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First examples of neutral rhenium(V) complexes with a novel semi-rigid ligand containing a P,N,N,S donor atom set: Synthesis, characterisation and crystal structure

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Abstract

A new PN₂S ligand, *N*-[2-(diphenylphosphino)phenyl]-2-[(*S*-trityl)acetylaminomethanamide] [Ph-P(Ph₂)N₂S(Trt)], was synthesised and reacted with Re^V precursors. The reaction of both tritylated and detritylated ligands with ReOCl₃(PPh₃)₂ gave the same expected neutral complex [ReO{Ph-P(Ph₂)N₂S}] (**4**) in good yield. An unexpected neutral and diamagnetic species, [ReN{Ph-P(Ph₂)N₂S(Trt)}] (**5**), has been isolated during the complexation of the tritylated ligand with ReNCl₂(PPh₃)₂. The complexes, characterized by classical spectroscopic methods and X-ray analysis for **4**, are the first examples of neutral semi-rigid-PN₂S rhenium(V) complexes.

Keywords: Tetradentate PN₂S ligand; Rhenium complexes; Crystal structure; Phosphine

1. Introduction

Rhenium(V) complexes are of interest because of the potential use of ^{186/188}Re in nuclear medicine and the chemical similarity of Re/Tc, largely used for the design of ^{99m}Tc radiopharmaceuticals [1]. Consequently, inorganic chemistry studies with the long-lived β-emitting isotope ^{99g}Tc (weak β⁻emitter, *E*_{max} = 0.294 MeV, *t*_{1/2} = 2.12 × 10⁵ years) or with the naturally occurring non-radioactive rhenium isotopes (¹⁸⁵Re: 37.07%, ¹⁸⁷Re: 62.93% abundance) are still very attractive in order to clearly establish the molecular structure of ^{99m}Tc- and ^{186/188}Re-based radiopharmaceuticals. One of the most important prerequisites

in the design of new classes of technetium/rhenium ligands is the development of highly stable complexes with these metals and the elucidation of their structures [2]. In a previous work, we have developed a new family of tetradentate semi-rigid ligands, Ph-XN₂S(Trt) [3]. We have shown that the incorporation of an aromatic ring fused into the chelate backbone imparted rigidity to a portion of the ligand, enhancing the formation and stability of the resulting complex by an entropy effect. Moreover, we have demonstrated that the nature of the donor atom set and more particularly the nature of the X aromatic function influenced the stability of the corresponding metallic complexes. Thus, coordination of Ph-XN₂S-type ligands acting as a tetraanionic ligand X⁻N⁻N⁻S⁻ (X = O, S, NH, NMe) towards the usual rhenium precursor ReOCl₃(PPh₃)₂ in the presence of sodium acetate gave straightforwardly highly stable anionic complexes of the general formula [Na][ReO(Ph-XN₂S)] under mild conditions [4]. In return, we never have been able to isolate

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the stable analogous neutral ReO complexes starting with Ph-XN₂S-type ligands acting as a trianionic ligand XN⁻N⁻S⁻ (X = OMe, SMe, NMe₂).

Due to their tendency to delocalize the electron density on the metal – a result of their σ -donor and π -acceptor character – phosphines often lead to the stabilization of the complexes in which they are contained [5]. This led us to anticipate that the incorporation of one phosphine group in the chelate ring should enhance the reactivity of the ligand towards the MO³⁺ core (M = Tc or Re) and consequently increase the stability of the resulting neutral metallic complexes. This expectation has been realized in the isolation of two neutral semi-rigid PN₂S rhenium(V) complexes and the structural characterization of one of them, [ReO{Ph-P(Ph₂)N₂S}] (4). To our knowledge, these compounds are the first Re^VN and Re^VO species including a semi-rigid PN₂S framework, the only previous examples in ReO chemistry being the PN₂S-tetradentate monooxo-rhenium complexes obtained with the non-semi-rigid ligands 3-diphenylphosphinoglycyl-L-(S-protected)cysteine and its methyl ester [6]. It is noteworthy that a Re^VO species including a semi-rigid Ph-P₂N₂ framework has been reported by Tisato et al. [7].

