Synthesis, Solution-State and Solid-State Structural Characterization of Monocationic Nitrido Heterocomplexes $[M(N)(DTC)(PNP)]^+$ (M = ^{99}Tc, Re; DTC = Dithiocarbamate; PNP = Heterodiphosphane)

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Mono-cationic nitrido heterocomplexes of general formula $[M(N)(DTC)(PNP)]^+$ (where M is ^{99}Tc or Re, DTC is the monoanionic form of a dithiocarbamate ligand, and PNP is a diphosphane ligand with a tertiary amine-containing five-membered spacer) were prepared by ligand-exchange reactions with the labile precursors $[M(N)Cl_2(PPh_3)_2]$ in dichloromethane/alcohol mixtures. The molecular structure of the representative rhenium complex $[Re(N)(dedc)(pnp2)][PF_6]$ (**1**) displays a distorted, square-pyramidal geometry with the dithiocarbamate sulfur and the diphosphane phosphorus atoms spanning the four coordination positions on the equatorial plane. If the additional interactions between the nitrido nitrogen and the weakly bonded *trans N*-diphosphane heteroatom, the molecular geometry can be viewed as pseudo-octahedral. The structure in solution, as established by multinuclear NMR spectroscopy and ESI spectrometry, is monomeric, and identical to that shown in the solid state. Replacement of the phenyl groups on the phosphorous atoms in complexes **1**, **2**, **5**, and **6** with alkyl groups modified neither the course of the reaction nor the composition of the resulting complexes. These results, together with the observation that no symmetrical complexes containing two identical bidentate ligands were produced in these reactions, strongly supports the conclusion that a mixed coordination sphere, composed by a combination of π-donor and π-acceptor atoms around the $[M{\equiv}N]^{2+}$ group, constitutes a highly stable system. Compounds containing dangling alkyl-substituted groups in the outer sphere (**3**, **4**, **7**, and **8**) were fully characterized by multinuclear NMR spectroscopy and ESI mass spectrometry.

Introduction

Radioactive isotopes of the two elements technetium and rhenium play an important role in nuclear medicine for diagnostic and therapeutic applications. In particular, the γ-emitting radionuclide ^{99m}Tc has almost ideal properties (E_γ = 142 keV, $t_{1/2}$ = 6.06 h) for the imaging of internal organs. Similarly, the β-emitting radionuclide ^{188}Re is currently considered to be an important candidate for the development of therapeutic agents for the treatment of degenerative diseases. Selective uptake into the target organ is one of the key issues that should be always considered in the development of effective diagnostic or therapeutic agents. Ultimately, this requires the design of radiopharmaceuticals possessing specific molecular features. Metal complexes of technetium and rhenium characterized by a selective reactivity toward a selected set of coordinating atoms are currently attracting much interest as suitable precursors for the design and preparation of new radiopharmaceuticals.[1−3] These complexes can be viewed as being composed of a robust metal-containing fragment with a few substitution-labile coordination positions, spanned by some weakly bound ancillary ligands. It turns out that these ancillary substituents can be easily replaced by ligands which only carry a specific set of coordinating atoms. The metal unit, therefore, manifests a selective reactivity towards a specific class of ligands, and is almost completely inert towards other types of reagents. Examples of this specific class include the low-valent aqua-carbonyl $[Tc^I(CO)_3(OH_2)_3]^+$ complex[4,5] and high-valent, nitrido-diphosphane $[Tc(N)(PNP)Cl_2]$ complexes.[6,7] In these complexes, the $[Tc(CO)_3]^+$ and $[Tc(N)(PNP)]^{2+}$ fragments are the stable molecular units. In contrast, the water and halide

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ligands can be efficiently substituted by a series of bi-functional tridentate σ-donor ligands (L) and bidentate π-donor ligands (L′), respectively, to yield mixed heterocomplexes of the type $[Tc(CO)_3(L)]^+$ [8,9] and [Tc(N)(PNP)(L′)].[10,11]

In the last few years, we have investigated the design of nitrido-containing species by exploiting the strong electrophilic character exhibited by the $[M(N)(PNP)]^{2+}$ metal fragment, which selectively reacts with nucleophilic bidentate ligands having a π-donor set of coordinating atoms. In particular, emphasis was placed on bidentate ligands containing both heteroatomic chelating sites (such as cysteine, thiocarboxylic acids, and aminothiols) and homoatomic sites (such as dithiols and dithiocarbamates). For example, small peptides having a terminal cysteine residue have been efficiently labeled with the $[^{99m}Tc(N)(PNP)]^{2+}$ complex at a high-specific-activity level.[10] A cysteine-conjugated 2-methoxyphenylpiperazine ligand was linked to the same metal fragment to investigate the binding affinity of the resulting heterocomplex for 5-HT_{1A} receptors in the central nervous system.[12]

Within the class of homoatomic bidentate ligands, monoanionic dithiocarbamates (DTC) were found to possess a strong affinity for the $[^{99m}Tc(N)(PNP)]^{2+}$ complex. Reactions with these ligands, carried out at tracer level (μM concentrations), yielded mono-cationic nitrido heterocomplexes, thought to be of general formula $[^{99m}Tc(N)(DTC)(PNP)]^+$. Biological evaluation of these new products demonstrated that they selectively accumulate in the myocardium of rats. For some derivatives, retention in this region was accompanied by a very fast blood, lung and liver clearance, suggesting that these tracers could be potentially utilized for obtaining SPECT myocardial images of superior quality compared to those obtained using currently available commercial agents.[13,14] The elucidation of the molecular structure of these compounds, therefore, appears to be of utmost importance for the comprehension of their peculiar biological properties. For this reason, we synthesized and structurally characterized a series of nitrido heterocomplexes of technetium and rhenium, obtained by treating the nitrido precursors $[M(N)Cl_2(PNP)]$ (M = Re, Tc) with the appropriate dithiocarbamate ligand.

The present study describes the synthesis, and solid-state and solution-state determination of the molecular structure of ^{99}Tc and Re mono-cationic compounds $[M(N)(DTC)(PNP)]^+$, where DTC indicates the derivatives diethyldithiocarbamate (dedc) and *N*,*N*′-bis(ethoxyethyl)dithiocarbamate (dbodc), and PNP represents the diphosphane ligands bis[(diphenylphosphanyl)ethyl]methoxyethyl-

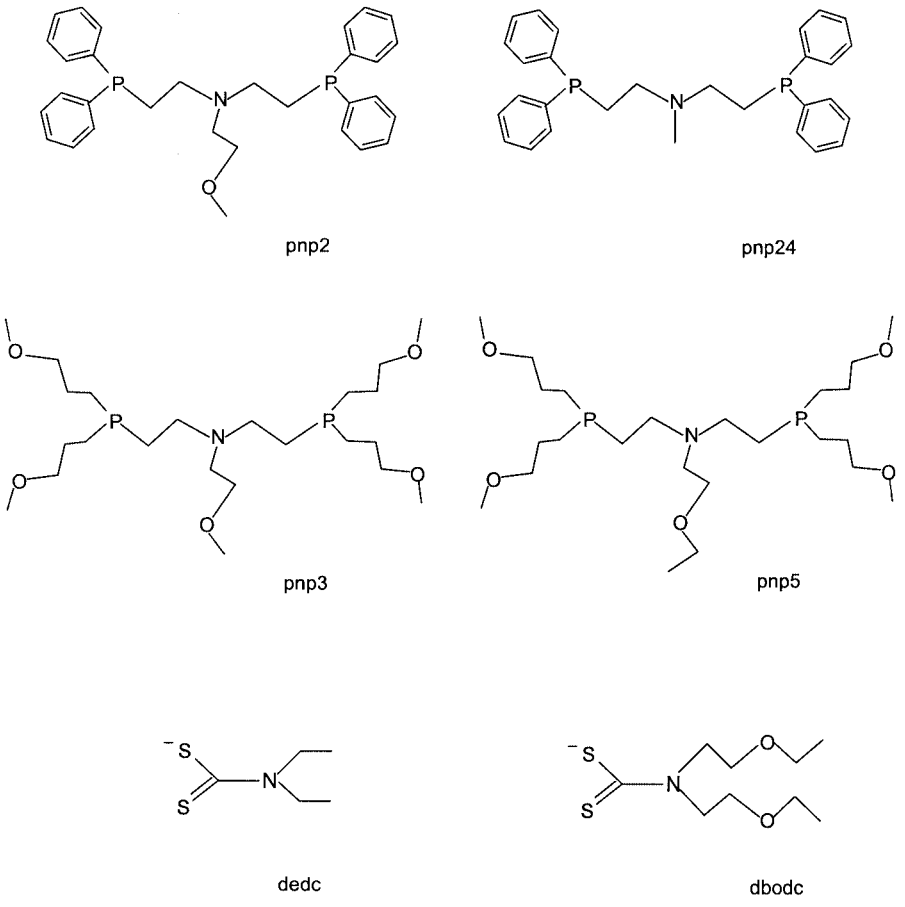
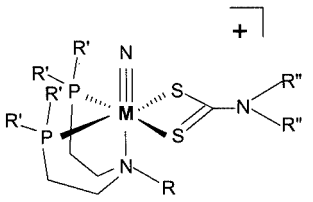


Figure 1. PNP and DTC ligands utilized in this study

amine (pnp2), bis[(diphenylphosphanyl)ethyl]methylamine (pnp24), bis[(dimethoxypropylphosphanyl)ethyl]methoxyethylamine (pnp3) and bis[(dimethoxypropylphosphanyl)-ethyl]ethoxyethylamine (pnp5). The dithiocarbamate and heterodiphosphane ligands utilized here are depicted in Figure 1, and the molecular structure of the $[M(N)(DTC)(PNP)]^+$ complexes is outlined in Figure 2.



