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Synthesis and Structural Characterization of Novel Re(I) Tricarbonyl Complexes Anchored on a Phosphinoarylbenzylamine and a Phosphinoaryloxazoline Generated in Situ

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Reduction of the amide or replacement of the hydroxyl by a bromide in 2-(diphenylphosphanyl)-*N*-(2-hydroxyethyl)-benzamide (**H_2PNO**) yielded the compounds 2-(diphenylphosphanyl)-*N*-(2-hydroxyethyl)benzylamine (**H_2CH_2PNO**, **1**) and *N*-(2-bromoethyl)-2-(diphenylphosphanyl)benzamide (**HPNBr**, **2**), respectively. Compound **2** is obtained in low yield and, depending on the reaction conditions, is mixed with starting material or with a product which has been identified as 2-(2-diphenylphosphinophenyl)oxazoline (**PPh_3oxaz**, **3**). Compounds **1** and **2** react with $(NEt_4)_2[ReBr_3(CO)_3]$, leading to the complexes $[Re(CO)_3(\kappa^2\text{-}H_2CH_2PNO)Br]$ (**4**) and $[Re(CO)_3(\kappa^2\text{-}PPh_3oxazBr)]$ (**5**), fully characterized by ^{1}H and ^{31}P NMR spectroscopy and X-ray crystallographic analysis. Complex **5** is the first example of a Re(I) tricarbonyl anchored on a phosphorus–oxazoline ligand, which has been generated during the course of complex formation. In the unexpected and unusual complex **5**, the Re atom is stabilized by a bidentate 2-(2-diphenylphosphinophenyl)oxazoline, by a bromide, and by three facially arranged carbonyl groups. In complex **4**, the carbonyl groups are also facially coordinated to the metal center and the other three remaining coordination positions are occupied by a bromide and by the bidentate (P, N) ligand 2-(diphenylphosphanyl)-*N*-(2-hydroxyethyl)-benzylamine.

Introduction

There has been an increasing interest in the development of new specific radiopharmaceuticals based on the low oxidation states of rhenium and technetium, which arises mainly from the introduction of straightforward methods of conversion of $[MO_4]^-$ to the highly stable organometallic precursors *fac*-$[M(CO)_3(H_2O)_3]^+$ (M = Tc, Re) under aqueous conditions.[1−4] Several bifunctional chelating agents, which allow the simultaneous stabilization of the metallic center and attachment to relevant biomolecules, have been explored.[5−14] However, further chelating agents are still needed in order to prepare complexes with different physicochemical properties, an important issue for their in vivo stability and pharmacokinetics. The number of bifunctional P-containing ligands useful for the stabilization of the organometallic core *fac*-$[M(CO)_3(H_2O)_3]^+$ is still limited.[15−17]

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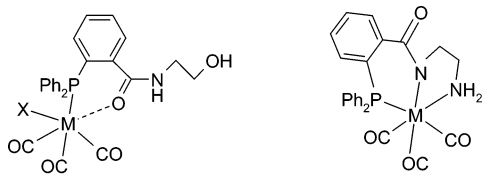
Chart 1. M(I) Tricarbonyl Complexes (M = ^{99m}Tc, Re) with **H_2PNO** and **H_2PN_2**



In our group, we have synthesized a new family of phosphine-containing ligands, and their coordination capabilities toward the *fac*-$[M(CO)_3]$ and the $[M(O)]^{3+}$ moieties (M = Re, ^{99m}Tc) have been explored.[18−23] In the case of tricarbonyl complexes, we have shown that the bi(tri)dentate heterofunctionalized phosphines **H_2PNO** (2-(diphenylphosphanyl)-*N*-(2-hydroxyethyl)benzamide) and **H_2PN_2** (*N*-(2-aminoethyl)-2-(diphenylphosphanyl)benzamide) react stoichiometrically with the synthon $[M(CO)_3]^+$ (M = Re, ^{99m}Tc), yielding the complexes $[M(CO)_3(\kappa^2\text{-}H_2PNO)X]$ and $[Re(CO)_3(\kappa^3\text{-}HPN_2)]$, respectively (Chart 1).[18,19]

By use of a triphenylphosphanyl-substituted benzamine, a reduced form of **H_2PNO**, the coordination behavior toward Re(I) should change, and by conversion of the hydroxyl function of the **H_2PNO**, which is not involved in the complexation, into a more reactive group, the coupling to bioactive molecules would be easier. With this aim, we synthesized the 2-(diphenylphosphanyl)-*N*-(2-hydroxyethyl)-benzylamine (**H_2CH_2PNO**, **1**) and the *N*-(2-bromo)-2-(diphenylphosphanyl)benzamide (**HPNBr**, **2**). Herein, we report on the synthesis and characterization of these new compounds as well as on the synthesis and structural characterization of the novel complexes *fac*-$[Re(CO)_3(\kappa^2\text{-}H_2CH_2PNO)Br]$ (**4**) and *fac*-$[Re(CO)_3(\kappa^2\text{-}PPh_3oxaz)Br]$ (**5**). Complexes **4** and **5** were obtained by reacting the organometallic precursor $[NEt_4]_2[Re(CO)_3Br_3]$ with **1** and **2**, respectively. The unusual and unexpected complex **5** is the first Re complex anchored on a phosphorus−oxazoline ligand, which has been generated during the complex formation.

