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New Water-Soluble Rhenium Complexes with 1,3,5-Triaza-7-phosphaadamantane (PTA) – X-ray Crystal Structures of [ReNCl$_2$(PTA)$_3$], [ReO$_2$Cl(PTA)$_3$], [ReCl$_3$(PTA)$_2$(PPh$_3$)], and [Re$_2$N$_2$Cl$_3$(Et$_2$dtc)(PTA)$_4$]

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The new water-soluble nitrido complex [ReNCl$_2$(PTA)$_3$] (**1**) was obtained by treatment of [ReNCl$_2$(PPh$_3$)$_2$] with four equivalents of PTA (1,3,5-triaza-7-phosphaadamantane). The reaction of [ReOCl$_2$X(PPh$_3$)$_2$] (X = Cl$^-$, EtO$^-$) with six equivalents of PTA gave the neutral dioxido species [ReO$_2$Cl(PTA)$_3$] (**2**). The formation of a rhenium(III) species of formula [ReCl$_3$(PTA)$_2$(PPh$_3$)] (**3**) is also described. The reaction of **1** with Na[Et$_2$dtc] (Et$_2$dtc = *N*,*N*-diethyldithiocarbamate) yielded the neutral compound [ReNCl(Et$_2$dtc)(PTA)$_2$] (**4**). Recrystallization of **4** afforded an unexpected dinuclear species [Re$_2$N$_2$Cl$_3$(Et$_2$dtc)(PTA)$_4$] (**5**), containing an asymmetric Re≡N–Re group. The nitrido compound [ReN(Et$_2$dtc)$_2$(PTA)] (**6**), was obtained by adding two equivalents of Na[Et$_2$dtc] to complex **1** or one equivalent to complex **4**. The X-ray crystal structures of the new PTA complexes **1**, **2**, **3**, and **5** have been determined.

Introduction

Rhenium coordination chemistry has attracted attention in view of the development of therapeutic agents. In fact, two isotopes of rhenium are β-emitters (^{186}Re, E_{max} = 1.1 MeV, $t_{1/2}$ = 90.64 h; ^{188}Re, E_{max} = 2.1 MeV, $t_{1/2}$ = 17 h) and therefore they are suitable candidates for therapeutic applications by means of β-irradiation in radiotherapy. In particular, the availability of a ^{188}W/^{188}Re generator[1] makes rhenium-188 the more promising choice for the development of radiopharmaceuticals for cancer therapy.[2] Also, ^{186}Re has a photon emission at approximately the same energy as ^{99m}Tc (γ = 137 keV) allowing the radioisotope to be imaged by γ-cameras utilized in ^{99m}Tc diagnostic imaging. The periodic relationship between Tc and Re suggests that ^{99m}Tc diagnostic agents may be used as a model in the design of ^{186,188}Re radiopharmaceuticals which may possess similar biodistribution properties[3]; the reverse case is also true. A rhenium radiopharmaceutical, ^{186}Re-HEDP, has been developed for the palliation of painful bone metastases.[4]

Rhenium and technetium show a very rich coordination chemistry due to their variety of stable oxidation states ranging from –1 to +7; moreover they are able to coordinate different ligands giving complexes with various coordination geometries. This versatility is stressed in particular cores which have been studied for developing new radiopharmaceuticals. These are oxido-Tc/Re^V [M=O]$^{3+}$,[5] nitrido-[M≡N]$^{2+}$,[6] hydrazino-metal(III) [MNNR]$^{n+}$[7], and more recently, carbonyl-Tc/Re^I *fac*-[M(CO)$_3$]$^+$[8] cores. Since the chemical species eluted from the radionuclide generator are [MO$_4$]$^-$, many studies have been focused on oxido-metal(V) complexes containing the [M=O]$^{3+}$ fragment, which is readily obtained by facile reduction of Tc and Re permetalates. In the +5 oxidation state, Tc and Re complexes are five- or six-coordinate species showing square pyramidal, trigonal bipyramidal, and octahedral geometries. The most-common starting materials for Re^V chemistry are represented by the oxido-Re^V complex [ReOCl$_3$(PPh$_3$)$_2$] and the nitrido complex [ReNCl$_2$(PPh$_3$)$_2$]. They are the synthetic precursors of a wide variety of well-characterized oxido and nitrido compounds, obtained by ligand-exchange reactions. These precursors, as well as many of their derivatives, include PPh$_3$ in their coordination sphere. It is well known that aryl- or alkylphosphanes are common ligands which influence both steric and electronic properties of metal complexes and stabilize low oxidation states. On the other hand, the hydrophobicity, high molecular weight, and low biocompatibility of arylphosphanes makes their complexes unsuitable for medical purposes; for this reason the replacement of PPh$_3$ with more hydrophilic and biocompatible phosphanes is a very important challenge.

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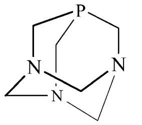
The solubility in water of phosphanes can be achieved by introducing polar or ionic substituents such as sulfonate, carboxylate groups. Examples of water-soluble arylphosphanes are represented by the sulfonated analogues of the corresponding mono-, bi- or tridentate arylphosphanes.

The water solubility of coordination compounds can be also enhanced utilizing water-soluble cage-like phosphanes.

PTA (1,3,5-triaza-7-phosphaadamantane, IUPAC nomenclature: 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane) is a cage-like, adamantane-type phosphane. Synthesized by Daigle in 1974,[9] PTA and its derivatives received renewed interest in the 1990s with the development of research of water-soluble metallo-phosphane catalysts.[10] They are also excellent hydrophilic components of transition-metal compounds for applications in medicine and biology. The high hydrophilicity and small size of PTA combined with its chemical and thermal stability makes this phosphane unique in comparison with other alkyl or arylphosphanes.



PTA
1,3,5-triaza-7-phosphaadamantane

An exhaustive report of the chemistry of PTA towards transition metals, its applications in homogeneous catalysis and in medicinal chemistry has been recently published by Peruzzini et al.[11] To date ruthenium and platinum compounds[12] have been the focus of interest in relation to use of PTA complexes as medicinal compounds although ^{99m}Tc complexes such as ^{99m}Tc-fosfim® and ^{99m}Tc-furifosfim® are currently used in diagnostic nuclear medicine for myocardial perfusion.[5a]

In an effort to develop new water-soluble precursors of rhenium for radiopharmaceutical applications, we attempted to exchange PPh_3 with PTA in $[ReOCl_3(PPh_3)_2]$ and $[ReNCl_2(PPh_3)_2]$. The syntheses of the nitrido $[ReNCl_2(PTA)_3]$ and dioxido $[ReO_2Cl(PTA)_3]$ complexes, their characterization by spectroscopic techniques and their reactivity with sodium *N*,*N*-diethyldithiocarbamate are described herein.