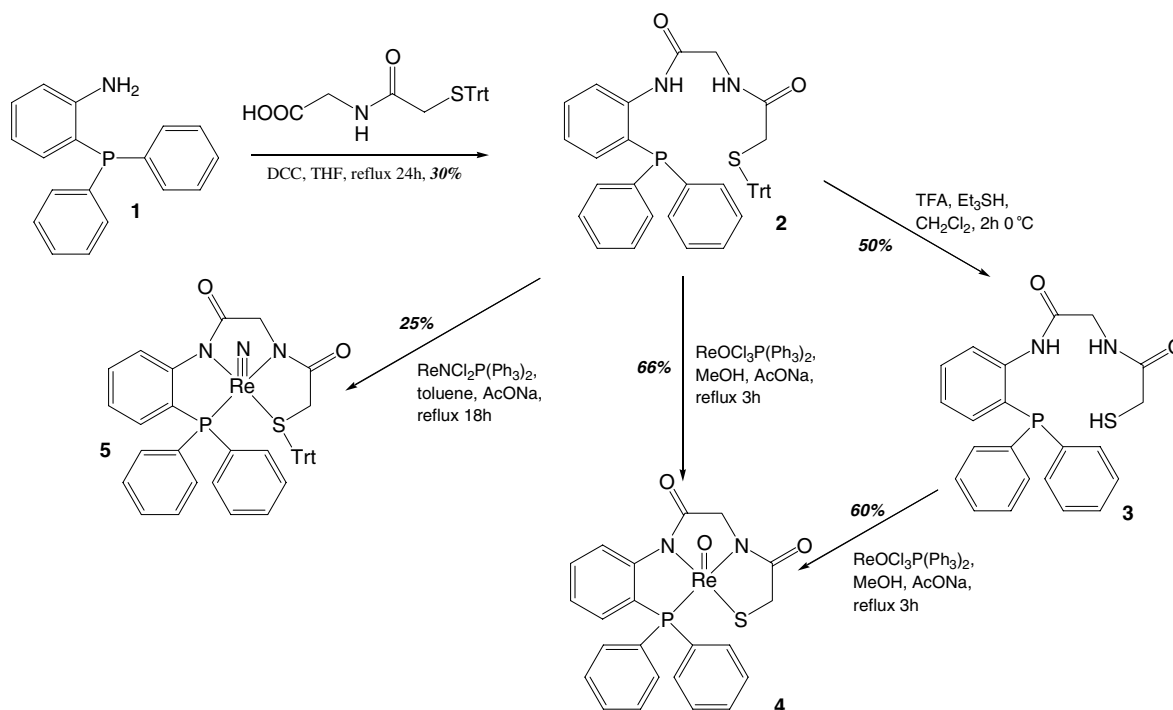
2. Results and discussion

The ligands of this study have been prepared under a strictly inert atmosphere according to the method outlined in Scheme 1. Thus, reaction of 2-iodoaniline with diphenylphosphine in the presence of NEt₃ and Pd(PPh₃)₄ as a catalyst in warm acetonitrile afforded the 2-diph-

enylphosphinoaniline (1), in quite good yield [8]. A conventional carbodiimide amide coupling of *N*-[(S-trityl)acetyl]glycine [3b] with 1 in THF, followed by the cleavage of the trityl group under acidic conditions (TFA, Et₃SiH) [9] gave the ligands [Ph-P(Ph₂)N₂S(Trt)] (2) and [Ph-P(Ph₂)N₂SH] (3), respectively. The ligands showed good solubility in methanol, ethanol, dichloromethane, chloroform and acetonitrile. They were characterized by elemental analysis, ¹H and ³¹P NMR spectroscopy, all consistent with the formula shown in Scheme 1. In particular, the ³¹P spectra of 2 and 3 revealed only one peak at ≈ -21.5 ppm corresponding to P^{III} species. The IR spectrum of 3 exhibited an absorption band at 2482 cm⁻¹, which corresponds to the S-H stretching vibration.

Ligand-exchange reactions in warm methanol of labile ReOCl₃(PPh₃)₂ with a slight excess of the relevant tritylated or detritylated ligand (1:1.2 metal:ligand ratio) in the presence of a methanolic sodium acetate solution as a deprotonating agent led to the same neutral complex 4 in satisfactory yield (Scheme 1). The cleavage of the trityl group of 2, accomplished during the coordination of the ligand to the ReO³⁺ core, is explained by the acidic contribution of the metal (Lewis acid) in the mechanism of sulfur detritylation. Complex 4 crystallised from CH₂Cl₂/hexane solution by slow evaporation and afforded purple crystals suitable for X-ray analysis.