Complex	PNP	DTC
$[Re(N)(dedc)(pnp2)]^+$ **1**	$R = (CH_2)_2OCH_3$ $R' = Ph$	$R'' = CH_2CH_3$
$[Re(N)(dedc)(pnp24)]^+$ **2**	$R = CH_3$ $R' = Ph$	$R'' = CH_2CH_3$
$[Re(N)(dedc)(pnp3)]^+$ **3**	$R = (CH_2)_2OCH_3$ $R' = (CH_2)_3OCH_3$	$R'' = CH_2CH_3$
$[Re(N)(dbodc)(pnp5)]^+$ **4**	$R = (CH_2)_2OCH_2CH_3$ $R' = (CH_2)_3OCH_3$	$R'' = (CH_2)_2OCH_2CH_3$
$[Tc(N)(dedc)(pnp2)]^+$ **5**	$R = (CH_2)_2OCH_3$ $R' = Ph$	$R'' = CH_2CH_3$
$[Tc(N)(dedc)(pnp24)]^+$ **6**	$R = CH_3$ $R' = Ph$	$R'' = CH_2CH_3$
$[Tc(N)(dbodc)(pnp3)]^+$ **7**	$R = (CH_2)_2OCH_3$ $R' = (CH_2)_3OCH_3$	$R'' = (CH_2)_2OCH_2CH_3$
$[Tc(N)(dbodc)(pnp5)]^+$ **8**	$R = (CH_2)_2OCH_2CH_3$ $R' = (CH_2)_3OCH_3$	$R'' = (CH_2)_2OCH_2CH_3$

Figure 2. Sketch of the molecular structure of $[M(N)(TDC)(PNP)]^+$ complexes

Results and Discussion

Synthesis of Technetium and Rhenium Complexes

Technetium and rhenium nitrido heterocomplexes containing one diphosphane and one dithiocarbamate ligand bound to the same Tc≡N group were prepared by a one-pot procedure, as shown in Scheme 1. Reaction of equimolar amounts of $[M(N)Cl_2(PPh_3)_2]$ and the relevant diphosphane ligand in dichloromethane/ethanol yielded the intermediate precursor $[M(N)Cl_2(PNP)]$, which in turn provided the mixed-ligand complex on treatment with a slight excess of dithiocarbamate. Formation of the corresponding bis-substituted complexes with two identical polydentate ligands was not observed, even when 3:1 or 1:3 PNP/DTC ratios were used.

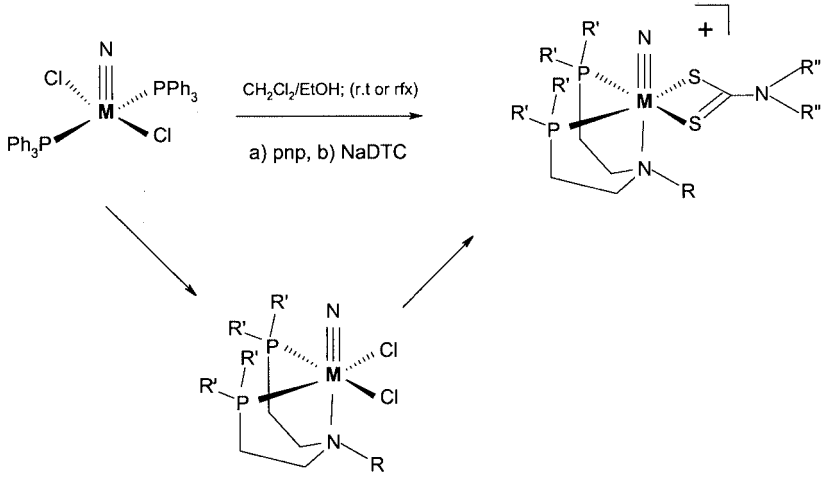
The reaction was faster for the technetium species, and afforded nearly quantitative yields. The preparation of the rhenium analogues required more drastic conditions (i.e. prolonged reflux), and yields dropped sharply, owing to the concomitant production of unstable side-products.

Characterization of the Complexes

The complexes were characterized by elemental analysis, spectroscopic methods and, in the case of complex **1**, X-ray diffraction. The IR spectra of both **1** and **2** exhibit bands of medium intensity at ca. 1060 cm^{-1}, attributable to the $\nu_{Re\equiv N}$ stretching vibration. Complex **1** displays an additional strong vibration at 840 cm^{-1}, characteristic of the hexafluorophosphate counter-anion.

X-ray Crystal Structure of $[Re(N)(dedc)(pnp2)][PF_6]$ (1)

Figure 3 shows the molecular structure of complex **1**, together with the essential numbering scheme. Relevant bond lengths and angles are given in Table 1. Crystallographic and structure refinement data are summarized in Table 2 (see Exp. Sect.).



Scheme 1. Reaction pathway for the preparation of mixed nitride-M(V) heterocomplexes **1**–**8**

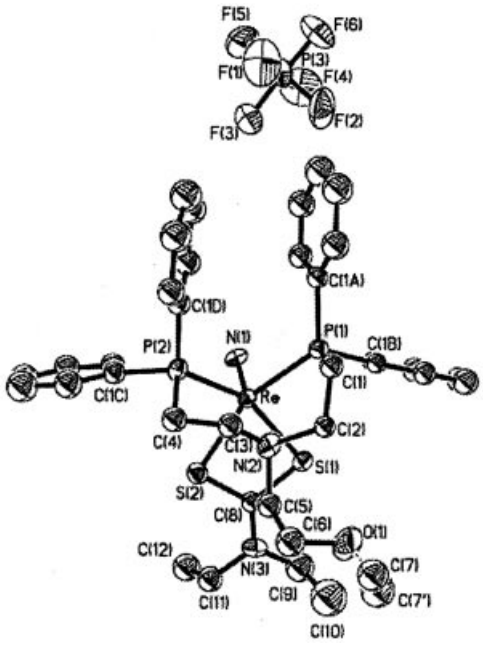


Figure 3. An ORTEP view of complex **1** with essential atom numbering. Hydrogen atoms have been omitted for clarity; displacement ellipsoids have been drawn at the 40% probability level

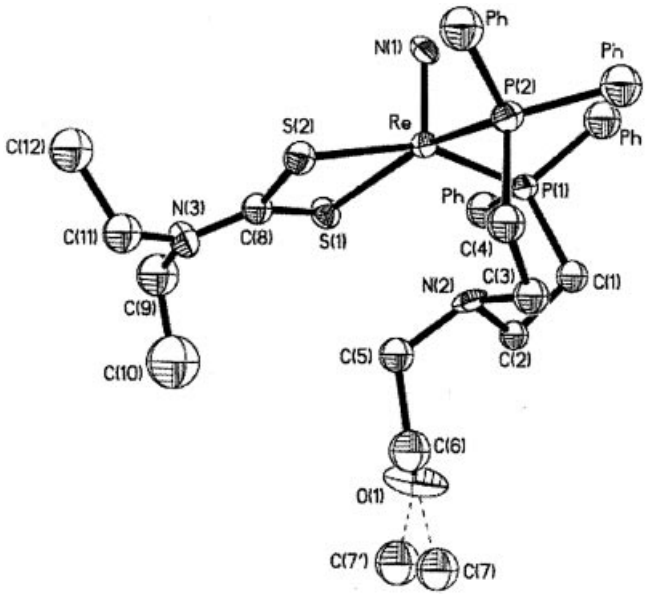


Figure 4. A close view of complex **1**. The phenyl rings have been replaced by pseudo atoms labelled as Ph. The C(7) atom position is split in two positions, each with an occupancy factor of 0.5

Table 1. Selected Bond lengths (Å) and Angles (°) for complex **1**

Re−S(1)	2.425(3)	Re−S(2)	2.413(3)
Re−P(1)	2.408(3)	Re−P(2)	2.396(3)
Re−N(1)	1.660(9)	Re···N(2)	2.73(1)
S(1)−C(8)	1.75(1)	S(2)−C(8)	1.72(1)
S(1)−Re−S(2)	72.5(1)	N(1)−Re−P(1)	93.3(4)
P(1)−Re−P(2)	101.2(1)	N(1)−Re−P(2)	96.8(3)
N(1)−Re−S(1)	105.4(3)	N(1)−Re···N(2)	164.4(5)
N(1)−Re−S(2)	106.4(4)	S(1)−C(8)−S(2)	110.9(7)

Crystalline **1** is made up of well-separated mono-cationic units and PF_6^- anions, which do not show any interaction below the sum of the van der Waals radii. The environment around the Re atom is square pyramidal, or pseudo-octahedral if we consider the additional weak interaction of N(2) with the metal, with the base plane defined by the P(1), S(1), S(2) and P(2) atoms (Figure 4).

None of these atoms deviate more than 0.02 Å from the mean plane, whereas Re is located 0.41 Å above the plane, towards N(1). The Re≡N(1) distance of 1.660(9) Å is close to the average of 1.675 Å found for terminal nitride-Re^V compounds (29 entries in the Cambridge Structural Database[15]). A similar search for the diphenylphosphinorhenium(v) synthon gave an average value of 2.484 Å for the Re^V-PPh_2R bond (25 entries), a distance markedly longer than those found for **1** [for which Re−P(1) and Re−P(2) are 2.408(3) and 2.396(3) Å, respectively). This shortening can be ascribed to the cationic nature of the complex, as previously observed for similar [Re(N)(pnp2)(L)][BF_4] and [Re(N)(pnp2)(POP)][BF_4] compounds (L = *S*-methyl 2-methyldithiocarbazate monoanion, POP = bis[(diphenylphosphanyl)ethyl]ether).[7] The S(1)−Re−S(2) bite angle of 72.5(1)° and the Re−S(1) and Re−S(2) bond lengths of 2.425(3) and 2.413(3) Å are in agreement with the reported data (average Re−S distance and S−Re−S angle of 2.433 Å and 71.3°, respectively).