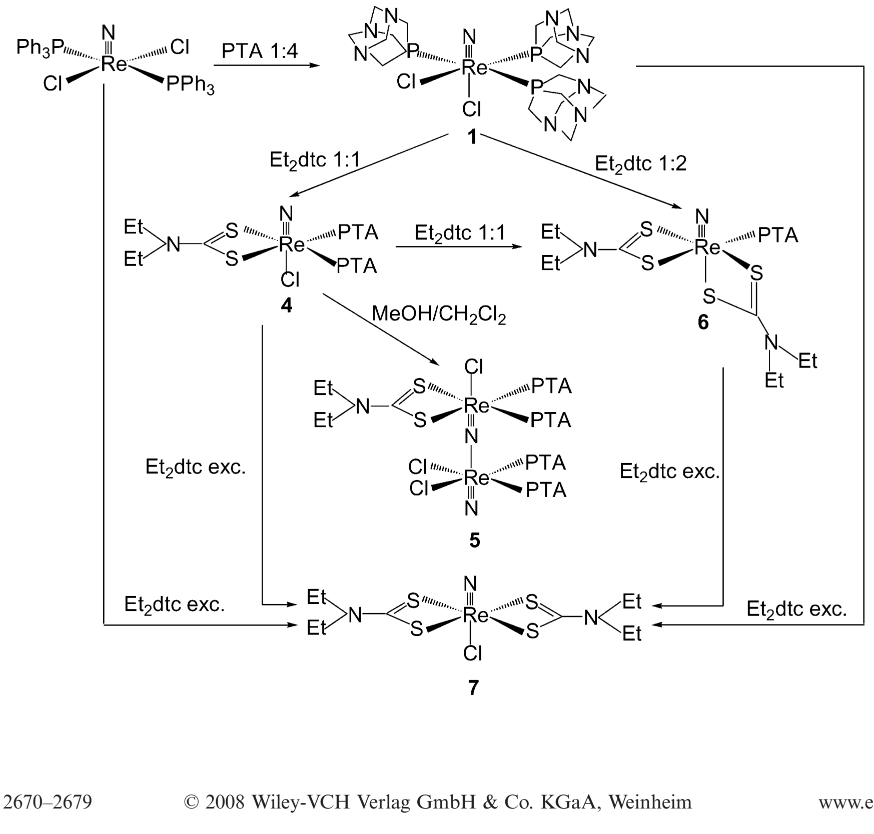
Finally, the X-ray crystal structures of four new PTA-Re complexes are reported.

Results and Discussion

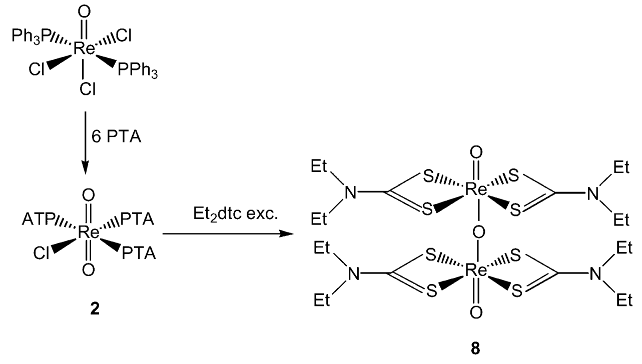
Synthesis and Characterization of Nitridorhenium(V) [ReNCl$_2$(PTA)$_3$] (1) and *trans*-Dioxidorhenium(V) [ReO$_2$Cl(PTA)$_3$] (2) Complexes

The nitridorhenium complex **1** was prepared by a ligand exchange reaction using $[ReNCl_2(PPh_3)_2]$ as the precursor in a 1:4 metal to PTA ratio (Scheme 1).

The *trans*-dioxidorhenium compound $[ReO_2Cl(PTA)_3]$ (**2**) was prepared in a similar manner using $[ReOCl_2X(PPh_3)_2]$ ($X = Cl^-$, OMe^-, OEt^-) as the precursor but in a 1:6 metal/PTA ratio (Scheme 2). An excess of PTA was required to minimize the formation of by-products. Complexes **1** and **2** were isolated as crystalline products from CH_2Cl_2/Me_2CO and $CH_2Cl_2/EtOH$ respectively and fully characterized also by X-ray crystallography. Both complexes are soluble in water ($S_{20\,°C} \approx 0.5\ g\,mL^{-1}$ for **1** and $S_{20\,°C} \approx 0.36\ g\,mL^{-1}$ for **2**) and slightly soluble in polar organic solvents.



Scheme 1.



Scheme 2.

Table 1. Selected bond lengths and angles [Å, °] for compound **1**.

Bond lengths	A	B		A	B
Re1–N1	1.708(4)	1.679(4)	Re1–P1	2.377(1)	2.386(1)
Re1–Cl1	2.634(1)	2.624(1)	Re1–P2	2.441(1)	2.453(1)
Re1–Cl2	2.444(1)	2.444(2)	Re1–P3	2.449(1)	2.439(1)
Angles					
N1–Re1–Cl1	168.7(2)	169.6(2)	Cl1–Re1–P3	92.96(4)	91.10(4)
N1–Re1–Cl2	104.1(2)	103.3(2)	Cl2–Re1–P1	163.19(5)	166.11(5)
N1–Re1–P1	92.6(2)	90.2(2)	Cl2–Re1–P2	85.11(6)	83.10(5)
N1–Re1–P2	90.5(2)	94.7(2)	Cl2–Re1–P3	81.61(5)	80.65(5)
N1–Re1–P3	92.2(2)	93.2(2)	P1–Re1–P2	96.48(4)	99.40(4)
Cl1–Re1–Cl2	86.61(5)	86.78(5)	P1–Re1–P3	96.39(4)	95.40(4)
Cl1–Re1–P1	76.80(5)	79.96(5)	P2–Re1–P3	166.71(4)	163.20(4)
Cl1–Re1–P2	86.75(5)	83.73(4)			

The infrared spectrum of **1** was dominated by the signals of coordinated PTA in the range 940–1015 cm^{-1} and 750–850 cm^{-1}. The proton NMR spectrum displayed complex multiplets at δ = 4.5–4.9 ppm caused by methylene protons of PTA, while no signal was observed in the typical range of aromatic protons of PPh_3. The ^{31}P NMR spectrum showed a doublet and a triplet at δ –78.2 and δ –74.5 ppm, respectively ($^2J_{PP}$ = 14.0 Hz), suggesting the presence of two equivalent and one different coordinated PTA ligands. On the basis of spectroscopic measurements together with analytical data, complex **1** was formulated as the Re^{V} neutral complex $[ReNCl_2(PTA)_3]$. The ^{31}P NMR spectrum is in agreement with two possible structures in which three PTA ligands are on the basal plane or two PTA are *trans* to each other on the basal plane and the third PTA is located in an apical position *trans* to the Re≡N multiple bond.

Nitrido complexes of rhenium with alkyl-/arylphosphanes such as $[ReNCl_2(PR_3)_3]$ (R = alkyl and/or aryl) were reported by Chatt and co-workers.[13] X-ray studies for the Re^{V} complex $[ReNCl_2(PR_3)_3]$ (R = Me_2PhP, Et_2PhP)[14] showed an octahedral geometry with PR_3/Me_2PhP groups on the basal plane and two halogen atoms in a *cis* position. The X-ray crystallographic analysis of complex $[ReNCl_2(PTA)_3]$, **1**, unambiguously showed that the same ligand disposition is present also in this case. An ORTEP diagram is shown in Figure 1 and selected bond lengths and angles are given in Table 1.

