$_2$(PPh$_3$)$_2$,[12] (AsPh$_4$)[ReOCl$_4$]·EtOH,[13] and 1-phenyl-2-(diphenylphosphino)ethanone[9] were prepared by literature methods.

Infrared spectra (4000−400 cm^{-1}) were recorded as KBr pellets on a Perkin-Elmer 1600 spectrometer. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at room temperature in CDCl$_3$ for **1** and CD$_2$Cl$_2$ for **2** on a Varian VXR-300 spectrometer. For ^{1}H NMR, the residual solvent signal ($\delta = 7.30$ ppm for CDCl$_3$ and 5.30 ppm for CD$_2$Cl$_2$) was used as internal standard, and the chemical shifts are reported with respect to Me$_4$Si. For ^{31}P{^{1}H} NMR, the external standard was H$_3$PO$_4$ (82% D$_2$O). Mass spectrometric data were obtained with a NERVAGR 10-10H spectrometer (DCI/NH$_3$ for **1** and FAB MNBA for **2**). Elemental analyses were carried out at the Laboratoire de Chimie de Coordination du CNRS, Toulouse, France.

Preparative Work. Chloro(oxo)bis[1-phenyl-2-(diphenylphosphino)ethenolato]rhenium(V) (1). To a solution of 0.46 g (0.60 mmol) of (AsPh$_4$)[ReOCl$_4$]·EtOH in hot EtOH (40 mL) was added 0.36 g (1.2 mmol) of ligand. The resulting solution was refluxed for 3 h. The green solid was filtered and dried in vacuo. Yield: 68%. Recrystallization from CHCl$_3$ afforded green crystals soluble in acetone, CH$_2$Cl$_2$, CHCl$_3$, and THF but insoluble in ethanol, ether, water, and toluene. Anal. Calcd (found) for C$_{40}$H$_{32}$ClO$_3$P$_2$Re: C 56.90 (56.66); H 3.82 (3.97). *m/z* = 845 (M + 1).

The same compound was obtained by adding the ligand (0.73 g, 2.4 mmol) to 1.00 g (1.2 mmol) of ReOCl$_3$(PPh$_3$)$_2$ and 0.25 g (2.5 mmol) of NEt$_3$ in ethanol (50 mL). The mixture was refluxed for 1 h. The green powder was filtered and dried. Yield: 42%

Nitridobis[1-phenyl-2-(diphenylphosphino)ethenolato]-(triphenylphosphine)rhenium(V) (2). A mixture of 0.15 g (0.19 mmol) of ReNCl$_2$(PPh$_3$)$_2$, 0.13 g (0.40 mmol) of ligand, and 0.053 g (0.50 mmol) of NEt$_3$ was stirred for 18 h in 50 mL of boiling ethanol. The yellow solid was filtered, washed with ether, and dried *in vacuo.* Yield: 50%. Anal. Calcd (found) for C$_{58}$H$_{47}$NO$_2$P$_3$Re: C 65.16 (65.21); H 4.43 (4.37); N 1.31 (1.25). *m/z* = 1070. **2** is soluble in CH$_2$Cl$_2$ and CHCl$_3$ but insoluble in ethanol, toluene, and ether. Recrystallization from CH$_2$Cl$_2$ gave yellow crystals of the disolvate, suitable for X-ray work.

Crystallographic Work. X-ray data for both compounds were collected in the open air with an Enraf-Nonius CAD-4 diffractometer. Cell parameters and other crystallographic data are listed in Table 1. The measured intensities were corrected for the effects of Lorentz, polarization and absorption (Gaussian integration, NRCVAX).[14]

For ReOCl(P⌒O)$_2$, the Niggli parameters of the reduced cell were not consistent with any symmetry higher than triclinic. The structure solved and refined normally in the centric $P\bar{1}$ space group. The Re atom was located by the direct methods of SHELXS-86.[15] All other non-hydrogen atoms were then found from structure-factor and ΔF-map calculations with the NRCVAX package.[14] Refinement was done by full-matrix least-squares procedures, the function minimized being $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/[\sigma^2(F_o) + (0.0001F_o)^2]$. In the final ΔF map, residual electron density of $\pm|2.2|$ e/Å^3 remained near Re atoms. The general background was below ±0.6 e/Å^3.