Experimental Section

General Techniques. All chemicals were of reagent grade. **H_2PNO** and $(NEt_4)_2[ReBr_3(CO)_3]$ were prepared as previously described.[23,24] Borane dimethyl sulfide complex and PBr_3 were purchased from Aldrich and used without further purification. The reactions were run in air unless otherwise indicated. ^{1}H and ^{31}P NMR spectra were recorded on a Varian Unity 300 MHz spectrometer; ^{1}H chemical shifts were referenced with the residual solvent resonance relative to tetramethylsilane, and the ^{31}P chemical shifts were measured with external 85% H_3PO_4 solution as reference. Chemical shifts are given in ppm. The NMR samples were prepared in $CDCl_3$ or $(CD_3)_2SO$. Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer 577 spectrometer using KBr pellets. Elemental analyses were performed on a Perkin-Elmer automatic analyzer.

2-(Diphenylphosphanyl)-*N*-(2-hydroxyethyl)benzylamine (H_2CH_2PNO) (1). To a solution of **H_2PNO** (0.50 g, 1.4 mmol) in dry toluene (40 mL), 1 M borane dimethyl sulfide solution in dichloromethane (2.8 mL, 2.8 mmol) was added at room temperature, under a nitrogen atmosphere with stirring. The solution was allowed to react for 30 min at room temperature and then refluxed for 24 h under a nitrogen atmosphere with stirring. The mixture was cooled, 20 mL of a 10% $NaHCO_3$ solution was added, and the mixture was refluxed again for 30 min. The solvents were evaporated in a vacuum to dryness, and the residue was treated with 10 mL of water and extracted with dichloromethane (3 × 20 mL). The organic phases were collected, dried over $MgSO_4$, and filtered, and the solvent was evaporated. The residue was chromatographed on a silica gel column with 95% chloroform−methanol to afford a colorless oil (0.282 g, 60%). IR (cm^{-1}): 3000, 1580, 1640, 1470, 1430, 740, 690. ^{1}H NMR (δ, $CDCl_3$): 7.45 (m, 1H, arom.), 7.38−7.20 (m, 12H, arom.), 6.95 (m, 1H, arom.), 4.03 (s, 1H, CH_2) 3.53 (s, 2H, CH_2), 2.72 (tr, 2H, CH_2). ^{31}P NMR (δ, $CDCl_3$): −15.1 ppm. ^{1}H NMR (δ, $[(CD_3)_2SO]$): 7.53 (m, 1H, arom.), 7.39−7.16 (m, 12H, arom), 6.75 (m, 1H, arom.), 4.41 (s, 1H, OH) signal disappears after shaking with D_2O, 3.83 (s, 2H, CH_2), 3.31 (tr, 2H, CH_2), 2.45 (tr, 2H, CH_2). Anal. Calcd for $C_{21}H_{22}NOP\cdot CH_2Cl_2$: C, 62.87; H, 5.76; N, 3.33. Found: C, 63.68; H, 5.90; N, 3.33.

***N*-(2-Bromoethyl)-2-(diphenylphosphanyl)benzamide (HPNBr) (2).** To a stirred solution of **H_2PNO** (0.35 g, 1 mmol) in chloroform (15 mL), PBr_3 (0.093 mL, 1 mmol) was added, and the mixture was allowed to reflux for 24 h. After cooling, the mixture was treated with 10% $NaHCO_3$ solution (10 mL) in chloroform (40 mL). The organic phase was collected, dried over $MgSO_4$, and filtered, and the solvent was removed. The residue was chromatographed on a silica gel column with 95% dichloromethane−ethyl acetate to afford a white solid identified as **H_2CPNBr** (0.091 g, 22%). IR (cm^{-1}, KBr): 3300 (NH); 1640 (C═O); 1550, 1430 (C═C); 1330, 1280, 750, 700, 510. ^{1}H NMR (δ, $CDCl_3$): 7.67 (m, 1H, arom.), 7.42−7.27 (m, 12H, arom.), 6.99 (m, 1H, arom.), 6.48 (s, br, 1H, NH), 3.71 (q, 2H, CH_2), 3.36 (tr, 2H, CH_2). ^{31}P NMR (δ, $CDCl_3$): −10.5 ppm. Anal. Calcd for $C_{21}H_{19}BrNOP$: C, 61.16; H, 4.61; N, 3.39. Found: C, 61.65; H, 4.41; N, 3.34.