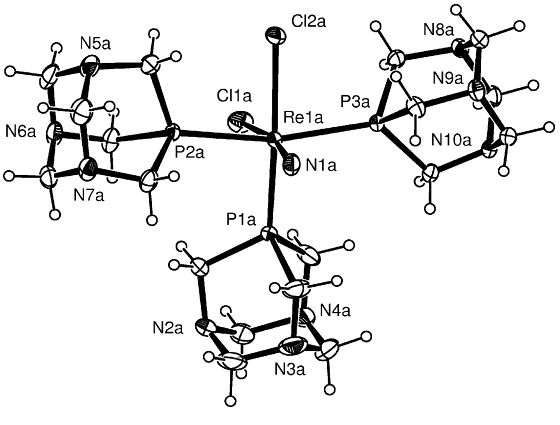


Figure 1. ORTEP view of molecule A of complex **1** displaying the thermal ellipsoids at 30% probability.

The asymmetric unit of **1** contains two molecular complexes and exhibits an approximately octahedral overall geometry around both Re^{V} atoms with the equatorial planes containing the three P atoms of PTA ligands and a chlorine atom, while the apical positions are occupied by a nitrido group and another Cl atom. In both molecules of the asymmetric unit the nitrido groups induce octahedral distortions, where the Re atoms are displaced by 0.1750(2) and 0.1927(2) Å, respectively, from the mean basal plane toward the N1 atoms. The Re1≡N1 triple bond lengths of 1.708(4) and 1.679(4) Å are in accordance with those of other similar derivatives showing distances in the range 1.67–1.71 Å.[14a,15] The Re1–Cl1 bond lengthening of 2.634(1) and 2.624(1) Å can be ascribed to the well-known strong *trans* influence exerted by the nitrido group. Similar distances, in the range 2.50–2.71 Å, can be observed in the previously quoted structures.[14a,15] With respect to the Re1–P1 distances of 2.377(1) and 2.386(1) Å, where P1 is *trans* to Cl2, the Re1–P2 and Re1–P3 bonds show significant lengthening, in the range 2.439(1)–2.453(1) Å, which can be ascribed to the mutual *trans* influence of the P atoms. Each molecule of the asymmetric unit is surrounded by water molecules linked, by hydrogen bond, mostly to the nitrogen atoms of PTA groups.

Dioxidorhenium(V) complexes $[ReO_2L_2]^+$ [L = 1,2-bis(diphenylarsane)ethane, 1,2-bis(diphenylphosphane)ethane, diphosphane tetraphosphonates] are known and fully characterized.[16] Infrared spectra of these compounds exhibited strong absorption bands in the range 780–840 cm^{-1} and were assigned to ν_{asym}(Re=O) stretching typical of the O=Re=O unit. A comparison between the IR spectra of **1** and **2** allowed the assignment of the Re≡N and Re=O stretching at 1050 cm^{-1} and at 788 cm^{-1}, respectively. Multiplets at δ = 4.4–5.0 ppm were observed in the proton NMR spectrum of **2**, while a doubled-triplet pattern at δ = –85.5 and δ = –70.5 ppm ($^2J_{PP}$ = 7.5 Hz) was displayed in the ^{31}P NMR spectrum. These data support the proposed formulation for complex **2**, confirmed by X-ray crystal structure. Figure 2 shows the perspective drawing of the $[ReO_2Cl(PTA)_3]$ complex and a selected list of bond lengths and angles are given in Table 2.

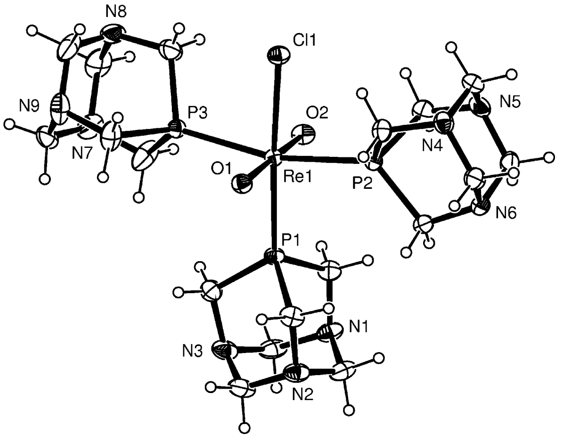


Figure 2. ORTEP view of complex **2** displaying the thermal ellipsoids at 30% probability.

Table 2. Selected bond lengths and angles [Å, °] for compound **2**.

Bond lengths			
Re1–O1	1.781(3)	Re1–P1	2.401(1)
Re1–O2	1.780(3)	Re1–P2	2.469(1)
Re1–Cl1	2.510(1)	Re1–P3	2.475(1)
Angles			
O1–Re1–O2	177.2(2)	O2–Re1–P3	87.4(1)
O1–Re1–Cl1	91.4(1)	Cl1–Re1–P1	176.74(4)
O1–Re1–P1	89.2(1)	Cl1–Re1–P2	81.56(4)
O1–Re1–P2	92.7(1)	Cl1–Re1–P3	85.38(4)
O1–Re1–P3	91.4(1)	P1–Re1–P2	95.22(4)
O2–Re1–Cl1	91.0(1)	P1–Re1–P3	97.79(4)
O2–Re1–P1	88.4(1)	P2–Re1–P3	166.41(4)
O2–Re1–P2	89.1(1)		

The coordination polyhedron for compound **2** is a distorted octahedron where the P atoms of PTA ligands and Cl1 atoms define the equatorial plane and the two O atoms are situated at the apical positions. The central Re^V atom is displaced by 0.0484(1) Å toward the O1 atom. The greatest molecular distortions are determined by the repulsions between PTA ligands causing, for instance, a significant enlargement of P1–Re1–P2 and P1–Re1–P3 angles to 95.22(4) and 97.79(4)°, respectively. The Re-dioxido moiety exhibits Re=O distances of 1.781(3) and 1.780(3) Å, in agreement with a number of Re-dioxido phosphane derivatives where these bond lengths are in the range of 1.75–1.81 Å.[17]

In accordance with the structure of **1**, the Re1–P1 and Re1–P3 bonds, in mutual *trans* positions, display longer distances of 2.470(1) and 2.475(1) Å, with respect to the Re1–P1 bond *trans* to the Cl1 atom, showing a distance of 2.401(1) Å.

The molecules of the complex in the crystals are linked, in chains, by means of water molecules that act as bridges between O1 and O2 oxygen atoms of two vicinal molecules through hydrogen bonds: O3(w)···O1 2.836(6) Å and O3(w)···O2($-x$, $y - 1/2$, $172 - z$) = 2.827(6) Å.

Stability Tests of 1 and 2 in Water and Physiological Solution by ^{31}P NMR Spectroscopy

The stability of Re-PTA complexes in aqueous solutions is crucial for radiopharmaceutical purposes. By studying their aqueous solution behavior at the macroscopic level it is possible to obtain useful information concerning the ^{188}Re-labeled-PTA species. For phosphane-metal complexes, ^{31}P NMR spectroscopy is an important analytical tool for detecting ligand replacements by the solvent or decomposition processes.