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Table 1. Crystal Data

	$\mathrm{ReOCl(P{}^\frown O)_2}$ (**1**)	$\mathrm{ReN(PPh_3)(P{}^\frown O)_2 \cdot 2CH_2Cl_2}$ (**2**)
formula	$\mathrm{C_{40}H_{32}ClO_3P_2Re}$	$\mathrm{C_{60}H_{51}Cl_4NO_2P_3Re}$
fw	844.29	1239.01
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	11.306(3)	15.779(6)
b, Å	12.084(2)	12.328(4)
c, Å	15.390(3)	27.839(13)
α, deg	105.01(2)	90.0
β, deg	93.98(2)	98.08(3)
γ, deg	116.30(2)	90.0
V, Å^3	1779.0(7)	5362(4)
Z	2	4
T, K	278(2)	220(2)
D_{calcd}, g/cm^3	1.576	1.535
F(000)	836	2488
radiation	Cu Kα	Cu Kα
λ, Å	1.54056	1.54056
μ, mm^{-1}	8.29	7.36
no. of reflcs measd	13262	37947
no. of independent reflcns	6736	10143
no. of obsd reflcns	5650	6574
rejection criterion, $I/\sigma(I)$	3.0	2.0
R[a]	0.046	0.065
weighted R	0.051[b]	0.155[c]
goodness-of-fit ratio S,[d]	1.90	0.908

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [d] $S = [\sum w||F_o| - |F_c||^2/(\text{no. of reflcns - no. of params})]^{1/2}$.

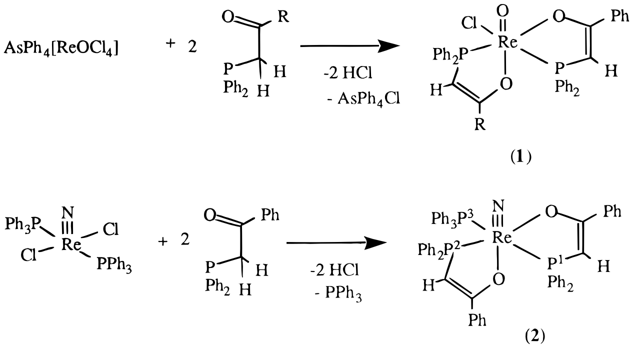
For $\mathrm{ReN(PPh_3)(P{}^\frown O)_2 \cdot 2CH_2Cl_2}$, space group $P2_1/c$ was unambiguously established from Laue symmetry and systematic absences. The Re atom was positioned by the direct methods of SHELXS-86[15] and the remaining atoms were found from ΔF syntheses calculated with SHELXL-93,[16] which was also used for refinement by full-matrix least-squares procedures. The function minimized was $\sum w(F_o^2 - F_c^2)^2$, the weights being calculated from $w = 1/[\sigma^2(F_o^2) + (0.0884P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. The asymmetric unit was found to contain two lattice $\mathrm{CH_2Cl_2}$ molecules: Cl1−C5−Cl2 was ordered, but Cl3−C6−Cl4 was disordered over two equally populated orientations. The Cl3 site was common to both orientations, whereas resolved positions were found for C6/C6′ and Cl4/Cl4′. To refine these fractional atoms, constraints were imposed on the C−Cl and Cl−Cl separations, a common occupancy factor and a common temperature factor were refined for each individual (C6/Cl4 and C6′/Cl4′), and the sum of occupancies was normalized to unity. All other non-hydrogen atoms were independently refined anisotropically. Hydrogens were fixed at idealized positions. In the final ΔF map, residual electron density of $\pm|1.5-2.3|$ e/Å^3 remained near the Re and the solvent Cl atoms. The general background was below ±0.8 e/Å^3.