The spectroscopic characteristics of the oxo-rhenium complex 4 of the general formula [ReO{Ph-P(Ph₂)N₂S}], as evident from the elemental analysis, were similar to the analogous anionic complexes described previously [3b,10], i.e. (i) the characteristic rhenium(V) oxo isotopic pattern



Scheme 1. Synthesis of compounds 4 and 5.

consistent with the presence of a neutral mononuclear complex ($[M+H^+] = 607/609$), (ii) an intense band in the IR spectrum attributable to the Re=O stretching vibration at 966 cm^{-1} , (iii) a non-equivalence of the two hydrogens of each methylene group (AX pattern) of the tetradentate ligand framework in the proton NMR spectrum, the downfield signal of both AX patterns being assigned to the *endo* protons (*syn* to the Re=O group) and the upfield signals to the *exo* ones (*anti* to the Re=O group) [6b,11]. The ^{31}P NMR spectrum showed a singlet peak in agreement with phosphine coordination, [12] the pertinent peak moving downfield to the +38.7 ppm positive region from the -21.6 and -21.2 ppm values exhibited by the uncoordinated detriylated and triylated ligands, respectively. Thus only one single isomer was produced. The formation of a single isomer is important as isomerism can markedly influence the pharmacokinetics of a radiopharmaceutical [13].

As shown in Fig. 1, the crystal structure of **4** consists of a discrete monomeric and neutral monooxo complex packed with no intermolecular contacts shorter than the van der Waals radii sum. Selected interatomic distances and bond angles are listed in Table 2. The coordination geometry about the metal is distorted square pyramidal with the phosphorous of the linked phosphine, the two amide nitrogen and the sulfur atom occupying the equatorial plane and the oxo group directed in the apical position. The description in terms of a square pyramid is supported by the nearly equal N(2)-Re(1)-S(1) and N(1)-Re(1)-P(1) angles, leading to a very low trigonality index τ of 0.05 (N(2)-Re(1)-S(1) = $135.91(15)^\circ$ and N(1)-Re(1)-P(1) = $138.88(14)^\circ$) [14]. This value is similar to those found for our analogous anionic complexes ($0.00 < \tau < 0.07$) [4,10] and the semi-rigid neutral complex [ReO{Ph-N₃O}] recently developed by Papachristou et al. [15] ($\tau = 0.01$). The Re atom lies 0.78 Å above the basal plane, which is reflected by the O=Re-N and O=Re-S/P angles ranging from $106.73(15)^\circ$ to $114.1(2)^\circ$. This value is in agreement with the displacement normally observed for square-pyramidal rhenium complexes [4,16]. The tetradentate coordination mode of the triply deprotonated ligand leads to a

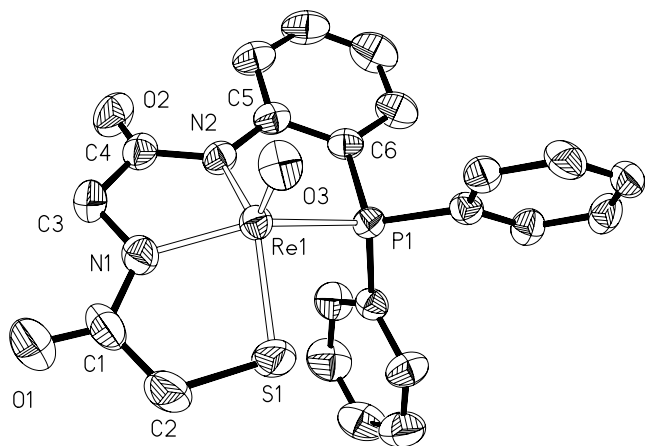


Fig. 1. ORTEP diagram of **4** with 50% probability thermal ellipsoids showing the atomic labelling scheme.

three (5,5,5)-membered chelate ring system around the rhenium atom. The two phenyl rings of the phosphine are roughly perpendicular to the Ph-PN₂S plane; the mean planes passing through them make angles of 87.9° and 125.0° with the pyramidal basal plane. The same planes define an angle to each other of 64.2° .