In order to evaluate the stability of **1** and **2**, we performed some ^{31}P NMR experiments both in water and physiological solution (0.154 mol L^{-1}). When a freshly prepared solution of **1** in water (0.036 mol L^{-1}) was observed by ^{31}P NMR, the spectrum showed the signal of uncoordinated PTA at δ = –96.5 ppm and three broad bands at –69.4, –71.3, and –74.7 ppm. ^{31}P NMR spectra were then monitored after 3 h and 24 h, but the relative intensities of the signals were not time-dependent.

The weak singlet at δ = –69.4 ppm could be tentatively assigned to species generated by loss of PTA or its replacement by water. The two more intense signals at –71.3 and –74.7 ppm look similar to the doublet–triplet pattern of **1** in $CDCl_3$ (–74.5 and –78.2 ppm). The signal broadening and downfield shift could be ascribed to a network of hydrogen bonds established between coordinated PTA and water.

The hypothesis of a partial PTA dissociation was confirmed by the following experiment, which showed that the process is reversible. The aqueous solution of **1** was carefully dried in vacuo, the solid residue was then redissolved in $CDCl_3$ and the ^{31}P NMR spectrum collected again. The typical doublet–triplet pattern of **1** at δ = –78.2 (d) and δ = –74.5 (t) reappeared, while the peak of free PTA was no longer observed.

These experiments were repeated under the same conditions replacing water with a physiological solution as a solvent: the ^{31}P NMR spectra do not show any difference with respect to the behavior previously observed in pure water.

With the same purpose, complex **2** was also dissolved both in water and in physiological solution (0.036 mol L^{-1}) and ^{31}P NMR spectroscopic data were collected as above. A downfield-shifted doublet–triplet pattern, less resolved in comparison with the spectrum of **2** in $CDCl_3$, was observed at δ = –83.6 and –68.3 ppm. A small signal at δ = –81.25 ppm and the presence of uncoordinated PTA at δ = –96.5 ppm seemed to indicate also in this case partial loss or replacement of a PTA ligand, reversible by changing water with chloroform.

In conclusion, these NMR experiments seem to indicate that **1** and **2** in water undergo a partial PTA dissociation, which can be reverted by the elimination of water, followed by re-dissolution in organic solvent.

Synthesis and Characterization of Rhenium(III) $[ReCl_3(PTA)_2(PPh_3)]$ (3)

Numerous investigations have been carried out on rhenium(III) phosphane complexes of the type [ReX$_3$-

$(PR_2PhP)_3]$ (X = Cl, Br; R = alkyl) and several X-ray crystal structures were determined.[18] Usually, these complexes were prepared by exchange/reduction reactions of $[ReCl_4(PPh_3)_2]$ or by reduction reactions from the $[ReO_4]^-$ anion.[18b,19] Under similar reaction conditions, it was not possible to isolate the analogous complex $[ReCl_3(PTA)_3]$, indicating the poor reducing properties of PTA in comparison with other alkyl- and arylphosphanes. The complex **3** reported herein, was prepared by ligand-exchange reaction starting from the Re(III) precursor $[ReCl_3(NCMe)(PPh_3)_2]$. In contrast to the above-reported reactions with $[ReOCl_3(PPh_3)_2]$ and $[ReNCl_2(PPh_3)_2]$, in this case only one out of two triphenylphosphane ligands were substituted by PTA. The product is an orange-yellow solid, soluble in CH_2Cl_2, $CHCl_3$, moderately soluble in water and ethanol, insoluble in acetone and benzene. The presence of both phosphanes was confirmed by the observation, in the infrared spectrum, of absorption bands at 1097 cm^{-1}, typical of PPh_3, and in the range 950–1015 cm^{-1}, characteristic of PTA. As expected, the proton NMR spectrum of complex **3** showed a pattern characteristic of paramagnetic compounds in agreement with a d^4 octahedral configuration. Both the signals of the protons of PPh_3 and those of PTA appeared as well-defined sharp bands. The aromatic protons of PPh_3 resonated at δ = 14.95 and at δ = 7.92 ppm in a 4:1 ratio due respectively to the protons in *ortho* and *meta* (12) and to those in *para* positions (3) of the aromatic rings. The methylene protons of PTA occurred at δ = 12.80, 11.00, 9.05, and 7.11 ppm as multiplets of equal intensity. As reported by Randall,[20] no phosphorus–proton coupling was observed, owing to rapid relaxation of the phosphorus nuclei. These observations, however, are in good agreement with the elemental analysis results, corresponding to $[ReCl_3(PTA)_2(PPh_3)]$. The X-ray structure analysis of **3** confirmed that the central metal atom is in an octahedral environment. An ORTEP view of complex **3** is shown in Figure 3 and selected bond lengths and angles are given in Table 3.

Table 3. Selected bond lengths and angles [Å, °] for compound **3**.

Bond lengths			
Re1–Cl1	2.351(1)	Re1–P1	2.439(1)
Re1–Cl2	2.353(1)	Re1–P2	2.426(1)
Re1–Cl3	2.464(1)	Re1–P3	2.428(1)
Angles			
C1–Re1–Cl2	174.64(3)	Cl2–Re1–P3	88.56(3)
Cl1–Re1–Cl3	93.18(4)	Cl3–Re1–P1	82.63(4)
Cl1–Re1–P1	85.93(4)	Cl3–Re1–P2	84.07(4)
Cl1–Re1–P2	83.87(4)	Cl3–Re1–P3	174.06(3)
Cl1–Re1–P3	92.33(3)	P1–Re1–P2	162.75(4)
Cl2–Re1–Cl3	86.17(3)	P1–Re1–P3	95.55(4)
Cl2–Re1–P1	99.24(4)	P2–Re1–P3	98.73(4)
Cl2–Re1–P2	90.76(4)		

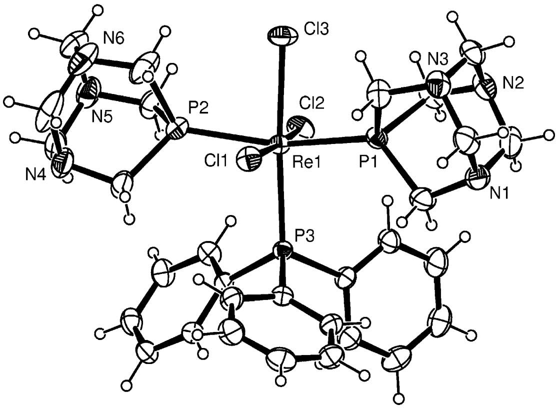


Figure 3. ORTEP view of complex **3** displaying the thermal ellipsoids at 30% probability.

Compound **3** is a Re^{III} complex with a *mer* arrangement of three chlorine atoms, two PTA ligands in mutual *trans* positions, and a PPh_3 group *trans* to a Cl atom. In the present compound and in other similar Re^{III} complexes no systematic *trans* influence exerted by P atoms can be observed.[18b,21] Accordingly, no lengthening of P1–Re1–P2 distances in mutual *trans* positions can be observed in complex **3**, only a small lengthening of the Re1–Cl3 bond length *trans* to a phosphane group is observed.