Full lists of atomic coordinates and thermal parameters for both structures are given in the supporting information. Those of the atoms in the coordination sphere are listed in Table 2.

Table 2. Refined Coordinates and Isotropic Temperature Factors for the Atoms in the Coordination Sphere

atom	x	y	z	B_{eq}
		$\mathrm{ReOCl(P{}^\frown O)_2}$ (**1**)		
Re	0.36513(3)	0.75462(3)	0.32022(2)	3.40(2)
Cl	0.5012(2)	0.6589(3)	0.3513(2)	6.65(16)
P1	0.2242(2)	0.8116(2)	0.2338(1)	3.25(9)
P2	0.2153(2)	0.6749(2)	0.4216(1)	3.59(10)
O1	0.4482(4)	0.7580(5)	0.2107(3)	3.8(3)
O2	0.2224(4)	0.5728(4)	0.2373(3)	3.5(2)
O3	0.4506(5)	0.9010(5)	0.4032(3)	5.1(3)
C1	0.3987(6)	0.7773(6)	0.1371(4)	3.4(4)
C2	0.2923(7)	0.7998(7)	0.1329(4)	3.7(4)
C3	0.1195(6)	0.4888(6)	0.2623(4)	3.5(4)
C4	0.0948(7)	0.5217(7)	0.3474(5)	4.0(4)
		$\mathrm{ReN(PPh_3)(P{}^\frown O)_2}$ (**2**)		
Re	0.70314(2)	0.35504(3)	0.136259(13)	2.002(12)
P1	0.69834(13)	0.3296(2)	0.04875(8)	2.44(5)
P2	0.70623(14)	0.1673(2)	0.15796(8)	2.69(5)
P3	0.75161(13)	0.4328(2)	0.21682(7)	2.34(4)
O1	0.7521(4)	0.5031(4)	0.1175(2)	2.35(12)
O2	0.8381(3)	0.3079(5)	0.1330(2)	2.58(12)
N	0.5974(5)	0.3649(6)	0.1386(2)	2.9(2)
C1	0.7698(5)	0.5234(7)	0.0726(3)	2.5(2)
C2	0.7506(5)	0.4522(7)	0.0357(3)	2.5(2)
C3	0.8656(5)	0.2103(7)	0.1445(3)	2.6(2)
C4	0.8141(5)	0.1316(7)	0.1602(3)	3.0(2)

Scheme 1



Results and Discussion

The reaction of 2 equivalents of 1-phenyl-2-(diphenylphosphino)ethanone ($\mathrm{P{}^\frown OH}$) with $\mathrm{(AsPh_4)[ReOCl_4]}$ in hot ethanol produced **1** as a green precipitate in 68% yield (Scheme 1). This compound was also obtained with a similar yield from $\mathrm{ReOCl_3(PPh_3)_2}$ in presence of $\mathrm{NEt_3}$. In the IR spectrum, **1** displayed a strong band at 973 cm^{-1}, typical of terminal Re═O stretching.[17] The same reaction with $\mathrm{ReNCl_2(PPh_3)_2}$ gave a yellow solid **2** in 50% yield. As usual, the ν(Re≡N) vibration could not be identified in the IR spectra, because vibrations of phenyl groups interfere.

The structures of **1** and **2** in solution were deduced from NMR data. The ^{1}H spectrum of **1** exhibits phenyl multiplets centered at 7.5 ppm, as well as two doublets at 5.5 ppm and 5.2 ppm with J_{HP} coupling constants of 4.9 and 3.7 Hz, respectively, showing that the ethylenic protons are not equivalent. The ^{31}P{^{1}H} spectrum shows two doublets at 8.4 and 15.7 ppm, respectively, with $J_{\mathrm{PP}} = 11$ Hz. These chemical shifts and coupling constant are similar to those observed for previously described halo(oxo)bis(ligand)rhenium(V) complexes with bidentate monobasic ligands.[3,5,18]