2-(2-Diphenylphosphinophenyl)oxazoline (PPh_3oxaz) (3). To a stirred solution of **H_2PNO** (0.350 g, 1 mmol) in chloroform (15 mL), PBr_3 (0.186 mL, 2 mmol) was added, and the mixture refluxed for 1 h. After treatment with 10% $NaHCO_3$ (10 mL) and chloroform (40 mL), the organic phase was separated, dried over $MgSO_4$, and filtered, and the solvent was removed. The residue was purified by chromatography on a silica gel column with 95% dichloromethane−ethyl acetate to afford two fractions, which correspond to **HPNBr** (0.040 g, 9.7% yield) and **PPh_3oxaz** (0.088 g, 26% yield). The former compound was obtained as an oil that crystallized to a white solid. IR (cm^{-1}, KBr): 1640 (C═N); 1425, 1340, 1080, 1040, 940, 740, 690. ^{1}H NMR (δ, $CDCl_3$): 7.92 (m, 1H, arom.), 7.41−7.29

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(m, 12H, arom.), 6.91 (m, 1H, arom.), 4.13 (tr, 2H, CH_2), 3.81 (tr, 2H, CH_2). ^{31}P NMR (δ, $CDCl_3$): − 4.00 ppm. Anal. Calcd for $C_{21}H_{18}NOP$: C, 76.13; H, 5.44; N, 4.23. Found: C, 75.78; H, 5.78; N, 4.19.

[Re(CO)$_3$(κ^2-H$_2$CH$_2$PNO)Br] (4). A solution of **H$_2$CH$_2$PNO** (0.060 g, 0.18 mmol) in methanol (4 mL) was added to a solution of $(NEt_4)_2[ReBr_3(CO)_3]$ (0.138 g, 0.18 mmol) in methanol (10 mL) at room temperature. After refluxing for 5 h, the mixture was cooled and the solvent evaporated to dryness. The obtained residue was chromatographed on a silica gel column with 90% dichloromethane−ethyl acetate. Complex **4** was obtained as a white solid (0.05 g, 41% yield). IR (cm^{-1}, KBr): 2020, 1920, 1880 (C═O); 1430 (C═C); 760, 690, 530. ^{1}H NMR (δ, $[(CD_3)_2SO]$): 7.62−7.48 (m, 9H, arom.), 7.35−7.21 (m, 4H, arom.), 6.70 (m, 1H, arom.), 5.13 (tr, 1H, OH) signal disappears by shaking with D_2O, 4.15 (m, 1H, CH), 4.07 (m, 1H, CH), 3.80 (m, 1H, CH), 3.57 (m, 1H, CH), 2.84 (m, 2H, CH_2). ^{31}P NMR (δ, $CDCl_3$): +11.8 ppm. Anal. Calcd for $C_{24}H_{22}BrNO_4PRe$: C, 42.05; H, 3.23; N, 2.04. Found: C, 41.84; H, 2.89; N, 1.83.

[Re(CO)$_3$(κ^2-PPh$_3$oxaz)Br] (5). A solution of **HPNBr** (0.062 g, 0.150 mmol) in methanol was added to a solution of $(NEt_4)_2[ReBr_3(CO)_3]$ (0.115 g, 0.150 mmol) in methanol (10 mL), and the mixture was refluxed overnight. After cooling, evaporation of the solvent afforded a residue, which was purified by chromatography on a silica gel column with 100% dichloromethane. The complex (0.090 g, 88%) was obtained as a pale-yellow solid. IR (cm^{-1}, KBr): 2010, 1910, 1870 (C═O); 1610, 1470 (C═C); 1430, 1370, 1950, 1120, 1090, 1050, 730, 690, 540. ^{1}H NMR (δ, $[(CDC_3)_2SO]$): 8.13 (m, 1H, arom.), 7.72−7.55 (m, 10H, arom.), 7.14 (m, 2H, arom.), 6.80 (m, 1H, arom.), 4.62 (m, 2H, CH_2), 4.26 (m, 1H, CH), 4.12 (m, 1H, CH). ^{31}P NMR (δ, $[(CD_3)_2SO]$): +9.8. Anal. Calcd for $C_{24}H_{18}BrNO_4PRe$: C, 42.29; H, 2.64; N, 2.05. Found: C, 41.84; H, 2.68; N, 1.88.

X-ray Crystallographic Analysis. Colorless crystals of **4** and **5**, suitable for X-ray diffraction analysis, were obtained from slow evaporation of methanolic solutions and were fixed inside thin-walled glass capillaries. Data were collected at room temperature on an Enraf-Nonius CAD4-diffractometer with graphite-monochromatized Mo Kα radiation, using a $\omega-2\theta$ scan mode. Unit cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections with $16.3 < 2\theta < 31.9°$ for **4** and $15.8 < 2\theta < 27.8°$ for **5**. A summary of the crystallographic data is given in Table 1. Data were corrected for Lorentz and polarization effects and for absorption by empirical corrections based on Ψ scans.[25] The heavy atom positions were located by Patterson methods using SHELXS-97.[26] The remaining atoms were located by sucessive difference Fourier techniques and refined by least-squares refinements on F^2 using SHELXL-97.[27] All the non-hydrogen atoms were refined with anisotropic thermal motion parameters, and the contribution of the hydrogen atoms was included in calculated positions. Atomic scattering factors and anomalous dispersion terms were taken from ref 25. The drawings were made with ORTEP-3.[28]