The valence bond distances are unexceptional and are within the range observed for Re-oxo (1.675(4) Å), Re-N_{amide} (ca. 1.99 Å) and Re-S_{thiolate} (2.2614(17) Å) bonds in ReO five-coordinate square-pyramidal complexes. The dominating feature of this structure is the Re-P distance. The latter is 2.4052(14) Å, and it is far shorter than that reported for the non-semi-rigid [ReO{P(Ph₂)N₂S}] compound developed by Mazzi et al. [6b] 2.4446(2) Å. The rigidity imposed by the aromatic ring conjugated with the strained five-membered chelate ring Re(1)-P(1)-C(6)-C(5)-N(2) instead of a six-membered chelate ring for the Mazzi complex explains this difference. Consequently, the P(1)-Re(1)-N(2) angle is shorter in our complex than in Mazzi's one ($78.84(14)^\circ$ versus $90.5(2)^\circ$). It is noteworthy that the length of the X-Re bond in our [ReO(Ph-XN₂S)] complexes (X = O, S, NH, PPh₂) is greatly influenced by the nature of the X atom. As expected, the bulkier is the X atom, the longer is the X-Re bond, with the following order: $d_{\text{N-Re}} 1.968(2)\text{Å} < d_{\text{O-Re}} 2.000(4)\text{Å} \ll d_{\text{S-Re}} 2.2969(18)\text{Å} < d_{\text{P-Re}} 2.4052(14)\text{Å}$. In return, there are no significant differences for the other Re-N or Re-S bonds.

By using the above coordination conditions, treatment of **2** with the ReNCl₂(PPh₃)₂ precursor afforded an intractable mixture, from which the isolation of pure and defined species was not possible. Surprisingly, use of solid sodium acetate as a deprotonating agent and toluene instead of methanol as the solvent allowed us to isolate an unprecedented non-detriylated neutral nitridorhenium(V) complex in 25% yield, as sketched in Scheme 1. [ReN{Ph-P(Ph₂)N₂S(Trt)}] (**5**) was characterized by spectroscopical methods, even though crystals suitable for X-ray work could not be obtained. In particular, both ^{31}P and ^1H NMR spectra demonstrated that **5** is diamagnetic, suggesting a low-spin d² configuration, typical of distorted octahedral or distorted square-pyramidal species bearing a multiple oxo- or nitrido-core [17]. The presence of the trityl group is revealed by the integration ratio of total aromatic/aliphatic protons (29/4), consistent with three more phenyl rings in the complex. As expected, the methylene protons of the tetradentate ligand framework were found to be diastereotopic (AX pattern) with coupling constants in the range 17.5–19.5 Hz (Fig. 2). The DCI-MS spectrum of complex **5** showed the production of molecular cations at m/z 848/850 ([M+H⁺]) and m/z 865/867 ([M+NH₄⁺]), with a detectable fragment ion at m/z 243 ([Trt⁺]), revealing the loss of the trityl group. The IR spectrum of **5** exhibited an absorption band at 1098 cm^{-1} assigned to the characteristic ReN stretching vibration. No multiple strong bands were detected in the ranges 1500–1560 and 3200–3400 cm^{-1} of complex **5**, confirming the deprotonation of the amide functions. The complex is