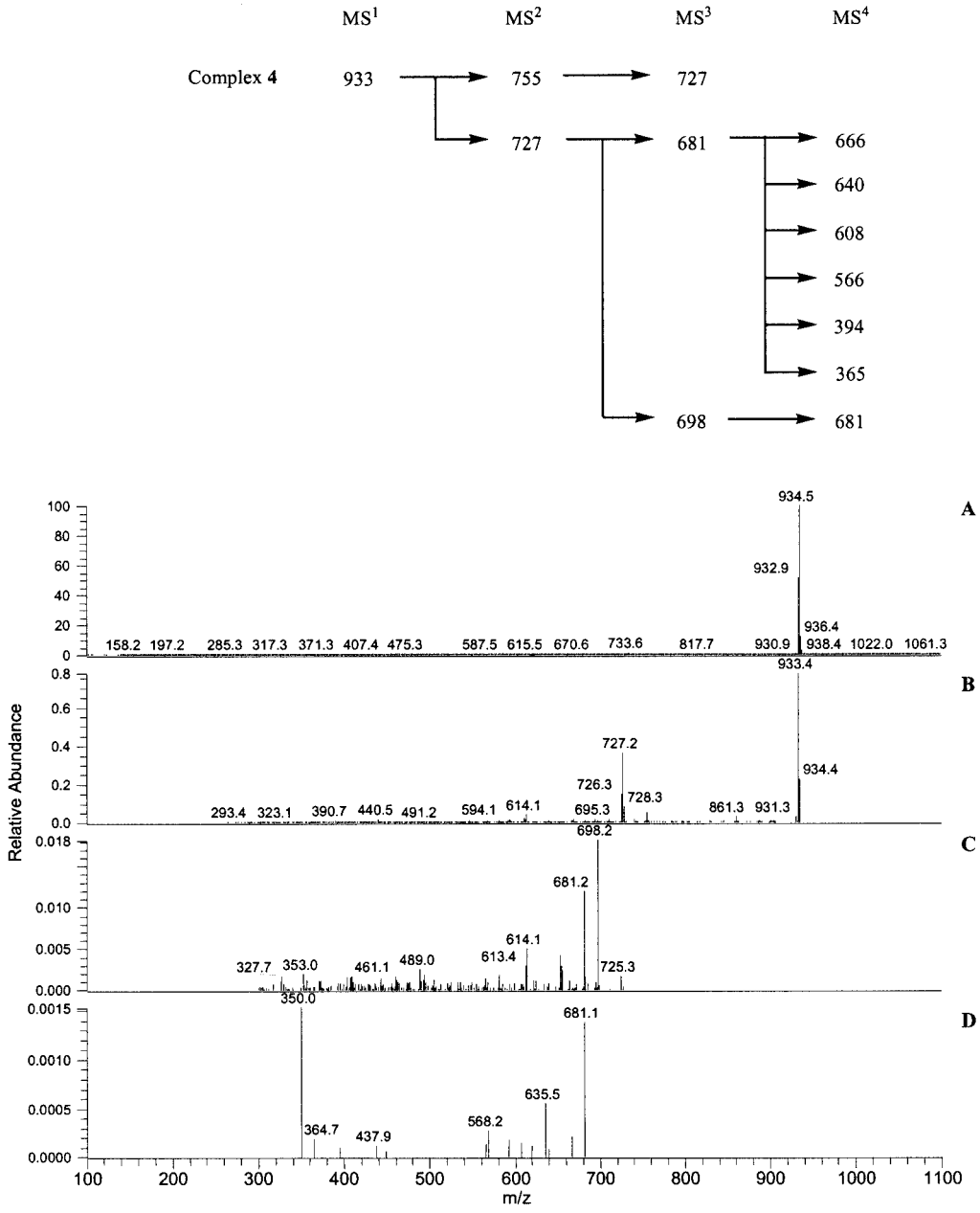
The position assumed by the phenyl rings bound to the phosphorous atoms deserves comment. The two facing phenyl groups (labeled as A and D in Figure 3) adopt the so-called "parallel displaced" arrangement, characterized by the X(A) and X(D) centroid distance of 4.11 Å, and the C(1A)−X(A)−X(D)−C(1D) "twist angle" of 24.1°. These values corroborate the hypothesis of a possible role for π-bonds in stabilizing the *cis*-P coordination. On the other hand, the two rings bound to each phosphorous atom are roughly orthogonal to each other, with dihedral angles of 83.9° and 103.9° between the mean planes of A and B, and C and D, respectively. The A, B, C, and D phenyl rings have dihedral angles with the S_2P_2 equatorial plane of 93.3, 117.0, 114.7, and 69.3,°respectively. This plane has a dihedral angle of 13.6° to the dithiocarbamate plane [sp^2 geometry at N(3)], defined by the six S(1), S(2), C(8), N(3), C(9), and C(11) atoms. The methylene carbons of the diphosphane chain, C(1), C(4), C(2), and C(3), are located, respectively, at 1.69, 1.81, 2.64 and 2.64 Å below the mean S_2P_2 basal plane, whereas N(2) faces this plane at the intermediate distance of 2.29 Å. This additional metal−N(2) interaction provides further thermodynamic stability to the system and contributes to the kinetic inertness shown by this class of mixed nitrido heterocomplexes.

ESI Mass Spectrometry

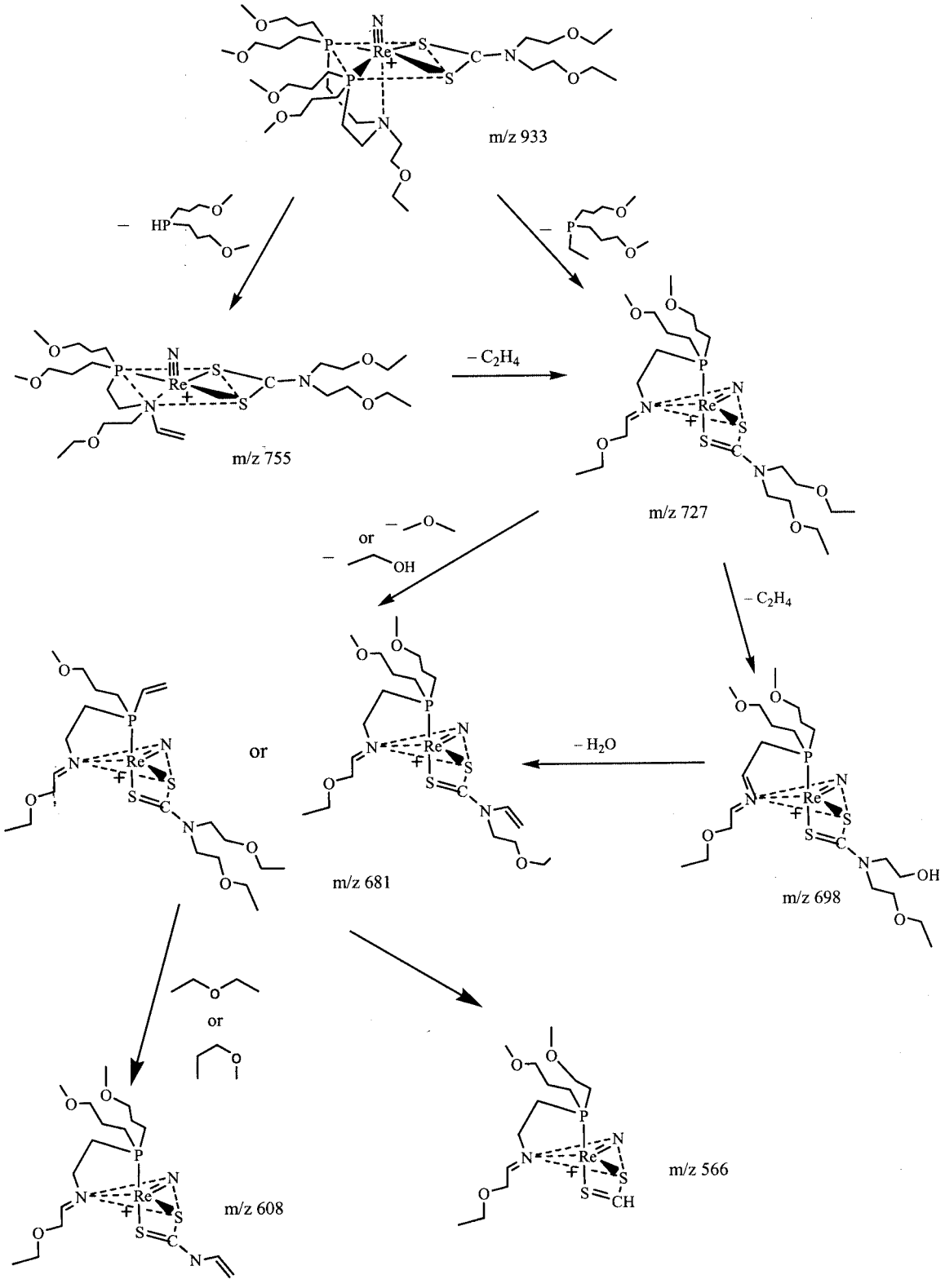
The ESI mass spectra of the rhenium complexes **1**−**4** each show a peak corresponding to the molecular ion with

no additional detectable fragments, indicating the high stability of the cation in the oxidative/reductive conditions typical of ESI experiments. To gain further information on the ligand-rhenium bond strengths, a series of collision experiments was undertaken. Such collisions (performed with an ion trap) inidicate the presence of decomposition channels with a low critical energy; the eventual products represent the more energetically favored pathways. For complex **4**, under these conditions, many fragment ions become detectable (as summarized in Scheme 2). The related collision-induced decomposition pathway is illustrated in Scheme 3. Collision of the molecular cation (m/z = 933) produces abundant fragments at m/z = 755 and 727, both corresponding to the unexpected loss of phosphorous-containing residues originating from the pnp5 ligand. As shown in Scheme 3, the resulting species at m/z = 727 most likely adopt a five-coordinate structure (the common arrangement for nitrido-containing rhenium compounds), in which a native bidentate *P*,*N*-phosphinoamine ligand shares the coordination positions around the Re=N group with the dithiocarbamate unit. It should be noted that this first fragmentation is identical to that exhibited by the isostructural technetium complex **8**, which was separately investigated in a previous study.[16]

No variation in the first collision-induced fragmentation profile is observed for any of the complexes investigated,



Scheme 2. MS^n data for complex **4** obtained by resonant excitation of the indicated precursor ion and of the main collision-generated fragment ions; below, **A**) ESI-MS spectrum of compound **4**; **B**) MS^2 spectrum of the molecular ion (m/z = 727); **C**) MS^3 spectrum of product ion at m/z = 698; **D**) MS^3 spectrum of the product ion at m/z = 681



Scheme 3. Fragmentation scheme proposed to rationalize the collision-induced decomposition behavior of complex **4**

either by decreasing the bulkiness at the dithiocarbamate ligand (bdodc → dedc, **4** → **3**), replacing dangling methoxyethyl substituents at the diphosphane phosphorous with rigid phenyl groups (pnp3 → pnp2, **3** → **1**), or by diminishing the steric hindrance at the *N*-diphosphinoamine function (pnp2 → pnp24, **1** → **2**).