Results and Discussion

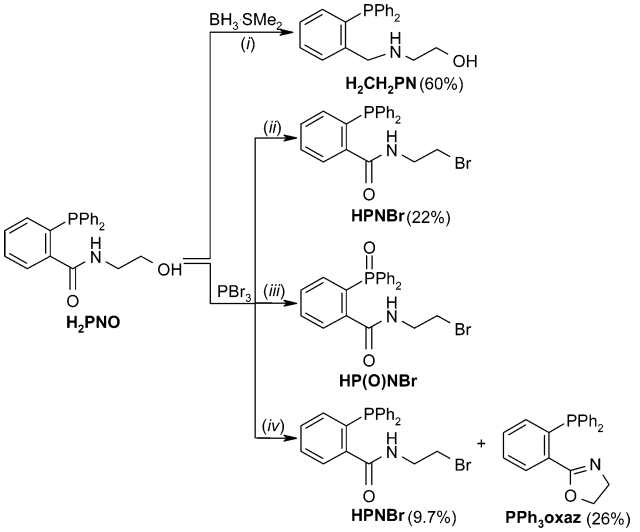
To broaden the type of phosphine-containing ligands useful for stabilizing the $[M(CO)_3]^+$ core (M = Re, Tc), the basic framework of the previously described **H$_2$PNO** ligand was changed following two different approaches. One comprises the reduction of the amide group to a secondary amine and the other the substitution of the hydroxyl group by a bromide for an easier coupling to biomolecules. As depicted in Scheme 1, **H$_2$PNO** reacts with $BH_3{\cdot}SMe_2$ or with PBr_3, leading to the new compounds **H$_2$CH$_2$PNO** (**1**) and **HPNBr** (**2**), respectively. After appropriate workup and purification by chromatography on a silica gel column, **1** was obtained as a colorless oil and **2** as a white solid. The synthesis of **H$_2$CH$_2$PNO** in 60% yield was more or less straightforward, but in the case of **HPNBr**, prepared by nucleophilic substitution of the hydroxyl group with PBr_3, the reaction was not so clean. In fact, when **H$_2$PNO** reacted with an equimolecular amount of PBr_3 in refluxing $CHCl_3$ for 24 h, the alkyl bromide ligand is formed, but in a very low yield (22%), being a significant amount of unreacted starting

Table 1. Crystal Data for $[Re(CO)_3(\kappa^2\text{-}H_2CH_2PNO)Br]$ (**4**) and $[Re(CO)_3(\kappa^2\text{-}PPh_3oxaz)Br]$ (**5**)

complex	**4**	**5**
empirical formula	$C_{24}H_{22}BrNO_4PRe$	$C_{24}H_{18}BrNO_4PRe$
crystal size, mm^3	0.36 × 0.36 × 0.14	0.72 × 0.34 × 0.17
formula weight	685.51	681.47
crystal system	monoclinic	triclinic
space group	$P2_1/c$	$P1$
a, Å	11.2777(10)	11.2502(11)
b, Å	10.3652(8)	14.7436(15)
c, Å	20.7153(17)	15.029(2)
α, deg		71.370(11)
β, deg	105.742(7)	88.316(10)
γ, deg		87.786(8)
volume, Å^3	2330.7(3)	2360.0(5)
Z	4	4
$\rho_{calc.}$, g cm^{-3}	1.954	1.918
μ (Mo Kα), mm^{-1}	7.028	6.940
no. reflns measd	5866	12195
no. unique reflns	5590 [R_{int} = 0.0350]	11785 [R_{int} = 0.0239]
R1[a]	0.0439	0.0590
wR2[b]	0.0887	0.1258

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$. The values were calculated for data with $I > 2\sigma(I)$.

Scheme 1. Preparation of **H$_2$CH$_2$PNO** (**1**) and **HPNBr** (**2**)[a]



[a] Key: (*i*) toluene, reflux; (*ii*) PBr_3, (1 equiv), $CHCl_3$, reflux, 24 h; (*iii*) PBr_3 (2 equiv), $CHCl_3$, reflux, 18 h; (*iv*) PBr_3 (2 equiv), $CHCl_3$, reflux, 1 h.