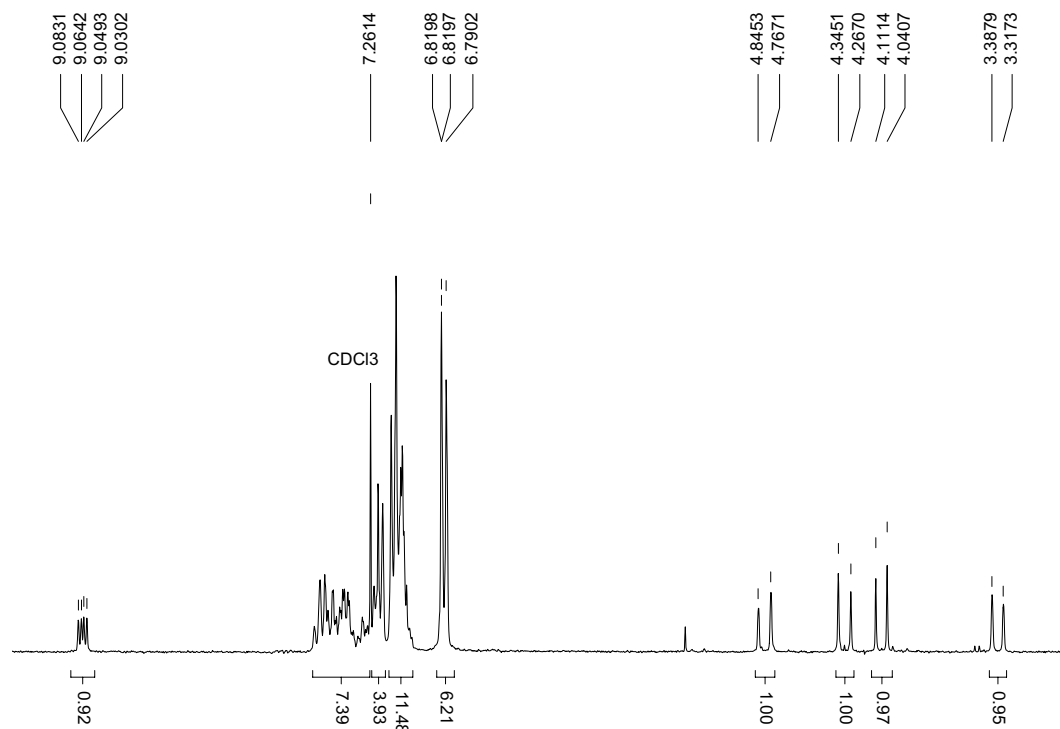


Fig. 2. ^1H NMR spectrum of $[\text{ReN}\{\text{Ph-P}(\text{Ph}_2)\text{N}_2\text{S}(\text{Trt})\}]$ (**5**) (CDCl_3 ; 250 MHz; 25 $^\circ\text{C}$).

non-conducting in acetonitrile solutions, as expected [18]. So, chelation of the ReN core proceeds by coordination with the PN_2S^{2-} donor atom set formed from one neutral phosphine, two deprotonated amide groups and one neutral thioether. This is the first example where metal catalysed removal of the trityl group does not occur during a Re^{V} complexation.

The isolation of these two complexes conjugated with the fact that we never succeeded in isolating a neutral Re^{V} complex with $[\text{Ph-X}(\text{Me})\text{N}_2\text{S}(\text{Trt})]$ ligands ($\text{X} = \text{O}$ or S) suggested that the phosphorus atom of the chelate (i) enhances the reactivity of the ligand towards the ReO^{3+} core, (ii) binds first to the metal and this bond acts as the driving force for coordination. The latter hypothesis is consistent with the mechanism proposed by Visentin et al. for their similar ReO complexes with a P,N,N,S donor atom set [6b]. Our complexes are extremely stable in the solid state as well as in organic solvents for long periods of time, as shown by NMR spectroscopy. Their stability is not affected by the presence of air. The mixing of a π -donor S atom with a π -acceptor P atom ensures an appropriate electronic balance around the ReO or ReN core and this event contributes to the overall robustness of the system.

3. Conclusion

In conclusion, the new semi-rigid PN_2S ligand studied here exhibits high chelating affinity for the rhenium(V) core. A neutral stable monooxorhenium(V) complex was produced as a single isomer by reacting the tritylated or detritylated ligand with a ReO precursor, in good yield. The high

affinity of the PN_2S set toward $\text{Re}^{\text{V}}\text{O}$ can be expected also for $^{99\text{m}}\text{TcO}$, making this ligand potentially useful as a $^{99\text{m}}\text{TcO}$ -based brain perfusion or brain receptor imaging agent. A radio-labelling study with $^{99\text{m}}\text{Tc}$ will start soon. Investigations on the unexpected neutral complex $[\text{ReN}\{\text{Ph-P}(\text{Ph}_2)\text{N}_2\text{S}(\text{Trt})\}]$, isolated during the complexation of the tritylated ligand with $\text{ReNCl}_2(\text{PPh}_3)_2$, are still going on to better understand the formation of this complex.