For **2**, the ^{1}H spectrum also shows phenyl multiplets between 6.3 and 8.2 ppm, as well as doublets at 4.89 and 4.95 ppm with $J_{\mathrm{HP}} = 3$ and 2 Hz, respectively, for nonequivalent ethylenic protons. The ^{31}P{^{1}H} NMR spectrum is more complicated than for **1**. The presence of three nonequivalent phosphorus atoms is deduced from the ABX pattern (A/B = mutually *trans* P1/P3 pair). P1 gives a downfield doublet of doublets at 35.5 ppm ($J_{\mathrm{P1-P2}} = 10$ Hz (*cis*); $J_{\mathrm{P1-P3}} = 210$ Hz, (*trans*)), P3 produces another doublet of doublets at 27.2 ppm ($J_{\mathrm{P3-P2}} = 13$ Hz (*cis*), $J_{\mathrm{P3-P1}} = 210$ Hz (*trans*)), whereas a broad upfield signal is observed at 12.3 ppm for P2. Assignment of the intermediate signal to $\mathrm{PPh_3}$ is based on the exchange reaction taking place slowly when free P(p-tolyl)$_3$ is added to the $\mathrm{CD_2Cl_2}$ solution.

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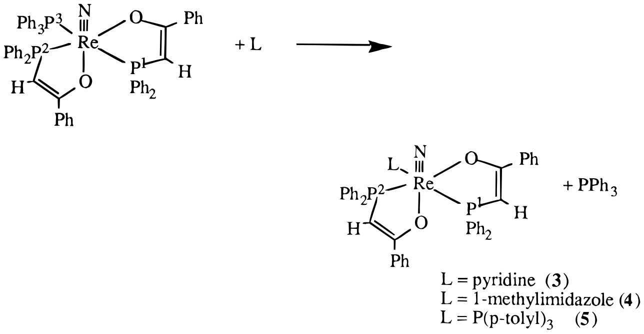
Scheme 2



As PPh$_3$ is displaced, another ABX spectrum develops for the new species ReN(PTol$_3$)(P⌒O)$_2$ (**5**) (Scheme 2): P1, dd, 35.0 ppm; P3, dd, 26.0 ppm; P2 s, br, 12.3 ppm; $J_{\mathrm{P1-P2}} = 10$ Hz (*cis*); $J_{\mathrm{P1-P3}} = 210$ Hz (*trans*). The middle resonance is assigned to the monodentate phosphine, because this signal undergoes the greatest displacement upon substitution and the upfield shift is consistent with the chemical shift difference between free PPh$_3$ (−5.0 ppm) and P(*p*-tolyl)$_3$ (−7.6 ppm). The outer signals due to the P donors in the chelate rings are virtually unmoved.

In the structure proposed here for **2**, which is confirmed by the X-ray work below, the P donors in the two P⌒O$^-$ ligands are *cis* as in complex **1** and the octahedral coordination is completed by PPh$_3$ sitting *trans* to P1 and *cis* to P2. There is no evidence for the presence of other isomers in solution. A single stereoisomer was also observed for the related complex with (2-hydroxyphenyl)diphenylphosphine,[5] but in the *mer*-(P,P,P) structure proposed, the PPh$_3$ ligand was assumed to be located *cis* to the two other phosphine groups. However, the pattern of NMR data reported for the latter complex is very similar to ours, and the possibility that identical structures be adopted by the two compounds cannot be ruled out.

The structure of **2** is also consistent with its behavior in the presence of pyridine and 1-methylimidazole in CD$_2$Cl$_2$ (Scheme 2). ^{31}P{^{1}H} NMR indicates that species **3** and **4** form quantitatively while triphenylphosphine is smoothly displaced over a period of 1−2 days at room temperature. AB spectra are obtained for **3** and **4**: P1, d, 30.1 ppm; P2, d, 19.0 ppm; $J_{\mathrm{P1-P2}} = 8$ Hz (*cis*) for **3**; P1, d, 30.7 ppm; P2, d, 18.0 ppm; $J_{\mathrm{P1-P2}} = 7$ Hz (*cis)* for **4.** The spectra also show a signal at −5 ppm for free PPh$_3$ In both cases, replacement of PPh$_3$ by the amine is accompanied by the disappearance of the intermediate doublet of doublets of **2**. Therefore, the labile PPh$_3$ ligand is stereoselectively substituted, since in the amine complex, a small *cis*-P1−P2 coupling is retained for the P donors of the two bidentate ligands.