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Table 2. ^{31}P NMR and IR Data

compound	^{31}P (ppm)	IR (cm^{-1})	ref
H_2PNO	−9.9[a]	1630, ν(CO)	23
H_2CH_2PNO (1)	−15.1[a]		*c*
HPNBr (2)	−10.5[a]	1640, ν(CO)	*c*
$H_2P(O)NBr$	+36.7[a]		*c*
PPh_3oxaz (3)	−4.0[a]	1640, ν(CN)	*c*
[Re(CO)$_3$(κ^2-H_2PNO)Br]	+11.8[a]	1598, ν(CO)	18
[Re(CO)$_3$(κ^2-H_2CH_2PNO)Br] (**4**)	+11.8[b]		*c*
[Re(CO)$_3$(κ^2-PPh_3oxaz)Br] (**5**)	+9.8[b]	1610, ν(CN)	*c*

[a] $CDCl_3$. [b] $[(CD_3)_2SO]$. [c] This work.

material recovered during workup. If more harsh reaction conditions are applied (2-fold molar excess of PBr_3, refluxing chloroform, overnight reaction), the main isolated product (77%) was identified as the phosphine oxide derivative **HP(O)NBr**, based on ^{1}H and ^{31}P NMR spectroscopy (^{31}P NMR: +36.7 ppm). In a third attempt, using a 2-fold molar excess of PBr_3 in refluxing chloroform for 1 h, the desired alkyl bromide **HPNBr** (**2**) ligand was isolated in 9.7% yield. However, a side product, which has been identified as 2-(2-diphenylphosphinophenyl)oxazoline (**PPh_3oxaz**), was also isolated (Scheme 1).

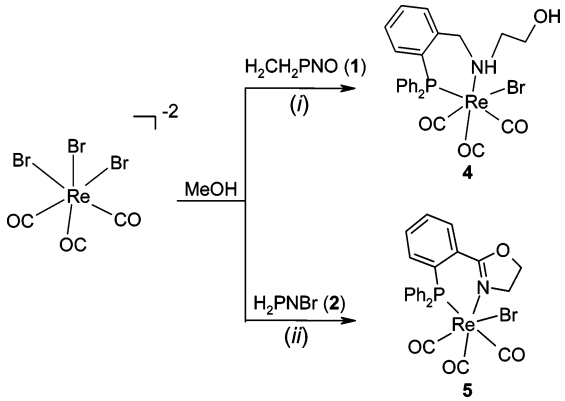
After separation by chromatography on a silica gel column, **PPh_3oxaz** was recovered as a white solid in 26% yield. The 2-(2-diphenylphosphinophenyl)oxazoline (**PPh_3oxaz**) is a compound already described but by a quite different synthetic method. It has been obtained through a two-step synthetic pathway, preparation of 2-(2-fluorophenyl)-oxazoline by one-pot condensation of the 2-fluorobenzoic acid with the corresponding amino alcohol followed by nucleophilic substitution with $LiPPh_2$.[29]

In our case, the compound **HPNBr** is certainly formed in a first step, but a deprotonation of the amide by the PBr_3 Lewis base promotes an intramolecular nucleophilic attack of the C═O group to the terminal ethylenic carbon atom.

Compounds **1**, **2**, and **3** were characterized by ^{31}P NMR and ^{1}H NMR spectroscopy, elemental analysis, and IR spectroscopy. In the IR spectrum of **H_2CH_2PNO** (**1**), no stretching bands in the range 1630−1640 cm^{-1} are found, confirming the absence of the carbonyl amide function.[23] For compound **HPNBr** (**2**), the ν(C═O) stretching vibration, assigned to the amide function, appears at 1640 cm^{-1}, and for the oxazoline **PPh_3oxaz** a band, which appears also in this range (1640 cm^{-1}), has been attributed to the ν(C═N) stretching vibration of the ring.[30]

As shown in Table 2, the ^{31}P NMR spectra of **H_2CH_2PNO** (**1**), **HPNBr** (**2**), and **PPh_3oxaz** (**3**) show only one peak at −15.1, −10.5, and −4 ppm, respectively. As expected, the chemical shift of the resonance found for **2** compares well with the value found for **H_2PNO**, but the ^{31}P NMR resonances found for **1** and **3** are, respectively**,** high-field and low-field shifted relative to the nonreduced form (**H_2PNO**: $\delta = -9.9$). The more and less shielded P atoms, respectively, in **1** and **3** are due to the absence of the electron withdrawing carbonyl group in **1** and to the presence of the heterocycle in complex **3**, which certainly promotes a significant electron delocalization.

Scheme 2. Preparation of the Complexes **4** and **5**.[a]



[a] Key: (*i*) Reflux, 5 h; (*ii*) reflux, 18 h.

In the ^{1}H NMR spectrum of **H_2CH_2PNO** ($[(CD_3)_2SO]$), the most characteristic peaks are two singlets at $\delta = 4.41$ and 3.83, assigned, respectively, to the OH group and to the new methylenic protons. The ^{1}H NMR spectrum of **HPNBr** agrees with the formulation, and no significant differences can be observed in the overall pattern when compared to that of the **H_2PNO** starting material. Unlike the **HPNBr** ligand, where a broad singlet assigned to the NH group ($\delta = 6.48$) together with a quartet ($\delta = 3.71$) and a triplet signal ($\delta = 3.36$) for the CH_2 groups appear in the ^{1}H NMR spectrum ($CDCl_3$), the cyclic oxazoline **PPh_3oxaz** presents in the same solvent two triplets of equal intensity ($\delta = 4.13$, 3.81) for the CH_2 protons of the heterocycle, and as expected, no resonance assigned to the NH group could be found.