Further MS^n experiments implied the loss of ethanol followed by release of other groups originating from the di-

thiocarbamate and/or the phosphinoamine ligands. In the latter case, the substituents begin to play a significant role in the decomposition pathways. For example, dedc complexes 1−3 always retain the dithiocarbamate ligand intact, in contrast to the dbodc complex **4**, which undergoes cleavage of the C−N bond C−N, with retention of carbon disulfide. Moreover, the bidentate P,N-phosphinoamine ligand in complexes **1** and **2** releases the diarylalkylphosphane arm and retains the amine group, whereas the reverse is observed for complexes **3** and **4**, which carry the more strongly donating trialkylphosphanes.

Multinuclear NMR Spectroscopy

The remarkable downfield shift of the ^{31}P signal from negative values typical of uncoordinated diphosphanes to positive values for these complexes is diagnostic of metal-phosphorus coordination. Consistent with the expected magnetic equivalence of the two diphosphane phosphorus atoms, complexes 1−8 exhibit a singlet in the ^{31}P NMR spectrum, the peak profile being narrow ($\nu_{1/2} \approx 25$ Hz) in the case of rhenium and broad ($\nu_{1/2} \approx 350$ Hz) in the case of technetium.

One-dimensional proton and carbon spectra are quite complicated owing to the presence of overlapping methyl and methylene signals. However, the use of several two-dimensional experiments including homonuclear ^{1}H-^{1}H COSY and heteronuclear ^{1}H-^{13}C HETCOR makes the assignment of each signal possible. By way of example, COSY and HETCOR maps and the corresponding proton and carbon spectra for the technetium complex **8** are shown in Figure 5.

The assignment was determined as follows. Methyl carbons may be distinguished from methylene carbons with the ^{13}C DEPT-135 experiment (as shown in the bottom right

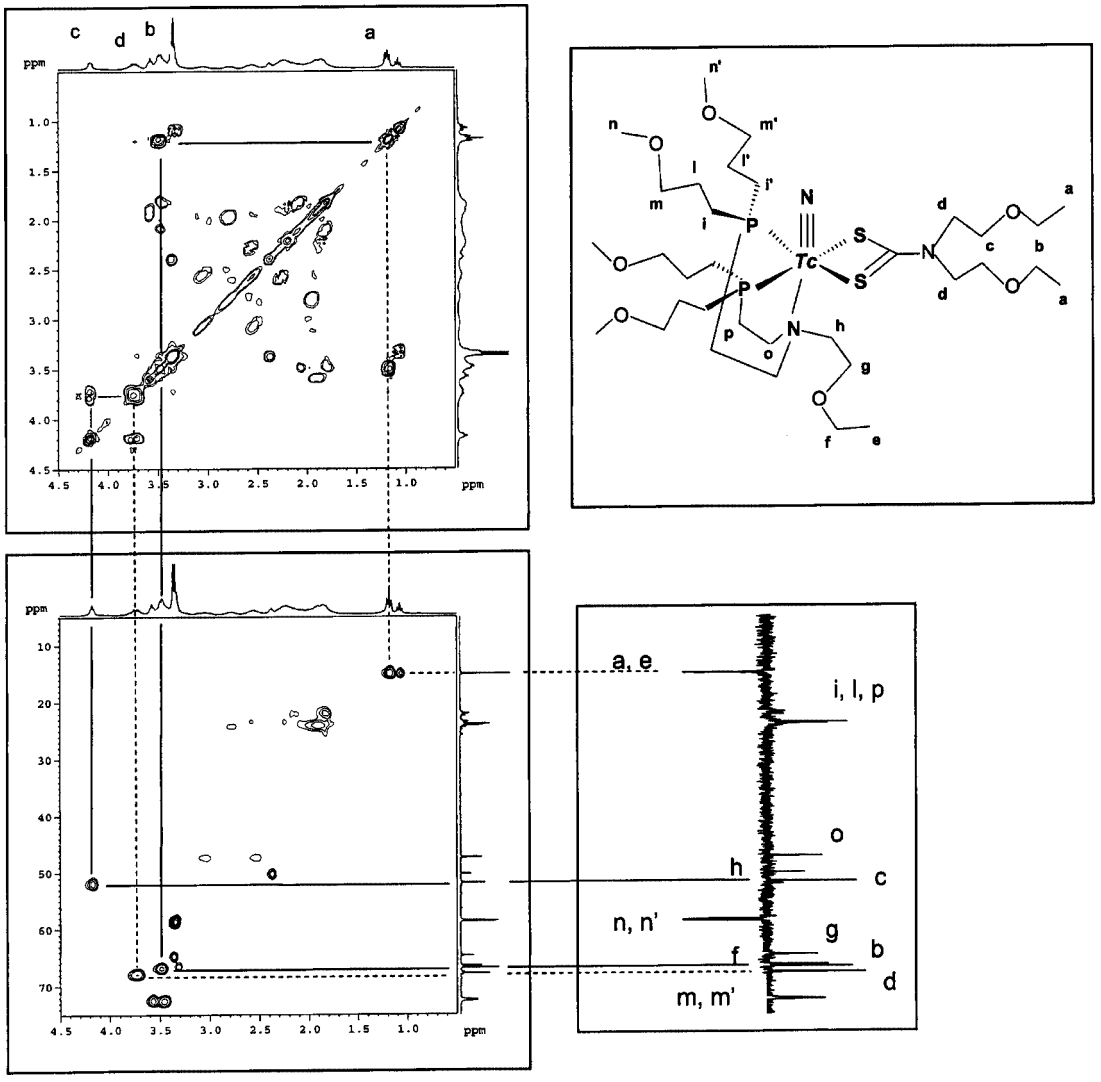


Figure 5. NMR spectra and maps of complex **8**; ^{1}H-^{1}H COSY spectrum (top left); ^{1}H-^{13}C HETCOR spectrum (bottom left); ^{13}C-DEPT 135 spectrum (bottom right); atom numbering scheme (top right); example of interpretation: carbon **b** is connected (solid line) with methylene protons **b** (multiplet at ca. 3.5 ppm) through a unique spot in the HETCOR map; protons **b** are coupled with methyl protons **a** (triplet at ca 1.20 ppm) in the COSY map; protons **a** are in turn connected with carbon **a** (dotted line) through another spot in the HETCOR map; the same interpretation strategy is applied for carbon and protons **c** and **d**, and for the other networks

diagram in Figure 5), the former being phased "down" (on the left of the spectrum, as shown) and the latter being phased "up" (on the right of the spectrum). The downfield-shifted methyl carbons correspond to the terminal methoxy groups of the phosphane substituents (C-n and C-n′); the splitting is determined by the relative *syn* and *anti* orientation of each substituent with respect to the Tc≡N core. The upfield-shifted methyl signal in the carbon spectrum consists of two overlapping signals (split correctly into two components in the proton spectrum), due to the presence of two chemically inequivalent ethoxy groups (Me-a and Me-e). The related methylene protons of the terminal ethoxy groups CH_2-b and CH_2-f, as well as the methylene network of the dithiocarbamate (CH_2-c and CH_2-d) are distinguished in the COSY spectrum. Analogously, the methylene chain of the pendant *N*-diphosphane ethoxyethyl fragment (CH_2-h and CH_2-g) shows cross peaks in the COSY spectrum, as well as two distinct peaks in the HETCOR spectrum. Regarding the terminal methoxy groups Me-n and Me-n′ outlined above, the diphosphane methoxypropyl chains are oriented *syn* and *anti* with respect to the Tc≡N core, giving two distinct proton networks (i, l and m, and i′, l′ and m′). The peaks due to the bridging diphosphane methylene protons (o and p) are widely separated and show a cross-peak in the COSY spectrum. The diastereotopic nature of the bridging methylene protons is clear from the HETCOR map, which shows two distinct spots for each bridging carbon.

Comments

The efficient synthesis of mono-cationic heterocomplexes $[M(N)(DTC)(PNP)]^+$ (M = Tc, Re) described here provides a clear example of reactions able to form complexes containing two different polydentate ligands coordinated to the same Tc≡N group. As previously noted for the similar compound $[M(N)(L)(POP)]^+$ [L = *S*-methyl 2-methyldithiocarbazate mono-anion, POP = bis[(diphenylphosphanyl)ethyl]ether],[7] the remarkable stability of this class of complexes results from a balance of π-acceptor and π-donor properties provided by the combination of the diphosphane and dithiocarbamate ligands bound to the same $[M{\equiv}N]^{2+}$ group. The exclusive formation of the mixed complexes $[M(N)(DTC)(PNP)]^+$, without the concomitant production of the symmetrical species $[M(N)(DTC)_2]$, is attributed to the strong electrophilic character of the metal fragment $[M(N)(PNP)]^{2+}$. This electrophilic character results from removal of electronic density from the two residual positions of the five-coordinate arrangement determined by the two π-acceptor atoms. As a consequence, these two bonding sites are activated only towards soft, π-donor atoms, and the whole metal fragment $[M(N)(PNP)]^{2+}$ becomes strongly stabilized upon substitution with an appropriate bidentate π-donor ligand. The additional contact between the metal center and the PNP diphosphane nitrogen helps to explain the remarkable kinetic inertness demonstrated by these class of heterocomplexes toward transchelation by other chelating agents.[14] In this regard, it should be mentioned that diphosphanes incorporating merely methylene groups in the spacer or diphosphanes carrying a quaternary ammonium group in the middle of the spacer yielded only mixtures from which the isolation of stable compounds was unsuccessful, thus supporting the view that contact of the lone pair of the amine nitrogen with the metal is important.