The structures of **1** and **2** were confirmed by X-ray diffraction work. ORTEP views are illustrated in Figure 1 and Figure 2. Selected bond distances and angles are listed in Tables 3 and 4.

Both complexes consist of monomeric molecules, as suggested by the mass spectrometric data. The overall geometry around the rhenium atom is best described as a highly distorted octahedron. With the axial direction being defined along the Re═O or Re≡N bond, one P⌒O$^-$ ligand lies in the equatorial plane, whereas the other spans an equatorial site (P *cis* to the other P atom) and an axial site (O *trans* to Re═O or Re≡N). The remaining equatorial position is occupied by Cl in **1** and by PPh$_3$ in **2**.

Inspection of the bond angles (Tables 3 and 4) shows that angular distortions in the Re coordination sphere are comparable in the two structures The metal is displaced above the equatorial plane toward the multiply bonded O and N atoms as usual (0.310(1) Å in **1** and 0.366(2) Å in **2**). On average, the ligand bite angles are slightly smaller in **2** (P1−Re−O1 = 79.8(2)°; P2−Re−O2 = 76.8(2)°) than in **1** (P1−Re−O1 = 81.3(1)°, P2−Re−O2 = 77.1(1)°), which likely reflects the greater steric demand of PPh$_3$ compared with Cl.

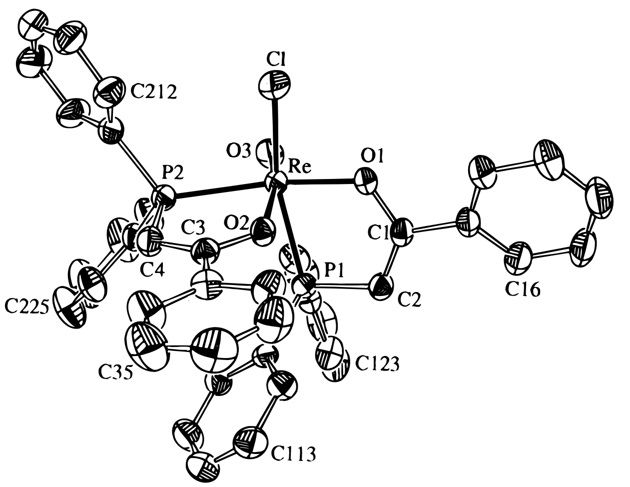


Figure 1. ORTEP view of ReOCl(P⌒O)$_2$ (**1**) with the atom labeling scheme. Hydrogens are omitted for clarity. Ellipsoids are drawn at 50% probability.

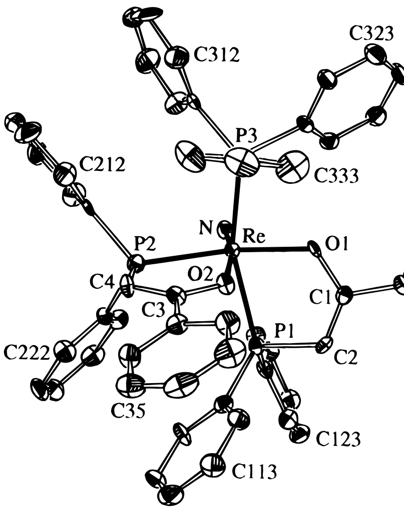


Figure 2. ORTEP view of ReN(PPh$_3$)(P⌒O)$_2$ (**2**) with the atom labeling scheme. Hydrogens are omitted for clarity. Ellipsoids are drawn at 40% probability.