The Re(I) tricarbonyl complex [Re(CO)$_3$(κ^2-H_2CH_2PNO)Br] (**4**) was obtained in moderate yield (41%) by stoichiometric reaction of the precursor $(NEt_4)_2[ReBr_3(CO)_3]$, in refluxing methanol for 5 h, with **H_2CH_2PNO (1)** (Scheme 2). Compound **4** is air and moisture stable, being soluble in MeOH and halogenated solvents and insoluble in water. Characterization of the complex was achieved by the usual analytical techniques, including X-ray diffraction analysis.

The Re(I) tricarbonyl complex [Re(CO)$_3$(κ^2-PPh_3oxaz)Br] (**5**) was unexpectedly obtained in high yield (88%) as a yellow solid by refluxing an analytically pure sample of **HPNBr**, with $(NEt_4)_2[ReBr_3(CO)_3]$ in methanol. Compound **5** was characterized by the usual analytical techniques; however, unambiguous evidence for its final structure was only achieved by X-ray diffraction analysis. In fact, there was no complex formed with a free bromoethyl side chain, and the rhenium complex contained a 2-aryloxazoline ligand, as depicted in Scheme 2.

Since the bromine-substituted ligand **HPNBr** was undoubtedly used as starting material, it must be assumed that the cyclization of the ligand has occurred in situ during complexation, most likely by the mechanism displayed in Scheme 3.

In this mechanism, we propose the formation of an intermediate (**I**), which is analogous to the previously isolated

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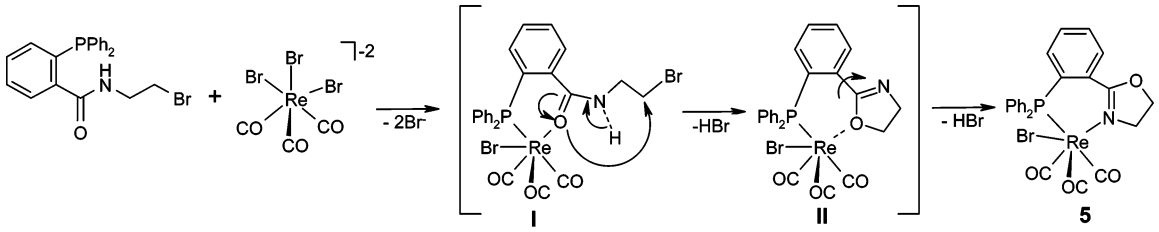
Scheme 3. Proposed Mechanism for the Formation of Complex **5**



$[Re(CO)_3(\kappa^2\text{-}H_2PNO)Br]$ complex.[18] The simultaneous effect of coordination of the ligand to the metal center and the presence of an electron withdrawing group in the ethyl chain (Br) promotes the deprotonation of the amide and subsequent nucleophilic attack of the carbonyl group to the terminal ethylenic carbon atom, with formation of the cyclic oxazoline group (**II**). Intramolecular rotation of the oxazoline residue around the C−C bond followed by coordination of the nitrogen atom to the metal yields then complex **5**. As far as we are aware, no Re tricarbonyl complex anchored by a phosphorus oxazoline bidentate ligand has been described and no examples exist of in situ generation of this type of ligands during d-transition-complex formation.

Strong ν(CO) stretching bands appear in the IR spectra of **4** (2020, 1920, and 1880 cm^{-1}) and **5** (2010, 1910, and 1870 cm^{-1}), these values being within the range normally found for other complexes with the moiety *fac*-$Re(CO)_3$.[1−23] The coordination of the phosphines is also confirmed by two strong absorption bands at ca. 730 and 690 cm^{-1}, associated with the C−H and C−C out-of-plane bending vibrations of monosubstituted benzene rings.[18,23] For compound **5**, a strong band appears at 1610 cm^{-1}, which has been attributed to the ν(C═N) stretching. This band is shifted toward lower frequency ($\Delta = 30$ cm^{-1}) relative to the free **PPh_3oxaz** (**3**), which is in accordance with the general trend observed for other metal−oxazoline complexes.[30]

The ^{1}H NMR spectrum of **4** in $[(CD_3)_2SO]$ shows four multiplets, integrating for one proton each, at 4.15, 4.07, 3.80, and 3.57 ppm and one multiplet of intensity 2 at $\delta = 2.84$. The four multiplets of intensity 1 were assigned to the four diastereotopic methylenic protons near the coordinated amine, and the resonance at 2.84 ppm was attributed to the methylenic protons near the hydroxyl group. A signal at 5.13 ppm, which disappears after treatment with D_2O, was attributed to the OH proton. The ^{31}P NMR spectrum shows only one singlet at +11.8 ppm, downfield shifted relative to the free compound **H_2CH_2PNO** ($\Delta = 26.9$ ppm), confirming the coordination to the metal.

The ^{1}H NMR spectrum of **5** in $[(CD_3)_2SO]$ shows one multiplet for a CH_2 group ($\delta = 4.62$) and two multiplet signals, integrating for one proton each, for the other two protons of the oxazoline fragment ($\delta = 4.26, 4.12$). The ^{31}P NMR signal for **5** appears at +9.8 ppm, downfield shifted relative to the free **PPh_3oxaz** (**3**) ($\Delta = 13.8$ ppm).