4. Experimental

4.1. General methods

All preparations and manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. All chemicals were of the highest purity commercially available. Rhenium(VII) oxide was purchased from Aldrich Chem. Co. It was converted to $\text{ReOCl}_3(\text{PPh}_3)_2$ and $\text{ReNCl}_2(\text{PPh}_3)_2$ according to published protocols [19]. Solvents were dried and distilled by standard methods before use and stored over 0.3 nm molecular sieves. 2-(diphenylphosphino)aniline (**1**) [8] and N -[(S -trityl)acetyl]glycine [3b] were prepared as described previously. Silica gel (0.060–0.200 nm) was purchased from Acros. TLC was performed using precoated Kieselgel 60 plates F_{254} (TLC plates, Merck) and was visualised by UV or iodine. Column chromatography was carried out using “gravity” silica (Merck). Infrared spectra (4000–400 cm^{-1}) were recorded as KBr pellets on a Vector 22 Bruker spectrophotometer. NMR spectra were recorded on a Bruker AC 200 (81.015 MHz for ^{31}P) and AC 250

apparatus (250.133 MHz for ^1H). Chemical shifts are indicated in δ values (ppm) downfield from internal TMS. For the $^{31}\text{P}\{^1\text{H}\}$ spectra the external standard was H_3PO_4 (82% D_2O , $\delta = 0.0$ ppm). DCI-Mass spectra were obtained on a NERMAG R10-10 mass spectrometer. Microanalysis was performed by the Microanalytical Department of the Ecole Nationale Supérieure de Chimie de Toulouse.

4.2. Synthetic work

4.2.1. *N*-[2-(diphenylphosphino)phenyl]-2-[(triphenylmethylmercapto)methylcarbonylamino]ethanamide (**2**)

N-[(*S*-trityl)acetyl]glycine (1.957 g, 5 mmol) and **1** (1.385 g, 5 mmol) were dissolved in anhydrous degassed THF (25 mL). Dicyclohexylcarbodiimide (1.135 g, 5.5 mmol) was added and the mixture was heated at reflux for 24 h. After cooling to room temperature, the insoluble dicyclohexylurea was removed by filtration and the filtrate evaporated under reduced pressure. The obtained brown oil was dissolved in AcOEt (20 mL) and cooled at 0°C . A white solid was collected by filtration and washed with cold AcOEt. The solid was purified by column chromatography on silica gel (eluent: $\text{CH}_2\text{Cl}_2/\text{AcOEt}$, 96/4) to give **2** as a white powder (1.002 g, 30%).

Anal. Calc. for $\text{C}_{41}\text{H}_{35}\text{N}_2\text{O}_2\text{PS}$: C, 75.67; H, 5.42; N, 4.30; S, 4.93. Found: C, 75.37; H, 5.22; N, 4.10; S, 5.22%; IR (KBr): ν (cm^{-1}) 3328, 3269 (NH); 3052 (CH_{Ar}), 1702, 1652 (CO); 1026 (P–C); MS (DCI/ NH_3) m/z 243 [Trt^+], 651 [$\text{M}+\text{H}^+$]; 667, [$\text{M}+\text{NH}_4^+$]; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ (ppm): -21.2 (s); ^1H NMR (CDCl_3) δ (ppm): 3.15 (s, 2H, SCH_2); 3.49 (d, 2H, $J = 5.5$ Hz, CH_2N); 6.42 (broad s, 1H, NH); 6.85–7.56 (m, 28H, CH_{Ar}); 8.09 (broad s, 1H, NH); 8.22 (m, 1H, CH_{Ar}).

4.2.2. *N*-[2-(diphenylphosphino)phenyl]-2-[mercaptomethylcarbonylamino]ethanamide (**3**)

To a chilled solution of **2** (0.250 g, 0.38 mmol) in degassed CH_2Cl_2 (30 mL) were added TFA (13 mL) and triethylsilane (121 μL , 0.76 mmol). The solution became colourless and it was stirred for 2 h. After removal of the solvents under vacuum, the resulting residue was crystallised as a white powder upon addition of hexane (77 mg, 50%).

Anal. Calc. for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_2\text{PS}$: C, 64.69; H, 5.18; N, 6.86; S, 7.85. Found: C, 64.80; H, 5.01; N, 6.50; S, 7.64%; IR (KBr) ν (cm^{-1}) 3338, 3241 (NH); 2482 (SH); 1696, 1640 (CO); MS (DCI/ NH_3): m/z 409 [$\text{M}+\text{H}^+$]; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ (ppm): -21.6 (s); ^1H NMR (CDCl_3) δ (ppm): 1.33 (t, 1H, $J = 8.8$ Hz, SH); 3.22 (d, 2H, $J = 8.8$ Hz, SCH_2); 3.93 (d, 2H, $J = 5.5$ Hz, CH_2N); 6.90 (m, 1H, NH); 6.92 (m, 1H, CH_{Ar}); 7.06–7.41 (m, 11H, CH_{Ar}); 7.55 (m, 1H, CH_{Ar}); 8.10 (broad s, 1H, NH); 8.35 (m, 1H, CH_{Ar}).