Reactivity of $[ReNCl_2(PTA)_3]$ (1) and $[ReO_2Cl(PTA)_3]$ (2) Complexes with $NaEt_2dtc$

The syntheses, structural characterizations, and reactions of rhenium and technetium nitrido complexes have been described in a great number of papers. The N^{3-} anion is one of the strongest π-donor ligands and the M≡N (M = Re, Tc) core is very stable. Ligand-exchange reactions of phosphane complexes $[MNCl_2(PPh_3)_2]$ and $[MNCl_2(PR_3)_3]$ (R = alkyl, aryl) have been extensively exploited to study the reactivity of several M≡N-containing complexes. Among the substitution products, those containing dithiocarbamate ligands have been widely studied and fully characterized. In fact, the $M–S_2CNR_2$ fragment (M = Re, Tc) can include a variety of organic substituents useful for the development of new radiopharmaceuticals: e.g., nitrido complexes of technetium of the type $[TcN(S_2CNR_2)_2]$ have been studied as heart-imaging agents.[22] For these reasons, we have chosen *N*,*N*-diethyldithiocarbamate as a relevant and useful ligand for starting the investigation of the reactivity of the new Re-PTA complexes above described.

The reaction of **1** with one equivalent of $Na[Et_2dtc]$ at room temperature gave the neutral complex $[ReNCl(Et_2dtc)(PTA)_2]$ (**4**) in good yield (Scheme 1). The presence of two PTA ligands makes **4** soluble in water. In the IR spectrum it was not possible to assign the Re≡N vibration in the typical range between 1000–1100 cm^{-1} because of the overlap with the absorption bands of PTA, while those observed at 1520 cm^{-1} and 1240 cm^{-1} could be assigned to ν(C–N) and ν(C–S), respectively. The ^1H NMR spectrum displayed a series of resonances in the range δ = 4.0–4.4 ppm caused by the methylene protons of PTA. The coordinated Et_2dtc resonated as a triplet at δ = 0.80 ppm (CH_3), while two quartets at δ = 2.95 and at δ = 3.22 ppm were attributed to the methylene protons. The integration of all these signals was in perfect agreement with the presence of coordinated PTA and Et_2dtc in a 2:1 ratio. Finally, the ^{31}P NMR showed a singlet at $\delta = -77.5$ ppm indicating that the two phosphane ligands were equivalent. Nitrido complexes of rhenium and technetium having this formulation are known and were obtained from $[MNCl_2(PMe_2Ph)_3]$ (M = Re, Tc).[23] By analogy, complex **4** could possess an octahedral geometry in which a Cl^- anion lies in a *trans* position to the Re≡N multiple bond, while bidentate Et_2dtc and two PTA occupy the four basal positions.[23a] Recrystallization of **4** from a mixture of CH_2Cl_2 and MeOH induced its transformation into a new unexpected compound. In fact, the ^{31}P NMR pattern changed from a singlet at $\delta = -77.5$ ppm to a series of four doublets at $\delta = -89.5$ and -84.8 ($^2J_{PP} = 10$ Hz), and at $\delta = -85.2$ and -71.4 ($^2J_{PP} = 14$ Hz). A complex series of resonances in the range $\delta = 4.4$–4.8 ppm attributable to CH_2 protons of PTA were observed in the ^1H NMR spectrum together with multiplets at $\delta = 1.42$ and 3.68–4.10 ppm caused by methyl and methylene protons of the dithiocarbamate ligand. On the basis of these data and elemental analysis we tentatively identified complex **5** as a dinuclear species having formula $[Re_2N_2Cl_3(Et_2dtc)(PTA)_4]$.

The formation of multinuclear complexes with bridging nitrido ligands between rhenium atoms Re≡N–Re has been observed before, when the complex $[ReN(Et_2dtc)_2(Me_2PhP)]$ reacted with TlCl or $Pr(O_3SCF_3)_3$.[24] *cyclo*-$[ReN]_4$ was formed when the nitrido starting material $[ReNCl_2(PPh_3)_2]$ reacted with 1.5 equiv. of *N*,*N*-diethyldithiocarbamate ligand in methanol[25] or when the complex $[ReN(Et_2dtc)_2(Me_2PhP)]$ reacted with $SbCl_3$.[26] Detailed studies of these reactions have been described by Abram and co-workers and some of the complexes were structurally characterized.[27]

The X-ray crystal structure of complex **5** has been determined, an ORTEP view is depicted in Figure 4 and selected bond lengths and angles are given in Table 4.

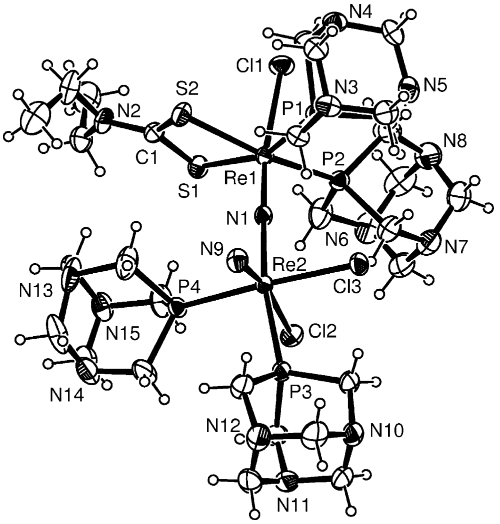


Figure 4. ORTEP view of complex **5** displaying the thermal ellipsoids at 30% probability.

Table 4. Selected bond lengths and angles [Å, °] for compound **5**.

Bond lengths			
Re1–N1	1.696(4)	Re2–N1	2.070(4)
Re1–Cl1	2.568(2)	Re2–N9	1.621(11)
Re1–P1	2.405(1)	Re2–Cl2	2.633(3)
Re1–P2	2.423(1)	Re2–Cl3	2.444(2)
Re1–S1	2.446(1)	Re2–P3	2.453(3)
Re1–S2	2.424(1)	Re2–P4	2.385(2)
C1–S1	1.720(5)		
C1–S2	1.711(7)		
Angles			
N1–Re1–Cl1	171.6(1)	N1–Re2–N9	99.5(6)
N1–Re1–P1	93.0(1)	N1–Re2–Cl2	86.2(2)
N1–Re1–P2	93.4(1)	N1–Re2–Cl3	86.0(1)
N1–Re1–S1	103.0(1)	N1–Re2–P3	167.0(1)
N1–Re1–S2	102.8(1)	N1–Re2–P4	89.7(1)
Cl1–Re1–P1	82.39(5)	N9–Re2–Cl2	169.0(4)
Cl1–Re1–P2	80.38(5)	N9–Re2–Cl3	100.6(6)
Cl1–Re1–S1	83.24(5)	N9–Re2–P3	92.5(6)
Cl1–Re1–S2	84.44(5)	N9–Re2–P4	90.5(6)
P1–Re1–P2	98.74(5)	Cl2–Re2–Cl3	89.1(1)
P1–Re1–S1	159.32(5)	Cl2–Re2–P3	82.9(1)
P1–Re1–S2	91.88(5)	Cl2–Re2–P4	80.1(1)
P2–Re1–S1	93.42(5)	Cl3–Re2–P3	86.71(6)
P2–Re1–S2	160.10(5)	Cl3–Re2–P4	168.64(7)
S1–Re1–S2	71.97(5)	P3–Re2–P4	95.33(6)
Re1–N1–Re2	173.1(3)	Re1–S2–C1	87.9(2)
Re1–S1–C1	87.0(2)	S1–C1–C2	113.0(3)