Despite the increasing interest on the coordination chemistry of phosphino-oxazoline ligands, mainly as chiral auxiliaries in transition-metal-catalyzed asymmetric organic syntheses, not many examples of Re complexes with this type of ligand have been described.[30,31] To the best of our knowledge, **5** is the first example of a Re complex anchored on a bidentate phosphorus-oxazoline ligand. Concerning the Re(I), two families of complexes of the type $[ReX(CO)_3L]$ (X = halide) have been described, one in which L = 2-methylthiomethyl-4-(S)-methyl-1,3-oxazoline[32] and another in which L = 2,6-bis[(4S)-isopropyloxazoline-2-yl]pyridine).[33,34] Concerning M(V) (M = Re, Tc), neutral monooxo complexes of the type $[M(O)XL_2]$ (X = halide; HL = 2-(2′-hydroxyphenyl)-2-oxazoline) and the cationic monooxo $[Re(O)(H_2O)L_2]^+$ have been described.[35,36]

Description of the Structures. The structures of complexes $[Re(CO)_3(\kappa^2\text{-}H_2CH_2PNO)Br]$ (**4**) and $[Re(CO)_3(\kappa^2\text{-}PPh_3oxaz)$ Br] (**5**) consist of discrete mononuclear units. Complex **5** possesses two molecules per asymmetric unit which are crystallographically independent but chemically equivalent. ORTEP views of the molecular structures of **4** and **5** are given in Figures 1 and 2, respectively. Selected bond distances and angles are given in Tables 3 and 4.

In both compounds, the Re atom is six-coordinated, displaying a slightly distorted octahedral coordination geometry. The three carbonyl ligands occupy one triangular face of the polyhedron; the other three remaining coordination sites are occupied by the bromide and by the phosphorus and nitrogen atoms of the bidentate ligands **H_2CH_2PNO** and **PPh_3oxaz** in **4** and **5**, respectively. In both complexes, the axial

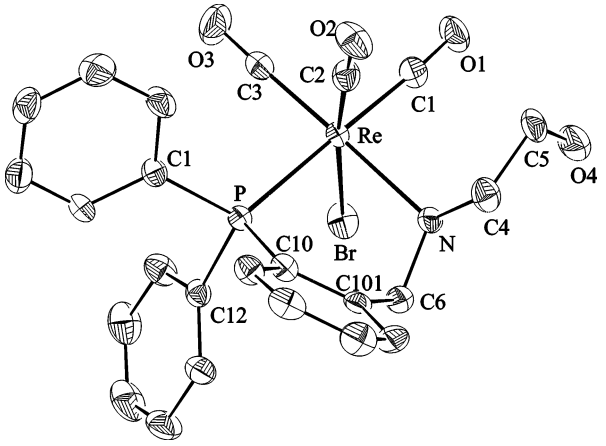


Figure 1. ORTEP drawing of complex **4**. Thermal ellipsoids are drawn at the 40% probability level.

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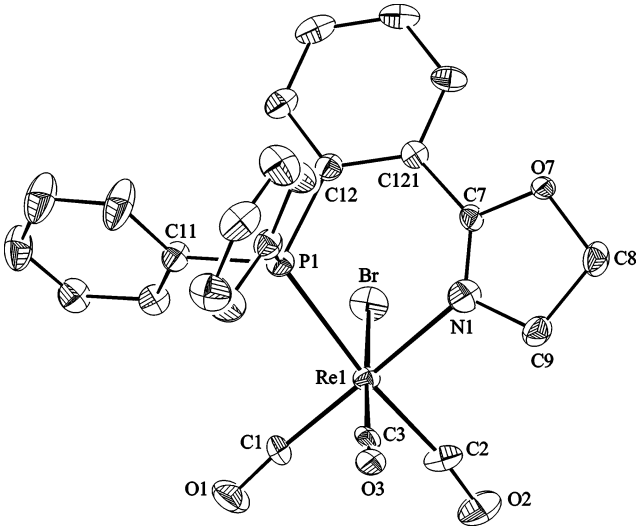

Figure 2. ORTEP drawing of molecule 1 of complex **5**. Thermal ellipsoids are drawn at the 30% probability level.