The high chemical stability of mono-cationic $[M(N)(DTC)(PNP)]^+$ heterocomplexes is also partially responsible for their interesting biological properties. These complexes showed selective localization into the myocardium of rats and retention in this region for a prolonged time.[13,14] Modification of the outer sphere pendant groups was found to influence both the kinetics of uptake by the heart and clearance from the background organs, giving unprecedentedly high heart/liver and heart/lung uptake ratios.[14] Hence, the prototype agent $[^{99m}Tc(N)(dbodc)(pnp5)]^+$ was proposed as a potential candidate for the development of a new myocardial perfusion tracer.[17] These findings prompted us to prepare and characterize macroscopic amounts of the corresponding ^{99}Tc and Re complexes with the aim to elucidate their molecular structure. As outlined in Figure 4, the solid-state geometry exhibited by the representative rhenium complex **1** is distorted square pyramidal [or pseudo-octahedral if we consider the additional Re−N(2) contact]. However, the flexiblity of the methoxypropyl groups made it impossible to grow crystals suitable for X-ray diffraction studies. Therefore, we were forced to characterize alkyldiphosphane-containing compounds in the solution state by means of combined mass spectrometry and multinuclear NMR investigations. These experiments confirmed that the molecular structure of these complexes (shown in Figures 2 and 5) is monomeric and, most importantly, identical to that shown by the aryldiphosphane-containing species (Figure 4). In particular, the diphosphane phosphorous atoms, as well as the pendant arms of the dithiocarbamate unit, were found to be magnetically equivalent, whereas the

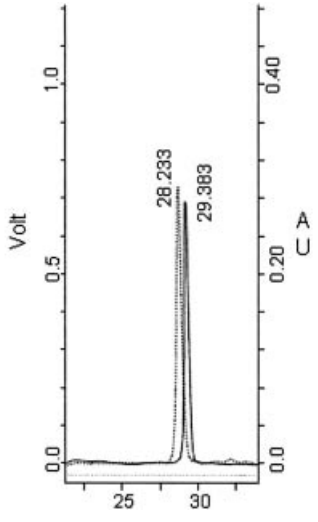


Figure 6. HPLC co-injection profiles for the complexes $[^{99m}Tc(N)(dbodc)(pnp5)]^+$ and $[^{99}Tc(N)(dbodc)(pnp5)]^+$ **8** (solid line, radiometric trace; dashed line, UV/Vis trace)

methoxypropyl substituents on the phosphorous atoms were magnetically inequivalent, and oriented *syn* and *anti* with respect to the terminal nitrido group.

Strong support for the conclusion that the chemical nature of the complex $[^{99m}Tc(N)(dbodc)(pnp5)]^+$ (prepared at tracer level) is similar to that of the corresponding ^{99m}Tc analogue (isolated in macroscopic amounts) was obtained by comparison of their chromatographic profiles after HPLC co-injection. As shown in Figure 6, the two species co-eluted at 29.38 min (radiometric trace) and at 28.23 min (UV/Vis trace).

Conclusion

A new family of cationic mixed nitrido heterocomplexes of general formula $[M(N)(DTC)(PNP)]^+$, where M is ^{99}Tc or Re, DTC is the mono-anionic form of a dithiocarbamate ligand and PNP is a heterodiphosphane incorporating a tertiary amine group in a five-membered spacer, has been synthesized and completely characterized both in the solid and in the solution state. The molecular structure of this class of mixed complexes is best described as pseudo-octahedral, with the diphosphane ligand facing the dithiocarbamate unit on the equatorial plane. The terminal nitrido and the weakly bound heterodiphosphane nitrogen complete the octahedron in a reciprocal *trans*-axial arrangement. The peculiar combination of π-acceptor phosphorous and π-donor sulfur around the M≡N group ensures remarkable thermodynamic stability and associated high kinetic inertness towards transchelation reactions. One of these complexes prepared at tracer level, $[^{99m}Tc(N)(dbodc)(pnp5)]^+$, has shown interesting biological properties in animal models.

Experimental Section

General Remarks: ***Caution!*** ^{99}Tc is a weak β-emitter (E_β = 0.292 MeV, $t_{1/2} = 2.12 \times 10^5$ years). All manipulations were carried out in laboratories approved for low-level radioactivity using monitored hoods and glove-boxes. When handled in milligram amounts, ^{99}Tc does not present a serious health hazard since common laboratory glassware provides adequate shielding. Bremsstrahlung radiation is not a significant problem due to the low-energy of the β-particles. However, normal radiation safety procedures must be used at all times, especially with solid samples, to prevent contamination and inhalation. Methanolic solutions (concentration ca. 2×10^{-6} M) were used for mass spectrometric measurements (ESI). For a 50-minute analysis at a flow-rate of 5 μL/min, the amount of ^{99}Tc injected into the mass spectrometer led to a radioactivity level lower than the environmental background.

Technetium (as $[NH_4][^{99}TcO_4]$) was obtained from Oak Ridge National Laboratory. Samples were dissolved in water and treated with excess aqueous ammonia and 30% H_2O_2 at 80 °C prior to use to eliminate residual TcO_2. Solid samples of purified ammonium pertechnetate were obtained by slow evaporation of the solvent at 40 °C. Literature methods were applied to prepare the starting compounds $[M(N)Cl_2(PPh_3)_2]$[18,19] and the intermediate species $[M(N)Cl_2(PNP)]$.[7] Finely powdered rhenium was obtained as a gift from H. C. Starck GmbH, Germany. Samples were first oxidized to perrhenate and then reduced to suitable Re^V compounds prior to use. Diethyldithiocarbamate sodium salt (dedcNa) was purchased from Aldrich Chimica and *N,N′*-bis(ethoxyethyl)dithiocarbamate sodium salt (dbodcNa) was prepared according to literature methods or obtained from Alchemy, Italy.[20] Aryl diphosphanes (pnp2 and pnp24) and alkyl diphosphanes (pnp3 and pnp5) were synthesized as reported previously[21,22] or purchased from Argus Chemicals, Italy. Aryl diphosphanes are stable both as solids and in solution, but alkyl diphosphanes are air and moisture sensitive, and should be handled carefully under a nitrogen atmosphere and stored under nitrogen at −20 °C to avoid oxidation of the tertiary diphosphane to the corresponding diphosphaneoxide. Common laboratory solvents and other chemicals were used as received.

Elemental analyses (C, H, N, S) were performed on a Carlo−Erba 1106 elemental analyzer. FT IR spectra were recorded on a Nicolet 510P Fourier-transform spectrometer in the range 4000−400 cm^{-1} in KBr mixtures using a Spectra-Tech diffuse-reflectance collector accessory for technetium compounds and on a Mattson 3030 Fourier-transform spectrometer in the range 4000−400 cm^{-1} in KBr pellets for rhenium compounds. Proton and ^{31}P NMR spectra were collected on a Bruker AC-300 instrument, using $SiMe_4$ as an internal reference (for ^1H) and 85% aqueous H_3PO_4 as an external reference (for ^{31}P). Mass spectrometric measurements were performed with a LCQ DECA instrument (ThermoFinnigan, Palo Alto, CA, USA) using ca. 5×10^{-6} M methanol solutions of rhenium complexes **1−4**, which were injected by a syringe pump at a flow rate of 5 μL/min. MS^n experiments were performed by selection of the ionic species of interest followed by collision with He inside the ion trap (He pressure 10^{-4} Torr) accomplished by resonant excitation. The supplementary rf voltage was in the range 0.25−4.00 V. Thin-layer chromatography (TLC) was performed using plates from Merck (Silica gel 60 F 254).

Ligands

Diphosphanes and Dithiocarbamates: The diphosphane ligands utilized in this work were prepared according to published methods.[21,22] The full NMR characterizations of these diphosphanes and of the branched dithiocarbamate Nadbodc are detailed below.

Bis[(diphenylphosphanyl)ethyl]methoxyethylamine (pnp2): ^1H NMR (300 MHz, Me_4Si, $CDCl_3$): δ = 2.07 [m, 4 H, N−(CH_2−CH_2−PPh_2)$_2$], 2.59 [m, 4 H + 2 H, N−(CH_2−CH_2−PPh_2)$_2$ and N−CH_2−CH_2−O−CH_3], 3.20 (s, 3 H, N−CH_2−CH_2−O−CH_3), 3.26 (t, ^3J = 9 Hz, 2 H; N−CH_2−CH_2−O−CH_3), 7.30−7.40 (−PPh_2, 20 H) ppm. ^{13}C NMR (300 MHz, Me_4Si, $CDCl_3$): δ = 25.0 (d, $^1J_{C,P}$ = 13 Hz; N−CH_2−CH_2−PPh_2), 50.1 (d, $^2J_{C,P}$ = 35 Hz; N−CH_2−CH_2−PPh_2), 52.8 (s, N−CH_2−CH_2−O−CH_3), 58.7 (s, N−CH_2−CH_2−OCH_3), 70.7 (s, N−CH_2−CH_2−OCH_3), 128.4 (d, $^3J_{C,P}$ = 8 Hz), 128.5 (s), 132.7 (d, $^2J_{C,P}$ = 22 Hz), 138.4 (d, $^1J_{C,P}$ = 8 Hz) (aromatic *C*) ppm. ^{31}P NMR (300 MHz, 85% H_3PO_4, $CDCl_3$): δ = −21.5 (s).