Compound **5** is a dinuclear Re^V complex where one molecule of $[ReNCl(Et_2dtc)(PTA)_2]$ coordinates with its nitrido ligand to the fragment $ReNCl_2(PTA)_2$. The resulting nitrido bridge is asymmetric with the distances Re1–N1 1.696(4) Å, Re2–N1 2.070(4) Å, and almost linear with a Re1–N1–Re2 bond angle of 173.1(3)°. These data are in perfect agreement with those of other similar bi or trinuclear Re complexes.[24,28] Both Re^V atoms assume a distorted octahedral geometry where Re1 is displaced by 0.3175(2) Å from the equatorial plane defined by the P1, P2, S1 and S2 atoms toward the nitrido N1 atom, while Re2 is displaced by 0.229(2) Å from the plane defined by P3, P4, Cl3, N1 atoms toward the N9 nitrido group. The Re1–Cl1 and Re2–Cl2 bond lengths *trans* to the nitrido groups display remarkable lengthening of 2.568(2) and 2.633(2) Å, respectively, as expected from the strong *trans* influence exerted by nitrido groups. Re1–S1 and Re1–S2 bond lengths compare very well with those in a similar Re^V compound where both S atoms are *trans* to phosphane groups.[24]

Neutral rhenium(V) and technetium(V) complexes of general formula $[MN(Et_2dtc)_2(Me_2PhP)]$ are known and were prepared by stepwise substitution reactions starting from $[MNCl_2(Me_2PhP)_3]$ or $[MNCl(Et_2dtc)(Me_2PhP)_2]$.[23b,29] The six-coordinate complex $[ReNCl(Et_2dtc)_2(PTA)]$ (**6**) was isolated in a similar way starting from $[ReNCl_2(PTA)_3]$ (**1**), or $[ReNCl(Et_2dtc)(PTA)_2]$ (**4**), with 2 and 1 equiv. of *N*,*N*-diethyldithiocarbamate, respectively (Scheme 1). In complex **6**, one PTA was retained as confirmed by the observation of a singlet at $\delta = -74.5$ ppm in the ^{31}P NMR spectrum. The ^{1}H NMR spectrum displayed the resonances of the CH_2 protons of PTA at δ = 4.6–4.0 ppm and those of ethyl protons of dithiocarbamate ligands. In fact, methyl protons resonated as four triplets at δ = 0.70 ppm (two overlapped triplets), δ = 0.85 ppm and 0.97 ppm, while the resonances due to the methylene protons appeared as four overlapped multiplets between δ = 3.6 and 2.8 ppm. These data support for **6** a six-coordinate disposition where one sulfur donor of a coordinated Et_2dtc is *trans* to the Re≡N multiple bond, like in the structurally characterized analogous complexes [MN(Et_2dtc)$_2$(Me_2PhP)] (M = Re, Tc).[6b,23b,29] The most reactive site in the complexes [$MNCl_2$(Me_2PhP)$_3$] (M = Re, Tc) is the Cl^- in a *trans* position to the nitride group. In the reactions with monoanionic bidentate ligands such as *N*,*N*-dialkyldithiocarbamates, one phosphane and one Cl^- anion are exchanged and the neutral species [MNCl(R_2dtc)(PMe_2PhP)$_2$] are formed. This substitution is followed by a rearrangement with migration of the remaining Cl^- *trans* to the nitrido ion. Thus, a second molecule of dithiocarbamate substitutes one phosphane and the *trans*-Cl^-.[27] More recently Dilworth and coworkers have reported diazenide-rhenium complexes with dithiocarbamate ligands of the formula [$ReNNC_6H_4$-4-OCH_3(dtc)$_2$(PPh_3)][30] in which the position *trans* to the diazenide ligand is occupied by a sulfur atom of one of the dithiocarbamate ligands. The treatment of **1**, **4**, or **6** with an excess of Na[Et_2dtc] gave rise to the displacement of all the coordinated PTA giving the known disubstituted five-coordinate complex [ReN(Et_2dtc)$_2$], **7**.[31]

Analogously, the *trans*-dioxidorhenium(V) complex [ReO_2Cl(PTA)$_3$] **2** reacted readily with an excess of Na[Et_2dtc] in aqueous solution at room temperature to yield the known μ-oxo complex [Re_2O_3(Et_2dtc)$_4$] (**8**) (Scheme 2) which was characterized by elemental analysis and IR and NMR techniques by comparison with a genuine sample.

Conclusions

We have described the syntheses of the new water-soluble nitrido-[$ReNCl_2$(PTA)$_3$] (**1**) and dioxido-[ReO_2Cl(PTA)$_3$] (**2**) complexes of rhenium(V). In water or physiological solution they undergo partial reversible PTA dissociation. The reactions of **1** with increasing quantities of sodium *N*,*N*-diethyldithiocarbamate gave the new complexes [ReNCl(Et_2dtc)(PTA)$_2$] (**4**) and [ReN(Et_2dtc)$_2$(PTA)] (**6**) and finally the known complex [ReN(Et_2dtc)$_2$], where the coordinated PTA are progressively replaced. The recrystallization of [ReNCl(Et_2dtc)(PTA)$_2$] (**4**) afforded an unexpected dinuclear species [$Re_2N_2Cl_3$(Et_2dtc)(PTA)$_4$] (**5**).

The reaction of complex [ReO_2Cl(PTA)$_3$] (**2**) gave exclusively the known μ-oxo complex [Re_2O_3(Et_2dtc)$_4$].

Although the chemical behavior of [$ReNCl_2$(PTA)$_3$] is very similar to analogous nitrido complexes containing alkylphosphanes [$ReNCl_2(PR_3)_3$], it may be noted that this new complex, as well as [ReO_2Cl(PTA)$_3$], is soluble in water and could be used as a starting precursor to develop a new chemistry of rhenium for applications of its radioisotopes Re-188/186 in nuclear medicine.

Experimental Section

General: Unless otherwise noted, all chemicals were of reagent-grade quality and used without further purification. The starting compounds [$ReNCl_2(PPh_3)_2$],[32] [$ReOXCl_2(PPh_3)_2$] (X = Cl^-, MeO^-, OEt^-),[33] [$ReCl_3$(NCMe)$(PPh_3)_2$],[34] and 1,3,5-triaza-7-phosphaadamantane (PTA),[35] were prepared according to literature procedures. Elemental analyses were performed using a Carlo–Erba Instruments model EA 1110. FT-IR spectra were recorded in a range 4000–200 cm^{-1} with a Nicolet 510 P FT-IR instrument in KBr, using a Spectra-Tech collector diffuse reflectance accessory. Proton spectra of $CDCl_3$, CD_3OD solutions of the compounds were examined with a Bruker AM 200 spectrometer with $SiMe_4$ as internal standard, ^{31}P NMR on the same instrument with an 85% H_3PO_4 solution as external standard.