Table 3. Selected Bond Lengths (Å) and Angles for (deg) for $[Re(CO)_3(\kappa^2\text{-}H_2CH_2PNO)Br]$ (**4**)

Re−C(1)	1.942(8)	Re−Br	2.6267(9)
Re−C(2)	1.892(9)	Re−N	2.275(6)
Re−C(3)	1.927(9)	Re−P	2.4661(18)
C(2)−Re−P(1)	90.2(3)	C(3)−Re−Br(1)	94.4(3)
C(3)−Re−P(1)	92.4(2)	C(1)−Re−Br(1)	83.6(3)
C(1)−Re−P(1)	176.6(3)	N(1)−Re−Br(1)	81.68(17)
N(1)−Re−P(1)	88.27(16)	P(1)−Re−Br(1)	93.01(5)
C(2)−Re−Br(1)	173.3(3)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Molecule 1 of $[Re(CO)_3(\kappa^2\text{-}PPh_3Oxaz)Br]$ (**5**)[a]

Re(1)−C(1)	1.914(10)	Re(1)−N(1)	2.193(8)
Re(1)−C(2)	1.976(11)	Re(1)−P(1)	2.446(2)
Re(1)−C(3)	2.034(11)	Re(1)−Br(1)	2.6093(13)
C(1)−Re(1)−N(1)	178.2(4)	C(1)−Re(1)−Br(1)	92.2(3)
C(2)−Re(1)−N(1)	94.4(4)	C(2)−Re(1)−Br(1)	85.6(3)
C(3)−Re(1)−N(1)	90.3(4)	C(3)−Re(1)−Br(1)	178.4(3)
C(1)−Re(1)−P(1)	97.2(3)	N(1)−Re(1)−Br(1)	89.1(2)
C(2)−Re(1)−P(1)	169.4(3)	P(1)−Re(1)−Br(1)	84.52(7)
C(3)−Re(1)−P(1)	96.8(3)	Re(1)−N(1)−C(7)	132.1(6)
N(1)−Re(1)−P(1)	81.6(2)	Re(1)−P(1)−C(12)	108.5(3)

[a] The structural parameters for molecule 2 are given in Supporting Information.

positions of the octahedron are defined by the phosphorus atom of the neutral and bidentate heterofunctionalized phosphines and by one carbonyl ligand. Deviations from the idealized octahedral geometry can be seen in the bond angles around the Re atom (Tables 3 and 4). The cis and trans bond angles are in the ranges 81.7−94.4° and 173.3−176.6° and 81.6−97.2 and 169.4−178.4° in **4** and **5**, respectively. Probably due to steric and/or electronic restrictions imposed by the oxazoline moiety, compound **5** presents a higher distortion than **4**, the values found for this one being comparable with the values previously found for the analogous $[Re(CO)_3(\kappa^2\text{-}H_2PNO)Br]$.[18]

Although there are different existing d-transition complexes anchored on polydentate nitrogen, oxygen, or phosphorus−oxazoline ligands, to the best of our knowledge, **5** is the only Re(I) complex anchored on a phosphorus−oxazoline ligand and, therefore, a comparison of structural data is difficult. However, concerning the structural parameters of the oxazoline moiety in complex **5**, they are comparable to the corresponding values found in other structurally characterized d-transition complexes.[30−32] For molecules 1 and 2, the bite angles N(1)−Re(1)−P(1), 81.6°, and N(2)−Re(2)−P(2), 83.6°, fall in the range 80−90° where the bite angles N−M−Y (Y = C, N, O, S, P) of other oxazoline complexes with five-, six-, and seven-membered cycles normally appear.[30,31] The Re−N−C bond angle is large (132.1(6)° in molecule 1 and 133.0(7)° in molecule 2) and out of the range 112.8−125.79° normally found in other oxazoline complexes, certainly due to the steric restrictions imposed by the diphenylphosphine moiety.

The relatively strong sigma-donor character of the phosphorus−oxazoline ligand compared with the phosphines **H_2PNO** and **H_2CH_2PNO** explains the longer Re−CO bond distances in **5** (molecule 1, 1.975(11) Å; molecule 2, 1.943(16) Å) than in **4** (1.920(9) Å) and also in the previously described $[Re(CO)_3Br(\kappa^2\text{-}H_2PNO)]$ (1.922(8) Å).[18]

The Re−P bond distance found in **5** (2.440(2) Å) is slightly shorter than the corresponding bond length in **4** (2.4661(18) Å), certainly due to the presence of the oxazoline moiety, which forms with the metal a strong Re−N bond (2.192(8) Å).

Concluding Remarks

We have synthesized and characterized a new family of bidentate P, N donor ligands (**H_2CH_2PNO**, **HPNBr**) and studied their coordination capabilities toward the *fac*-$[Re(CO)_3]^+$ moiety. By reaction of $[(NEt_4)_2[ReBr_3(CO)_3]$ with **H_2CH_2PNO**, the novel complex $[Re(CO)_3Br(\kappa^2\text{-}H_2CH_2PNO)]$ (**4**) has been formed. Unexpectedly, the same reaction with **HPNBr** led to $[Re(CO)_3Br(\kappa^2\text{-}PPh_3oxaz)]$ (**5**). Compound **5** is the first example of a Re(I) complex anchored on a phosphorus−oxazoline ligand, generated during the course of complex formation. All the compounds were fully characterized by ^1H and ^{31}P NMR spectroscopy and, in the case of **4** and **5**, by X-ray crystallographic analysis.

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Supporting Information Available: Crystallographic data for the structures **4** and **5**, in CIF format, can be obtained free of charge via the Internet at http://pubs.acs.org.

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