Bis[(diphenylphosphanyl)ethyl]methylamine (pnp24): ^1H NMR (300 MHz, Me_4Si, $CDCl_3$): δ = 2.14 [m, 4 H, N−(CH_2−CH_2−PPh_2)$_2$], 2.24 (s, 3 H, N−CH_3), 2.48 [m, 4 H, N−(CH_2−CH_2−PPh_2)$_2$], 7.30−7.41 (−PPh_2, 20 H) ppm. ^{13}C NMR (300 MHz, Me_4Si, $CDCl_3$): δ = 22.1 (d, $^1J_{C,P}$ = 18 Hz; N−CH_2−CH_2−PPh_2), 39.6 (s, N−CH_3), 52.7 (d, $^2J_{C,P}$ = 29 Hz, N−CH_2−CH_2−PPh_2), 128.9 (d, $^3J_{C,P}$ = 7 Hz), 129.5 (s), 132.7 (d, $^1J_{C,P}$ = 20 Hz), 135.6 (d, $^2J_{C,P}$ = 9 Hz) (aromatic *C*) ppm. ^{31}P NMR (300 MHz, 85% H_3PO_4, $CDCl_3$): δ = −21.5 (d) ppm.

Bis[(dimethoxypropylphosphanyl)ethyl]methoxyethylamine (pnp3): ^1H NMR (300 MHz, Me_4Si, $CDCl_3$): δ = 1.36−1.75 (4 H +16 H,

N−(CH2−CH2)2−[P−(CH2−CH2−CH2−O−CH3)2]2), 2.62 [m, 2 H +4 H, CH3−O−CH2−CH2−N−(CH2−CH2)2−P], 3.30 (s, 3 H +12 H, O−CH3), 3.38 (t, 3J = 9 Hz, 8 H, P−CH2−CH2−CH2−O−CH3), 3.42 (t, 3J = 9 Hz, 2 H, N−CH2−CH2−O−CH3) ppm. 13C NMR (300 MHz, Me4Si, CDCl3): δ = 23.4 (d, 1JC,P = 12 Hz, P−CH2−CH2−CH2−O−CH3), 24.2 [d, 1JC,P = 13 Hz; P−(CH2−CH2)2−N], 26.0 (d, 2JC,P = 13 Hz; P−CH2−CH2−CH2−O−CH3), 50.9 [d, 2JC,P = 21 Hz; P−(CH2−CH2)2−N], 52.5 (s, N−CH2−CH2−O−CH3), 58.5 (s, P−CH2−CH2−CH2−OCH3), 58.9 (s, N−CH2−CH2−OCH3), 71.1 (s, N−CH2−CH2−OCH3), 73.4−73.6 (P−CH2−CH2−CH2−OCH3) ppm. 31P NMR (300 MHz, 85% H3PO4, CDCl3): δ = − 34.4 (s).

Bis[(dimethoxypropylphosphanyl)ethyl]ethoxyethylamine (pnp5): 1H NMR (300 MHz, Me4Si, CDCl3): δ = 1.19 (t, 3J = 7 Hz, 3 H, P2N−CH2−CH2−O−CH2−CH3), 1.45 (m, 8 H, P−CH2−CH2−CH2−O−CH3), 1.54 [m, 4 H, (P−CH2−CH2)2N−), 1.68 [m, 8 H, P(CH2−CH2−CH2−O−CH3)2], 2.65 [m, 4 H + 2 H, P−(CH2−CH2)2−N−CH2−CH2−O−CH2−CH3], 3.33 [s, 12 H, P(CH2−CH2−CH2−O−CH3)2], 3.40 [t, 3J = 6 Hz, 8 H, P−(CH2−CH2−CH2−O−CH3)2], 3.49 (m, 2 H + 2 H, >N−CH2−CH2−O−CH2−CH3) ppm. 13C NMR (CDCl3, ppm): δ = 15.1 (s, >N−CH2−CH2−O−CH2−CH3), 23.4 (d, 1JC,P = 12 Hz; P−CH2−CH2−CH2−O−CH3), 24.3 [d, 1JC,P = 12 Hz; P−(CH2−CH2)2−N], 26.0 (d, 2JC,P = 14 Hz; P−CH2−CH2−CH2−O−CH3), 51.0 [d, 1JC,P = 21 Hz; P−(CH2−CH2)2−N], 52.5 (s, >N−CH2−CH2−O−CH2−CH3), 58.5 (s, P−CH2−CH2−CH2−O−CH3), 66.5 (s, >N−CH2−CH2−O−CH2−CH3), 69.0 (s, >N−CH2−CH2−O−CH2−CH3), 73.4 and 73.6 (P−CH2−CH2−CH2−O−CH3) ppm. 31P NMR (300 MHz, 85% H3PO4, CDCl3): δ = − 31.7 (s).

***N,N′*-Bis(ethoxyethyl)dithiocarbamate Sodium Salt (Nadbodc):** 1H NMR (300 MHz, D2O): δ = 1.20 [t, 6 H, S2CN(CH2−CH2−O−CH2−CH3)2], 3.62 [q, 4 H, S2CN(CH2−CH2−O−CH2−CH3)2], 3.85 [t, 4 H, S2CN(CH2−CH2−O−CH2−CH3)2], 4.29 [t, 4 H, S2CN(CH2−CH2−O−CH2−CH3)2] ppm. 13C NMR (300 MHz, D2O ppm): δ = 17.1 [s, S2CN(CH2−CH2−O−CH2−CH3)2], 57.2 [s, S2CN(CH2−CH2−O−CH2−CH3)2], 69.6 and 69.9 [s, S2CN(CH2−CH2−O−CH2−CH3)2], 213.9 [s, S2CN(CH2−CH2−O−CH2−CH3)2].

Synthesis of Technetium and Rhenium Complexes: A general one-pot procedure was adopted for the preparation of both technetium and rhenium complexes.

[M(N)(DTC)(PNP)][Cl] (M = 99Tc, Re) (1−8): A solution of the appropriate diphosphane (0.05 mmol) in ethanol (10 mL) was added under a nitrogen atmosphere to a three-neck round-bottomed flask containing a suspension of [M(N)Cl2(PPh3)2] (0.05 mmol) in dichloromethane (10 mL). The mixture was stirred for 60 min at room temperature (or at reflux for rhenium complexes) to give a clear bright yellow solution. A solution of DTC sodium salt (0.055 mmol) in ethanol (5 mL) was added, and, after reflux for an additional 60 min (overnight reflux is necessary for rhenium complexes), the yellow solution was cooled and the solvent removed by a gentle stream of nitrogen. The residue was treated with dichloromethane (5 mL) and a white precipitate was separated by filtration. The filtrate was again evaporated to dryness to give a pale yellow solid residue (for compounds containing aryl diphosphanes), or a yellow oil (for compounds containing alkyl diphosphanes). Technetium complexes **5** and **6** were purified by treating the residue with ethanol (3 mL). A yellow precipitate was collected by filtration, washed with diethyl ether (4 × 5 mL) and dried under vacuum. The oily products **7** and **8** were placed under vacuum overnight to afford pure compounds as a yellow-orange oils (yield >90%). For all rhenium complexes, column chromatography (described below) was necessary to separate the pure species. The filtrate was evaporated to dryness and then re-dissolved in the minimum amount of chloroform. The resulting solution was loaded onto a silica column (diameter 2 cm, length 30 cm) previously conditioned with chloroform. Elution was conducted with chloroform (100 mL) followed by a mixture of ethanol/chloroform/toluene/0.5 M ammonium acetate (5:3:3:0.5) to provide the pure compounds in low-to-moderate yields (25−40%). The light yellow residue obtained after chromatography of complex **1** was dissolved in methanol (2 mL) and added to an excess of NH_4PF_6 in methanol (3 mL). Trituration with diethyl ether (20 mL) yielded a yellow-orange powder, which was filtered off, washed with diethyl ether (2 × 5 mL) and dried under vacuum.

[Re(N)(dedc)(pnp2)][PF6] (1): $C_{36}H_{45}F_6N_3OP_3S_2Re$ (993.0): calcd. C 43.54, H 4.57, N 4.23, S 6.45; found C 43.72, H 4.51, N 4.41, S 6.63. IR (KBr): $\tilde{\nu}$ = 1434 cm^{-1} (s), 1100 (s, Re−P), 1061 [m, Re(N)], 840 (vs, PF_6), 693 (s). 1H NMR ($CDCl_3$, ppm): δ = 1.27 [t, 6 H, $S_2CN(CH_2-CH_3)_2$], 2.53 (t, 2 H, $P_2N-CH_2-CH_2-O-CH_3$), 3.00−3.51 [8 H, $(P-CH_2-CH_2)_2N-$], 3.27 (s, 3 H, $P_2N-CH_2-CH_2-O-CH_3$), 3.57 (t, 2 H, $P_2N-CH_2-CH_2-O-CH_3$), 3.70 [m, 4 H, $S_2CN(CH_2-CH_3)_2$], 6.95−7.94 (20 H, C_6H_5-P) ppm. 13C NMR ($CDCl_3$, ppm): δ = 12.5 [s, $S_2CN-(CH_2-CH_3)_2$], 25.1 [d, $J_{C,P}$ = 14 Hz; $P-(CH_2-CH_2)_2N-$], 45.0 (s, $S_2CN(CH_2-CH_3)_2$], 49.5 [s, $P(CH_2-CH_2)_2N-$], 50.9 (s, $P_2N-CH_2-CH_2-O-CH_3$), 58.9 (s, $P_2N-CH_2-CH_2-O-CH_3$), 67.2 (s, $P_2N-CH_2-CH_2-O-CH_3$), 128.8−134.0 (C_6H_5-P), 215.8 [s, $S_2CN-(CH_2-CH_3)_2$] ppm. 31P NMR ($CDCl_3$, ppm): δ = 18.3 (s), −144.0 (septet, PF_6). ESI MS (*m/z*): 848 $[M]^+$. Yield 35%.