4.2.3. [*N*-(2-diphenylphosphinophenyl)-2-(mercaptomethylcarbonylamino)ethanamido(4-)- $\kappa^4\text{P},\text{N},\text{N}',\text{S}$]nitridorhenate(V) or [*ReN*{*Ph*-*P*(*Ph*₂)*N*₂*S*}] (**4**)

Method 1: To a suspension of **2** (200 mg, 0.308 mmol) and $\text{ReOCl}_3(\text{PPh}_3)_2$ (307 mg, 0.370 mmol) in degassed

MeOH (30 mL) was added a 1 M solution of sodium acetate in degassed MeOH (3 mL, 3 mmol). After refluxing for 3 h, the solution turned violet and clear. After cooling, the solution was filtered off and evaporated to dryness. The obtained brown violet solid was recrystallised from $\text{CH}_2\text{Cl}_2/\text{hexane}$ (2/1) to afford **4** as a violet powder (123 mg, 66%).

Method 2: The same procedure as method 1 starting with **3** (50 mg, 0.122 mmol), $\text{ReOCl}_3(\text{PPh}_3)_2$ (122 mg, 0.147 mmol) and sodium acetate in MeOH (1 mL, 1 mmol). After recrystallisation, **4** was obtained as a violet powder (44 mg, 60%).

Anal. Calc. for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_3\text{PReS}$: C, 43.49; H, 2.99; N, 4.61; S, 5.28. Found: C, 43.60; H, 3.12; N, 4.58; S, 5.12%; IR (KBr): ν (cm^{-1}) 1665, 1647 (CO); 966 (ReO); MS (DCI/ NH_3): m/z (%) 607 (11), 609 (20) [$\text{M}+\text{H}^+$], 623 (1), 625 (2) [$\text{M}+\text{NH}_4^+$]; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ (ppm): 38.7 (s); ^1H NMR (CDCl_3) δ (ppm): 3.88 (d, 1H, $J = 17.4$ Hz, SCH_2); 4.04 (d, 1H, $J = 17.4$ Hz, SCH_2); 4.78 (d, 1H, $J = 19.0$ Hz, CH_2N); 5.22 (d, 1H, $J = 19.0$ Hz, CH_2N); 7.20 (t, 1H, $J = 7.3$ Hz, CH_{Ar}); 7.28–7.91 (m, 12H, CH_{Ar}); 9.10 (dd, 1H, $J_{\text{HH}} = 8.5$ Hz, $J_{\text{HP}} = 4.6$ Hz, CH_{Ar}).

4.2.4. [*N*-(2-diphenylphosphinophenyl)-2-[(triphenylmethylmercapto)methylcarbonylamino]ethanamido(4-)- $\kappa^4\text{P},\text{N},\text{N}',\text{S}$]nitridorhenate(V) or [*ReN*{*Ph*-*P*(*Ph*₂)*N*₂*S*(*Trt*)}] (**5**)

To a suspension of **2** (200 mg, 0.308 mmol) and $\text{ReNCl}_2(\text{PPh}_3)_2$ (294 mg, 0.370 mmol) in degassed toluene (30 mL) was added sodium acetate (304 mg, 3.7 mmol). After refluxing for 18 h the solution turned brown and clear. After cooling, the solution was filtered off and evaporated to dryness. Addition of ether (10 mL) gave a precipitate which was filtered off. The precipitate was dissolved in CH_2Cl_2 . Addition of hexane gave a precipitate which was filtered off. The filtrate was concentrated to give **5** as a red-dish-brown powder (65 mg, 25%).