Table 3. Selected Interatomic Distances (Å) and Bond Angles (deg) for ReOCl(P⌒O)$_2$ (**1**)

	Distances		
Re−Cl	2.386(2)	Re−O1	1.986(4)
Re−P1	2.435(2)	Re−O2	2.044(4)
Re−P2	2.435(2)	Re−O3	1.686(5)
	Angles		
Cl−Re−P1	159.89(7)	P1−Re−O3	96.4(2)
Cl−Re−P2	94.73(7)	P2−Re−O1	160.7(1)
Cl−Re−O1	81.7(1)	P2−Re−O2	77.1(1)
Cl−Re−O2	87.7(1)	P2−Re−O3	89.4(2)
Cl−Re−O3	99.5(2)	O1−Re−O2	83.8(2)
P1−Re−P2	97.72(6)	O1−Re−O3	109.8(2)
P1−Re−O1	81.3(1)	O2−Re−O3	165.2(2)
P1−Re−O2	79.8(1)		

The Re═O distance of 1.686(5) Å in **1** and the Re≡N distance of 1.683(7) Å in **2** are within the ranges found in Re(V) oxo and nitrido complexes and a clear indication for multiple bond character.[17] There is evidence for a large *trans* influence of the oxo and nitrido groups.[19] The *trans* Re−O bonds

Table 4. Selected Interatomic Distances (Å) and Bond Angles (deg) for $ReN(PPh_3)(P^\frown O)_2 \cdot 2CH_2Cl_2$ (**2**)

Distances			
Re−P1	2.447(2)	Re−N	1.683(7)
Re−P2	2.391(2)	Re−O1	2.077(5)
Re−P3	2.460(2)	Re−O2	2.221(5)

Angles			
P3−Re−P1	156.89(7)	P1−Re−N	98.9(2)
P3−Re−P2	98.87(8)	P2−Re−O1	156.8(2)
P3−Re−O1	78.9(2)	P2−Re−O2	76.8(2)
P3−Re−O2	87.8(2)	P2−Re−N	92.6(3)
P3−Re−N	96.9(2)	O1−Re−O2	80.0(2)
P1−Re−P2	97.15(7)	O1−Re−N	110.6(3)
P1−Re−O1	79.8(2)	O2−Re−N	169.0(3)
P1−Re−O2	79.7(2)		

(2.044(4) Å in **1** and 2.221(5) Å in **2**) are appreciably longer than the equatorial ones (1.986(4) Å in **1** and 2.077(5) Å in **2**), and the effect is particularly important in the nitride. The Re−P distances, identical in **1** (2.435(2) Å) and ranging from 2.460(2) Å (PPh_3) to 2.391(2) Å in **2**, are normal, as is the Re−Cl distance of 2.386(2) Å.

The distances and angles in the coordinated ligand show no unexpected features.[20] A close look at ligand conformation reveals that the orientation of the phenyl substituent on the double bond is not far from coplanar with the five-membered Re−O−C−C−P ring in both complexes: the dihedral angles are 21.7(4) and 7.8(4)° in **1,** and 17.3(4) and 1.5(4)° in **2**. As a result, π electrons are allowed to delocalize over the $C{=}C$ bond and into the empty Re orbitals, thus providing extra stabilization to the system.

To our knowledge, this is the first example of Re(V)−phosphine complexes where oxo and nitrido complexes with similar octahedral structures were isolated and characterized by X-ray diffraction. The structural similarity observed here suggests that the coordination geometry adopted by the hard Re(V) center is controlled by both steric and electronic features of the ligands. Therefore, with a suitable combination of ligands, similar structures can be obtained for the $Re{=}O$ and $Re{\equiv}N$ species. In the present case, a major driving force is the different nucleophilicity of the ligand donor atoms since, as reported for Re−oxo species, the stronger nucleophile always coordinates *trans* to the multiple group. We are showing here that this generalization can be extended to a Re(V)−nitrido complex, in which the presence of the unusual $N{\equiv}Re{-}O$ unit is unambiguously demonstrated.

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Supporting Information Available: Tables of crystallographic data, atom coordinates, anisotropic temperature factors, and distances and angles for both structures (18 pages). Ordering information is given on any current masthead page.

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