Synthesis and Characterization of Complexes 1–3

[$ReNCl_2$(PTA)$_3$] (1): A solution of PTA (110 mg, 0.70 mmol) in CH_2Cl_2 (20 mL) was added to a suspension of [$ReNCl_2(PPh_3)_2$] (140 mg, 0.18 mmol, 30 mL of CH_2Cl_2). The reaction mixture was refluxed for 1 h. The color changed from pink to bright yellow, and a solid precipitated upon evaporation of most of the solvent. The crude yellow-orange solid was collected and washed three times with Et_2O in order to eliminate PPh_3. Crystallization from CH_2Cl_2/EtOH gave **1** as a yellow powder, which was separated and washed with EtOH and Et_2O. Recrystallization of **1** from CH_2Cl_2/Me_2CO (1:1, v/v) gave suitable crystals for X-ray diffraction analysis (94 mg, 72% yield). $C_{18}H_{36}Cl_2N_{10}P_3Re$ (742): calcd. C 29.11, H 4.89, N 18.87; found C 29.20, H 4.75, N 18.90. IR (KBr): $\tilde{\nu}$ = 1281, 1242 ($\nu_{C–N}$), 1050 ($\nu_{Re\equiv N}$), 1015–940 (ν_{PTA}) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 4.5–4.9 (m, CH_2, PTA) ppm. ^{31}P NMR (81.15 MHz, $CDCl_3$, 25 °C): δ = –78.2 (d, $^2J_{PP}$ = 14.0 Hz), –74.5 (t, $^2J_{PP}$ = 14.0 Hz) ppm.

[ReO_2Cl(PTA)$_3$] (2): PTA (1.45 mmol) was dissolved in the minimum volume of CH_2Cl_2 and the solution was added to a suspension of [$ReOCl_2X(PPh_3)_2$] (X = Cl^-, MeO^-, EtO^-) (0.18 mmol) in CH_2Cl_2 (30 mL) at room temperature causing a color change to yellow-orange. The reaction mixture was stirred for 1 h, the volume of the solution was reduced in vacuo, and then EtOH (5 mL) was added. Slow evaporation of the solvent at room temperature gave product **2** as a red-orange solid, which was collected, washed with EtOH, and dried with Et_2O. Crystals of **2** suitable for X-ray crystallography were obtained by recrystallization from CH_2Cl_2/EtOH; yield 78.3 mg (60%). $C_{18}H_{36}ClN_9O_2P_3Re$ (725): calcd. C 29.80, H 5.00, N 17.38; found C 30.0, H 5.10, N 17.20. IR (KBr): $\tilde{\nu}$ = 940–1015 (ν_{PTA}), 788 ($\nu_{O=Re=O}$) cm^{-1}. ^{1}H NMR (200 MHz, CD_3OD, 25 °C): δ = 4.4–5.0 (m, 36 H, CH_2) ppm. ^{31}P NMR (81.15 MHz, CD_3OD, 25 °C): δ = –85.5 (d, $^2J_{PP}$ = 7.5 Hz), –70.5 (t, $^2J_{PP}$ = 7.5 Hz) ppm.

[$ReCl_3$(PTA)$_2$(PPh_3)] (3): PTA (73.2 mg, 0.48 mmol) dissolved in CH_2Cl_2 was added to a solution of [$ReCl_3$(NCMe)$(PPh_3)_2$] (100 mg, 0.12 mmol) in a 1:1 mixture of C_6H_6 and CH_2Cl_2. The reaction mixture was refluxed for 30 min under nitrogen. The solution was filtered and concentrated to small volume causing the precipitation of a red-orange solid which was collected, washed with EtOH, and dried with Et_2O. Crystals of this compound were grown from $CHCl_3$/Me_2CO (1:2, v/v); yield 55.3 mg (53%). $C_{30}H_{39}Cl_3N_6P_3Re$ (869): calcd. C 41.43, H 4.52, N 9.66; found C 41.52, H 4.61, N 9.60. IR (KBr): $\tilde{\nu}$ = 1281, 1242 ($\nu_{C–N}$), 1015–947 (ν_{PTA}), 1097 (ν_{PPh_3}) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 14.95 (s, 12 H, PPh_3), 12.80 (s, 6 H, CH_2, PTA), 11.00 (d, 6 H, CH_2, PTA), 9.05 (m, 6 H, CH_2, PTA), 7.92 (m, 3 H, PPh_3), 7.11 (d, 6 H, CH_2 PTA) ppm.

Tests of Stability of 1 and 2 in Water and Physiological Solution by ^{31}P NMR Spectroscopy: Solutions of **1** or **2** in water or in physiological solution (0.036 mol L^{-1}) with an internal capillary containing C_6D_6 for lock, were monitored by ^{31}P NMR after 5 min, 3 h, and 24 h at a constant $T = 298.15$ K.

1: δ = –96.5 (s, PTA); –74.7, –71.3, –69.4 ppm (broad signals).

2: δ = –96.5 ppm (s, PTA); –83.6, –81.25, –68.3 ppm (broad signals).

Synthesis and Characterization of Complexes 4–6

[ReNCl(Et$_2$dtc)(PTA)$_2$] (4) and [Re$_2$N$_2$Cl$_3$(Et$_2$dtc)(PTA)$_4$] (5): The complex [ReNCl$_2$(PTA)$_3$] (100 mg, 0.13 mmol) dissolved in CH_2Cl_2 (40 mL) was treated with a solution containing 1 equiv. of Na[Et$_2$dtc] dissolved in the minimum volume of acetone. The resulting orange solution was stirred at room temperature for 1 h. Solid NaCl was filtered off, the solvent was evaporated in vacuo and the solid residue dissolved in a 1:1 mixture of CH_2Cl_2 and acetone. Slow evaporation of the solvents at room temperature gave orange-yellow crystals of **4**; yield 75 mg (80 %). $C_{17}H_{34}ClN_8P_2ReS_2$ (698): calcd. C 29.23, H 4.91, N 16.05, S 9.17; found C 29.12, H 4.99, N 15.94, S 9.2. IR (KBr): $\tilde{\nu}$ = 1520 (ν_{C-N}, Et$_2$Dtc), 950–1015 (ν_{PTA}), 1240 (ν_{C-S}) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 2.95, 3.22 (m, 4 H, CH$_2$, Et$_2$dtc), 0.80 (t, 6 H, CH$_3$, Et$_2$dtc), 4.4–4.0 (m, 24 H, PTA) ppm. ^{31}P NMR (81.15 MHz, CDCl$_3$, 25 °C): δ = –77.5 (s) ppm.

Recrystallization of **4** (50 mg, 0.72 mmol) from CH_2Cl_2/MeOH (1:1, v/v) gave crystals of complex [Re$_2$N$_2$Cl$_3$(Et$_2$dtc)(PTA)$_4$] (**5**); yield 37 mg (80 %). $C_{29}H_{58}Cl_3N_{15}P_4Re_2S_2$ (1283): calcd. C 27.12, H 4.55, N 16.37, S 4.98; found C 27.15, H 4.50, N 16.29, S 4.80. ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 1.42 (m), 3.68–4.10 (m), 4.4–4.8 (m) ppm. ^{31}P NMR (81.15 MHz, CDCl$_3$, 25 °C): δ = –89.5 (d, $^2J_{PP}$ = 10 Hz), –85.2 (d, $^2J_{PP}$ = 14 Hz), –84.8 (d, $^2J_{PP}$ = 10 Hz), –71.4 (d, $^2J_{PP}$ = 14 Hz) ppm.