[Re(N)(dedc)(pnp24)][Cl] (2): $C_{34}H_{41}ClN_3P_2ReS_2$ (839.4): calcd. C 48.64, H 4.92, N 5.00, S 7.64; found C 48.78, H 5.01, N 5.21, S 7.88. 1H NMR ($CDCl_3$, ppm): δ = 1.28 [t, 6 H, $S_2CN(CH_2-CH_3)_2$], 2.09 (s, 3 H, $N-CH_3$), 2.86−3.56 [8 H, $(P-CH_2-CH_2)_2N-$], 3.70 [m, 4 H, $S_2CN(CH_2-CH_3)_2$], 6.96−7.95 (20 H, C_6H_5-P) ppm. 13C NMR ($CDCl_3$, ppm): 12.5 [s, $S_2CN-(CH_2-CH_3)_2$], 24.2 [d, $-P-(CH_2-CH_2)_2N-$], 44.6 (s, $N-CH_3$), 45.2 [s, $S_2CN(CH_2-CH_3)_2$], 50.3 [s, $P(CH_2-CH_2)_2N-$], 128.9−132.4 (C_6H_5-P), 212.5 [s, $S_2CN-(CH_2-CH_3)_2$] ppm. 31P NMR ($CDCl_3$, ppm): δ = 18.8 (s). ESI MS (*m/z*): 804 $[M]^+$. Yield 25%.

[Re(N)(dedc)(pnp3)][Cl] (3): $C_{28}H_{61}ClN_3O_5P_2ReS_2$ (867.5): calcd. C 38.76, H 7.09, N 4.84, S 7.39; found C 39.01, H 7.16, N 4.98, S 7.59. 1H NMR ($CDCl_3$, ppm): δ = 1.37 [t, 6 H, $S_2CN(CH_2-CH_3)_2$], 1.73 [m, 4 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2endo}$], 1.85 [m, 4 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2exo}$], 2.04 [m, 2 H + 2 H, $(P-CH_2-CH_2)_2N-_{endo}$ and $P(CH_2-CH_2-CH_2-O-CH_3)_2$], 2.31 [m, 4 H, $P(CH_2-CH_2-CH_2-O-CH_3)_2$], 2.42 (t, 2 H, $P_2N-CH_2-CH_2-O-CH_3$), 2.66 [m, 2 H, $(P-CH_2-CH_2)_2N-_{endo}$], 2.70 [m, 2 H, $P(CH_2-CH_2-CH_2-O-CH_3)_2$], 2.93 [m, 2 H, $(P-CH_2-CH_2)_2N-_{exo}$], 3.20 (s, 3 H, $P_2N-CH_2-CH_2-O-CH_3$), 3.22 [m, 2 H, $(P-CH_2-CH_2)_2N-_{exo}$], 3.35 [s, 6 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2endo}$], 3.37 [s, 6 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2exo}$], 3.38 (m, 2 H, $P_2N-CH_2-CH_2-O-CH_3$), 3.50 [m, 4 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2endo}$], 3.59 [m, 4 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2exo}$], 3.82 [m, 4 H, $S_2CN(CH_2-CH_3)_2$] ppm. 13C NMR ($CDCl_3$, ppm): δ = 12.6 (s, $S_2CN-(CH_2-CH_3)_2$], 22.9−26.1 [2 s and 3 d, $P(CH_2-CH_2-CH_2-O-CH_3)_{2endo/exo}$, $(P-CH_2-CH_2)_2N-$ and $P(CH_2-CH_2-CH_2-O-CH_3)_2$], 45.3 [s, $S_2CN(CH_2-CH_3)_2$], 48.7 [s, $P(CH_2-CH_2)_2N-$], 50.3 (s, $P_2N-CH_2-CH_2-O-CH_3$), 58.5 and 58.7 [2 s, $P(CH_2-CH_2-CH_2-O-CH_3)_2$], 58.8 (s, $P_2N-CH_2-CH_2-O-CH_3$), 66.9 (s, $P_2N-CH_2-CH_2-O-CH_3$),

72.3−72.5 [m, $P(CH_2-CH_2-CH_2-O-CH_3)_2$] ppm. ^{31}P NMR ($CDCl_3$, ppm): δ = 13.4 (s). ESI MS (*m*/*z*): 832 $[M]^+$. Yield 30%.

[Re(N)(dbodc)(pnp5)][Cl] (4): $C_{33}H_{71}ClN_3O_7P_2ReS_2$ (969.7): calcd. C 40.90, H 7.38, N 4.33, S 6.61; found C 41.08, H 7.46, N 4.28, S 6.86. ^1H NMR ($CDCl_3$, ppm): δ = 1.09 (t, 3 H, $P_2N-CH_2-CH_2-O-CH_2-CH_3$), 1.19 [t, 6 H, $S_2CN(CH_2-CH_2-O-CH_2-CH_3)_2$], 1.78 [m, 4 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2endo}$], 1.87 [m, 4 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2exo}$], 2.04 [m, 2 H, $(P-CH_2-CH_2)_2N-_{endo}$], 2.06 and 2.31 [m, 2 H + 4 H, $P(CH_2-CH_2-CH_2-O-CH_3)_2$], 2.45 (t, 2 H, $P_2N-CH_2-CH_2-O-CH_2-CH_3$), 2.67 [m, 2 H, $P(CH_2-CH_2-CH_2-O-CH_3)_2$], 2.70 [m, 2 H, $(P-CH_2-CH_2)_2N-_{endo}$], 2.90 [m, 2 H, $(P-CH_2-CH_2)_2N-_{exo}$], 3.23 [m, 2 H, $(P-CH_2-CH_2)_2N-_{exo}$], 3.32 (q, 2 H, $P_2N-CH_2-CH_2-O-CH_2-CH_3$), 3.35 [s, 6 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2endo}$], 3.37 [s, 6 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2exo}$], 3.39 (m, 2 H, $P_2N-CH_2-CH_2-O-CH_2-CH_3$), 3.50 [q + m, 4 H + 4 H, $S_2CN(CH_2-CH_2-O-CH_2-CH_3)_2$ + $P(CH_2-CH_2-CH_2-O-CH_3)_{2endo}$], 3.59 [m, 4 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2exo}$], 3.76 [m, 4 H, $S_2CN(CH_2-CH_2-O-CH_2-CH_3)_2$], 4.10 [m, 4 H, $S_2CN(CH_2-CH_2-O-CH_2-CH_3)_2$] ppm. ^{13}C NMR ($CDCl_3$, ppm): δ = 15.1 [s, $S_2CN-(CH_2-CH_2-O-CH_2-CH_3)_2$ + $P_2N-CH_2-CH_2-O-CH_2-CH_3$], 23.9−26.1 [2 s and 3 d, $P(CH_2-CH_2-CH_2-O-CH_3)_{2endo/exo}$, $(P-CH_2-CH_2)_2N-$)], 48.7 [s, $P(CH_2-CH_2)_2N-$], 50.4 (s, $P_2N-CH_2-CH_2-O-CH_2-CH_3$), 51.9 [s, $S_2CN(CH_2-CH_2-O-CH_2-CH_3)_2$], 58.5 and 58.7 [2 s, $P(CH_2-CH_2-CH_2-O-CH_3)_2$], 64.7 (s, $P_2N-CH_2-CH_2-O-CH_2-CH_3$), 66.5 (s, $P_2N-CH_2-CH_2-O-CH_2-CH_3$), 66.9 [s, $S_2CN-(CH_2-CH_2-O-CH_2-CH_3)_2$], 67.8 [s, $S_2CN-(CH_2-CH_2-O-CH_2-CH_3)_2$], 72.3−72.5 [m, $P(CH_2-CH_2-CH_2-O-CH_3)_2$], 220.2 [s, $S_2CN-(CH_2-CH_2-O-CH_2-CH_3)_2$] ppm. ^{31}P NMR ($CDCl_3$, ppm): δ = 13.4 (s). ESI MS (*m*/*z*): 933 $[M]^+$. Yield 30%.

[Tc(N)(dedc)(pnp2)][Cl] (5): $C_{36}H_{45}ClN_3P_2S_2Tc$ (780.2): calcd. C 54.30, H 5.69, N 5.28, S 8.05; found C 54.62, H 5.59, N 5.33, S 8.32. ^1H NMR ($CDCl_3$, ppm): δ = 1.22 (t, 6 H, $S_2CN(CH_2-CH_3)_2$], 2.45 (t, 2 H, $P_2N-CH_2-CH_2-O-CH_3$), 2.96−3.46 [8 H, $(P-CH_2-CH_2)_2N-$], 3.22 (s, 3 H, $P_2N-CH_2-CH_2-O-CH_3$), 3.50 (t, 2 H, $P_2N-CH_2-CH_2-O-CH_3$), 3.75 [m, 4 H, $S_2CN(CH_2-CH_3)_2$], 6.96−7.89 (20 H, C_6H_5-P) ppm. ^{13}C NMR ($CDCl_3$, ppm): δ = 12.5 [s, $S_2CN-(CH_2-CH_3)_2$], 24.0 [d, $J_{C,P}$ = 14 Hz; $P-(CH_2-CH_2)_2N-$], 44.8 [s, $S_2CN(CH_2-CH_3)_2$], 48.5 [s, $P(CH_2-CH_2)_2N-$], 50.9 (s, $P_2N-CH_2-CH_2-O-CH_3$), 58.9 (s, $P_2N-CH_2-CH_2-O-CH_3$), 67.4 (s, $P_2N-CH_2-CH_2-O-CH_3$), $S_2CN(CH_2-CH_3)_2$] ppm. ^{13}C NMR NMR ($CDCl_3$, ppm): δ = 29.9 (bs). Yield 80%.