Anal. Calc. for $\text{C}_{41}\text{H}_{33}\text{N}_3\text{O}_2\text{PReS}$: C, 58.00; H, 3.92; N, 4.95; S, 3.78. Found: C, 58.08; H, 4.20; N, 4.60; S, 3.56%; IR (KBr): ν (cm^{-1}) 3050 (CH_{Ar}); 1661, 1637 (CO); 1098 (ReN); MS (DCI/ NH_3): m/z (%) 243 (14) [Trt^+], 848 (60), 850 (100) [$\text{M}+\text{H}^+$], 865 (3), 867 (6) [$\text{M}+\text{NH}_4^+$]; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ (ppm): 39.0 (s); ^1H NMR (CDCl_3) δ (ppm): 3.31 (d, 1H, $J = 17.6$ Hz, SCH_2); 4.04 (d, 1H, $J = 17.6$ Hz, SCH_2); 4.26 (d, 1H, $J = 19.5$ Hz, CH_2N); 4.76 (d, 1H, $J = 19.5$ Hz, CH_2N); 6.70–6.82 (m, 6H, CH_{Ar}); 7.05–7.60 (m, 22H, CH_{Ar}); 9.05 (dd, 1H, $J_{\text{HH}} = 8.5$ Hz, $J_{\text{HP}} = 4.7$ Hz, CH_{Ar}). A_{M} (CH_3CN): $21.10 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ (neutral).

4.3. X-ray crystal structure determination of complex **4**

[$\text{ReO}\{\text{Ph}-\text{P}(\text{Ph}_2)\text{N}_2\text{S}\}$] (**4**) was crystallised by slow evaporation of a $\text{CH}_2\text{Cl}_2/\text{hexane}$ solution. A purple crystal of **4** thus produced was mounted on a Nonius Kappa CCD diffractometer equipped with a CDD detector, and was used for data collection. X-ray intensity data were collected with

Table 1
Summary of the crystal data for complex 4

Complex	[ReO{Ph-P(Ph ₂)N ₂ S}]
Empirical formula	C ₂₂ H ₁₈ N ₂ O ₃ PrReS
Molecular weight	607.635
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Crystal size (mm)	0.56 × 0.16 × 0.06
<i>a</i> (Å)	9.2572(6)
<i>b</i> (Å)	13.0513(3)
<i>c</i> (Å)	17.6436(14)
β (°)	100.107(6)
<i>V</i> (Å ³)	2098.6(2)
<i>Z</i>	4
<i>d</i> [g/cm ³]	1.923
<i>F</i> (000)	1176
Total reflections	39 174
Independent reflections	3621
Parameters	272
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	3621
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0351, <i>wR</i> ₂ = 0.0817
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0471, <i>wR</i> ₂ = 0.0917
Goodness-of-fit	1.109

Table 2
Selected bonds lengths (Å) and angles (°) for complex 4

Bond lengths			
Re(1)–O(3)	1.675(4)	C(2)–S(1)	1.821(7)
Re(1)–P(1)	2.4052(14)	C(1)–N(1)	1.364(9)
Re(1)–N(2)	2.046(5)	C(4)–N(2)	1.402(7)
Re(1)–N(1)	1.981(6)	C(6)–P(1)	1.806(6)
Re(1)–S(1)	2.2614(17)		
Bond angles			
O(3)–Re(1)–N(1)	113.8(2)	N(2)–Re(1)–N(1)	78.9(2)
O(3)–Re(1)–P(1)	106.73(15)	N(1)–Re(1)–S(1)	82.53(16)
O(3)–Re(1)–N(2)	114.1(2)	P(1)–Re(1)–S(1)	90.01(6)
O(3)–Re(1)–S(1)	110.00(17)	N(2)–Re(1)–S(1)	135.91(15)
P(1)–Re(1)–N(2)	78.84(14)	P(1)–Re(1)–N(1)	138.88(14)

graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at a temperature of 298 K. The most significant details of the crystallographic study are reported in Table 1. A collection of selected bond distances and angles are shown in Table 2. The structure was solved by direct methods. All the non-hydrogen atoms were refined anisotropically using the full-matrix, least-squares procedure based on *F*². Structure determination and refinement were performed using the MAXUS [20] and SHELX-97 [21] programs. 3621 independent reflections with *I* ≥ 2σ(*I*) were used for refinement of the unit cell ($\theta \leq 25^\circ$). Hydrogens for the mater molecule were not located.

Appendix A. Supplementary material

CCDC 651266 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data

Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2007.07.032](https://doi.org/10.1016/j.poly.2007.07.032).

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