[ReN(Et$_2$dtc)$_2$(PTA)] (6). Method A: One equivalent of Na[Et$_2$dtc] in acetone was added to a solution of [ReNCl(Et$_2$dtc)(PTA)$_2$] **4** (100 mg, 0.14 mmol) in CH_2Cl_2. The reaction mixture was refluxed for 1 h, concentrated under vacuo and the bright yellow solid of **6** was washed with EtOH and Et$_2$O; yield 77 mg (85 %).

Method B: Complex **6** may also be prepared under the same conditions as above adding 2 equiv. of Na[Et$_2$dtc] to a solution of [ReNCl$_2$(PTA)$_3$] (**1**) (100 mg, 0.13 mmol); yield 75 mg (88 %). $C_{16}H_{32}N_6PReS_4$ (654): calcd. C 29.36, H 4.93, N 12.84, S 19.57; found C 29.27, H 5.01, N 12.92, S 19.65. IR (KBr): $\tilde{\nu}$ = 1490, 1520 (ν_{C-N}), 950–1015 (ν_{PTA}), 1240 (ν_{C-S}) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 4.6–4.0 (m, 12 H, CH$_2$, PTA), 2.8–3.6 (m, 8, CH$_2$, Et$_2$dtc), 0.97 (t, 3 H, CH$_3$, Et$_2$dtc), 0.85 (t, 3 H, CH$_3$, Et$_2$dtc), 0.70 (m, 6 H, CH$_3$, Et$_2$dtc) ppm. ^{31}P NMR (81.15 MHz, CDCl$_3$, 25 °C): δ = –74.5 (s, PTA) ppm.

Reaction of 1, 4, or 6 with an Excess of Na[Et$_2$dtc]: Treatment of **1**, **4**, or **6** in CH_2Cl_2 with a ten-fold excess of Na[Et$_2$dtc] resulted in the formation of the known nitrido complex [ReN(Et$_2$dtc)$_2$] (**7**). The identity of this product was based on comparison of its spectroscopic properties and elemental analysis with those of an authentic sample;[31a] yield >70 %.

Reaction of 2 with an Excess of Na[Et$_2$dtc]: Na[Et$_2$dtc] (87 mg, 0.4 mmol) dissolved in water was added to an aqueous solution of [ReO$_2$Cl(PTA)$_3$] (**2**) (70 mg, 0.1 mmol). The reaction mixture was allowed to stir at room temperature for 30 min. A brown powder precipitated, which was collected and washed with ethanol. The product was then redissolved in CH_2Cl_2 and EtOH was added. Slow evaporation of the solvents at room temperature afforded brown-yellow crystals of [Re$_2$O$_3$(Et$_2$dtc)$_4$] (**8**). Analytical and spectroscopic data were coincident with those reported in the literature.[36]

Crystal Structure Determinations: Crystal data of compounds **1**, **2**, **3**, and **5** were collected with a Nonius Kappa CCD diffractometer

Table 5. Crystallographic data.

Compound	1	2	3	5
Formula	$C_{18}H_{36}Cl_2N_{10}P_3Re\cdot 4.5\,H_2O$	$C_{18}H_{36}ClN_9O_2P_3Re\cdot H_2O$	$C_{30}H_{39}Cl_3N_6P_3Re$	$C_{29}H_{58}Cl_3N_{15}P_4S_2Re_2\cdot 3\,H_2O$
M	823.65	743.13	869.13	1337.70
Space group	$P2_1/c$	$P2_12_12_1$	R-3	$P2_1/n$
Crystal system	monoclinic	orthorhombic	trigonal	monoclinic
a [Å]	14.8370(1)	11.6936(2)	39.7586(8)	12.1124(2)
b [Å]	21.2745(2)	13.0066(3)	39.7586(8)	23.3583(4)
c [Å]	20.7865(2)	17.0937(3)	10.9037(2)	17.9431(3)
α [°]	90	90	90	90
β [°]	93.0576(5)	90	90	106.5142(9)
γ [°]	90	90	120	90
V [Å^3]	6551.9(1)	2599.85(9)	15008.9(5)	4867.1(1)
Z	8	4	18	4
D_c [g cm^{-3}]	1.670	1.899	1.731	1.826
F(000)	3304	1480	7776	2640
μ(Mo-K_α) [cm^{-1}]	40.62	50.02	40.60	54.00
Measured reflections	59672	25361	37318	35554
Unique reflections	15793	7456	8037	11107
R_{int}	0.057	0.055	0.046	0.054
Obsd. reflections] [$I \geq 2\sigma(I)$]	11796	6628	6175	8107
θ_{min}–θ_{max} [°]	1.7–28.0	3.3–30.0	1.9–28.0	3.5–27.5
hkl ranges	–19,19; –28,28; –27,27	–15,16; –17,18; –23,24	–39,52; –50,52; –13,14	–15,15; –30,30; –21,23
$R(F^2)$ (obsd. reflections)	0.0403	0.0323	0.0317	0.0416
w$R(F^2)$ (all reflections)	0.1084	0.0689	0.0633	0.1081
Number of variables	691	324	388	552
Goodness of fit	1.057	1.032	1.048	1.019
$\Delta\rho_{max}$; $\Delta\rho_{min}$ [e Å^{-3}]	1.73; –1.77	1.33; –1.91	1.77; –1.48	1.40; –1.56

using graphite-monochromated Mo-K_α radiation ($\lambda = 0.7107$ Å) at room temperature (295 K). Data sets were integrated with the Denzo-SMN package[37] and corrected for Lorentz polarization and absorption effects.[38] The crystal parameters and other experimental details of the data collections are summarized in Table 5. The structures were solved by direct methods (SIR97)[39] and refined by full-matrix least square methods with all non-hydrogen atoms anisotropic and hydrogen atoms included on calculated positions, riding on their carrier atoms. The asymmetric unit of compound **1** contains two molecular complexes, differing slightly in the rotation of PTA ligands, and nine water molecules, three of them being disordered were refined over two positions with occupancy of 0.5 each. All the hydrogen atoms of water molecules could not be determined. In compound **5** the N9–Re2–Cl2 moiety, disordered over two opposite orientations, was refined over two positions with occupancies of 0.73 and 0.27, respectively. The asymmetric unit contains also three water molecules, two of them being disordered were refined over two positions with occupancies of 0.7 and 0.3. All the hydrogen atoms of water molecules could not be determined. All calculations were performed using SHELXL-97[40] and PARST[41] implemented in the WINGX system of programs.[42] ORTEP[43] views are shown in Figures 1, 2, 3, and 4. Selected bond lengths and angles are given in Tables 1, 2, 3, and 4.

Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC-670896 (for **1**), -670897 (for **2**), -670898 (for **3**), -670899 (for **5**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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