[Tc(N)(dedc)(pnp24)][Cl] (6): $C_{34}H_{41}ClN_3OP_2S_2Tc$ (768.1): calcd. C 54.28, H 5.49, N 5.58, S 8.52; found C 54.63, H 5.71, N 5.39, S 8.23. ^1H NMR ($CDCl_3$, ppm): 1.23 (t, 6 H, $N-CH_2-CH_3$), 1.98 (s, 3 H, $N-CH_3$), 2.23−3.35 [8 H, $(P-CH_2-CH_2)_2-N-$], 3.72 (m, 4 H, $N-CH_2-CH_3$), 6.97−7.89 (20 H, H_{arom}) ppm. ^{13}C NMR ($CDCl_3$, ppm): δ = 12.5 [s, $S_2CN-(CH_2-CH_3)_2$], 23.5 [d, $-P-(CH_2-CH_2)_2N-$], 43.5 (s, $N-CH_3$), 44.9 [s, $S_2CN(CH_2-CH_3)_2$], 49.8 [s, $P(CH_2-CH_2)_2N-$], 128.9−132.3 (C_6H_5-P), 210.5 [s, $S_2CN-(CH_2-CH_3)_2$] ppm. ^{31}P NMR ($CDCl_3$, ppm): δ = 34.4 (bs). Yield 78%.

[Tc(N)(dbodc)(pnp3)][Cl] (7): $C_{32}H_{69}ClN_3O_7P_2S_2Tc$ (868.3): calcd. C 44.25, H 8.01, N 4.84, S 7.38; found C 44.22, H 8.22, N 4.77, S 7.55. ^1H NMR ($CDCl_3$, ppm): δ = 1.15 [t, 6 H, $S_2CN(CH_2-CH_2-O-CH_2-CH_3)_2$], 1.84 [m, 4 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2endo}$], 1.90 [m, 4 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2exo}$], 2.10 [m, 2 H, $(P-CH_2-CH_2)_2N-_{endo}$], 2.14 and 2.24 [m, 2 H + 4 H, $P(CH_2-CH_2-CH_2-O-CH_3)_2$], 2.35 (t, 2 H, $P_2N-CH_2-CH_2-O-CH_3$), 2.54 [m, 2 H, $P(CH_2-CH_2-CH_2-O-CH_3)_2$], 2.56 [m, 2 H, $(P-CH_2-CH_2)_2N-_{endo}$], 2.76 [m, 2 H, $(P-CH_2-CH_2)_2N-_{exo}$], 3.03 [m, 2 H, $(P-CH_2-CH_2)_2N-_{exo}$], 3.14 (s, 3 H, $P_2N-CH_2-CH_2-O-CH_3$), 3.29 (t, 2 H, $P_2N-CH_2-CH_2-O-CH_3$), 3.31 [s, 6 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2endo}$], 3.33 [s, 6 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2exo}$], 3.40 (m, 2 H, $P_2N-CH_2-CH_2-O-CH_2-CH_3$), 3.45 [q + m, 4 H +4 H, $S_2CN(CH_2-CH_2-O-CH_2-CH_3)_2$ + $P(CH_2-CH_2-CH_2-O-CH_2-CH_3)_{2endo}$], 3.55 [m, 4 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2exo}$], 3.69 [m, 4 H, $S_2CN(CH_2-CH_2-O-CH_2-CH_3)_2$], 4.14 [m, 4 H, $S_2CN(CH_2-CH_2-O-CH_2-CH_3)_2$] ppm. ^{13}C NMR ($CDCl_3$, ppm): δ = 15.0 [s, $S_2CN-(CH_2-CH_2-O-CH_2-CH_3)_2$], 22.0−24.4 [2 s and 3 d, $P(CH_2-CH_2-CH_2-O-CH_3)_{2endo/exo}$, + $(P-CH_2-CH_2)_2N-$], 47.4 [s, $P(CH_2-CH_2)_2N-$], 50.2 (s, $P_2N-CH_2-CH_2-O-CH_3$), 51.9 [s, $S_2CN(CH_2-CH_2-O-CH_2-CH_3)_2$], 58.6 and 58.7 [2 s, $P(CH_2-CH_2-CH_2-O-CH_3)_2$], 66.8 (s, $P_2N-CH_2-CH_2-O-CH_3$), 67.0 [s, $S_2CN-(CH_2-CH_2-O-CH_2-CH_3)_2$], 67.8 [s, $S_2CN-(CH_2-CH_2-O-CH_2-CH_3)_2$], 72.3−72.5 [m, $P(CH_2-CH_2-CH_2-O-CH_3)_2$], 213.8 [s, $S_2CN-(CH_2-CH_2-O-CH_2-CH_3)_2$].$^{31}P$ NMR ($CDCl_3$, ppm): δ = 29.9 (bs). Yield 85%.

[Tc(N)(dbodc)(pnp5)][Cl] (8): $C_{33}H_{71}ClN_3O_7P_2S_2Tc$ (882.4): calcd. C 44.91, H 8.11, N 4.76, S 7.27; found C 45.32, H 8.33, N 4.67, S 7.44. ^1H NMR ($CDCl_3$, ppm): δ = 1.07 (t, 3 H, $P_2N-CH_2-CH_2-O-CH_2-CH_3$), 1.18 [t, 6 H, $S_2CN(CH_2-CH_2-O-CH_2-CH_3)_2$], 1.84 [m, 4 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2endo}$], 1.90 [m, 4 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2exo}$], 2.10 [m, 2 H, $(P-CH_2-CH_2)_2N-_{endo}$], 2.14 and 2.24 [m, 2 H + 4 H, $P(CH_2-CH_2-CH_2-O-CH_3)_2$], 2.38 (t, 2 H, $P_2N-CH_2-CH_2-O-CH_2-CH_3$), 2.53 [m, 2 H, $P(CH_2-CH_2-CH_2-O-CH_3)_2$], 2.56 [m, 2 H, $(P-CH_2-CH_2)_2N-_{endo}$], 2.77 [m, 2 H, $(P-CH_2-CH_2)_2N-_{exo}$], 3.04 [m, 2 H, $(P-CH_2-CH_2)_2N-_{exo}$], 3.32 (q, 2 H, $P_2N-CH_2-CH_2-O-CH_2-CH_3$), 3.34 [s, 6 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2endo}$], 3.36 [s, 6 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2exo}$], 3.40 (m, 2 H, $P_2N-CH_2-CH_2-O-CH_2-CH_3$), 3.50 [q + m, 4 H + 4 H, $S_2CN(CH_2-CH_2-O-CH_2-CH_3)_2$] + $P(CH_2-CH_2-CH_2-O-CH_3)_{2endo}$, 3.59 [m, 4 H, $P(CH_2-CH_2-CH_2-O-CH_3)_{2exo}$], 3.72 [m, 4 H, $S_2CN(CH_2-CH_2-O-CH_2-CH_3)_2$], 4.17 [m, 4 H, $S_2CN(CH_2-CH_2-O-CH_2-CH_3)_2$] ppm. ^{13}C NMR ($CDCl_3$, ppm): δ = 15.1 [s, $S_2CN-(CH_2-CH_2-O-CH_2-CH_3)_2$ + $P_2N-CH_2-CH_2-O-CH_2-CH_3$], 22.0−24.4 [2 s and 3 d, $P(CH_2-CH_2-CH_2-O-CH_3)_{2endo/exo}$, + $(P-CH_2-CH_2)_2N-$], 47.4 [s, $P(CH_2-CH_2)_2N-$], 50.3 (s, $P_2N-CH_2-CH_2-O-CH_2-CH_3$), 51.9 [s, $S_2CN(CH_2-CH_2-O-CH_2-CH_3)_2$], 58.6 and 58.7 [2 s, $P(CH_2-CH_2-CH_2-O-CH_3)_2$], 64.7 (s, $P_2N-CH_2-CH_2-O-CH_2-CH_3$), 66.5 (s, $P_2N-CH_2-CH_2-O-CH_2-CH_3$), 66.7 [s, $S_2CN-(CH_2-CH_2-O-CH_2-CH_3)_2$], 67.8 [s, $S_2CN-(CH_2-CH_2-O-CH_2-CH_3)_2$], 72.3−72.6 [m, $P(CH_2-CH_2-CH_2-O-CH_3)_2$], 214.0 [s, $S_2CN-(CH_2-CH_2-O-CH_2-CH_3)_2$] ppm. ^{31}P NMR ($CDCl_3$, ppm): δ = 30.2 (bs). ESI MS (*m*/*z*): 847 $[M]^+$. Yield 89%.

X-ray Crystallographic Study: Single crystals of complex **1** were grown by slow evaporation from DMSO solutions as light yellow blocks. Pertinent crystallographic data and structure refinement data are summarized in Table 2. The data set was collected at room temperature on a Nicolet Siemens R3m /V diffractometer with graphite-monochromatized Mo-K_α radiation. Cell parameters were obtained by fitting a set of 50 high-angle reflections. After Lorentz, polarization and absorption corrections (Ψ-scans method), the structure was solved using the SHELXTL NT computer program[23] and refined with SHELXL-97[24] by the full-matrix least-

Table 2. Crystallographic data for complex **1**

Formula	$C_{36}H_{45}F_6N_3OP_3ReS_2$
Formula mass	993.0
Cryst. syst.	monoclinic
Space group	$P2_1/c$ (No. 14)
a, Å	11.730(2)
b, Å	30.234(6)
c, Å	11.732(2)
β, °	93.44(3)
V, Å^3	4153(1)
Z, $D_{calcd.}$, g cm^{-3}	4; 1.588
μ (Mo-K_α), (cm^{-1})	32.0
T (°C)	23
λ (Mo-K_α), Å	0.71073
Θ_{max}, °	24
Obsd. reflections [$I > 2\sigma(I)$]	4809
$R1$[a]	0.053
$wR2$[b]	0.121
GOF[c]	1.045

[a] $R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w\ (F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] GOF = $\{\Sigma[w\ (F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ (n = reflections; p = parameters).

squares technique based on F^2. Figures were drawn with the ORTEP II program.[25] The final difference map was featureless, apart from a relevant residue in the vicinity of C(7) atom, indicating a possible second position [C(7′)]. This model was refined satisfactorily with occupancies of ca. 0.5. Anisotropy was applied only to non−carbon atoms to assure a good reflections/parameters ratio. CCDC-220372 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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