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# Synthesis and structural characterization of new oxorhenium and oxotechnetium complexes with $\text{XN}_2\text{S}$ -tetradentate semi-rigid ligands ( $\text{X} = \text{O}, \text{S}, \text{N}$ )

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Twelve novel oxo-technetium and oxo-rhenium complexes based on  $\text{N}_2\text{S}_2^-$ ,  $\text{N}_2\text{SO}^-$  or  $\text{N}_3\text{S}$ -tetradentate semi-rigid ligands have been synthesised and studied herein. By reacting the ligands with a slight excess of suitable  $[\text{MO}]^{3+}$  precursor ( $\text{ReOCl}_3(\text{PPh}_3)_2$  or  $[\text{NBu}_4][^{99\text{m}}\text{TcOCl}_4]$ ), the monoanionic complexes of general formula  $[\text{MO}(\text{Ph}-\text{XN}_2\text{S})]^-$  could be easily produced in high yield. The complexes have been characterized by means of IR, electrospray mass spectrometry, elemental analysis, NMR and conductimetry. The crystal structures of  $[\text{PPh}_4][\text{ReO}(\text{Ph}-\text{ON}_2\text{S})]$  **1b** and  $[\text{NBu}_4][^{99\text{m}}\text{TcO}(\text{Ph}-\text{ON}_2\text{S})]$  **1c** have been established. The  $[\text{MO}]^{3+}$  moiety was coordinated *via* the two deprotonated amide nitrogens, the oxygen and the terminal sulfur atoms in **1b** and **1c**. In both compounds, the  $\text{ON}_2\text{S}$  coordination set is in the equatorial plane, and the complexes adopted a distorted square-pyramidal geometry with an axial oxo-group. The chemical and structural identity of the different prototypic complexes (rhenium,  $^{99\text{m}}\text{Tc}$  complexes and their corresponding  $^{99\text{m}}\text{Tc}$  radiocomplexes) have been also established by a comparative HPLC study.

## Introduction

Technetium and rhenium are known for their useful applications in nuclear medicine.  $^{99\text{m}}\text{Tc}$  (140 keV  $\gamma$  emitter,  $t_{1/2}$  6.02 h, convenient availability from the  $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$  generator) is widely used for diagnostic imaging, while  $^{186}\text{Re}$  (1.07 MeV  $\beta^-$  emitter,  $t_{1/2}$  90 h) and  $^{188}\text{Re}$  (2.12 MeV  $\beta^-$  emitter,  $t_{1/2}$  17 h) are two of the most attractive isotopes for applications in targeted radionuclide therapy.<sup>1,2</sup> The efforts made in this field in recent years have led to the synthesis of novel, selective and effective chelates.<sup>2,3</sup> Among them,  $\text{N}_2\text{S}_2$ ,  $\text{N}_2\text{O}_2$  or  $\text{N}_3\text{S}$  frameworks are the most common chelate systems used to bind the  $[\text{TcO}]^{3+}$  and  $[\text{ReO}]^{3+}$  cores.<sup>4</sup>

In connection with our interest in the preparation of new substitution-inert technetium and rhenium compounds, we have recently reported the synthesis of a new family of semi-rigid  $\text{N}_2\text{S}_2$ ,  $\text{N}_2\text{OS}$  or  $\text{N}_3\text{S}$  tetradentate ligands, which are characterised by the presence of an aromatic cycle in the framework (Scheme 1). This design (i) enhances the  $\text{sp}^2$  character of the nitrogen atom bonded to the metal, (ii) promotes rigidity to the square-pyramidal base which can favour and stabilise the chelate ring by an entropic effect,<sup>5</sup> and (iii) avoids the formation of isomers. Thus, coordination of selected tetraanionic tetradentate ligands (Scheme 1) towards usual rhenium ( $\text{ReOCl}_3(\text{PPh}_3)_2$  or  $[\text{NBu}_4][\text{ReO}_4]$ ) and technetium ( $[\text{NBu}_4][^{99\text{m}}\text{TcOCl}_4]$ ) precursors gave straightforwardly complexes of the general formula  $[\text{C}][\text{MO}(\text{Ph}-\text{XN}_2\text{S})]$  (C is Na,  $\text{NBu}_4$ ,  $\text{Et}_3\text{NH}$ ,  $\text{PPh}_4$ ; X = O, S, NH, NMe) under mild conditions. Complexes  $[\text{PPh}_4][\text{ReO}(\text{Ph}-$

$\text{ON}_2\text{S})]$  **1b** and  $[\text{NBu}_4][^{99\text{m}}\text{TcO}(\text{Ph}-\text{ON}_2\text{S})]$  **1c** were characterised by single-crystal X-ray analyses, the latter constituting the first example of  $^{99\text{m}}\text{Tc}$  crystal structure with this kind of semi-rigid ligands.

The reactivity of these ligands with  $^{99\text{m}}\text{Tc}$  and the stability of the corresponding radiocomplexes, were also investigated. While trianionic tetradentate ligands gave quite stable  $[\text{M}^{3+}\text{TcO}]^{3+}$  complexes with two *syn/anti* epimers,<sup>6</sup> these tetraanionic tetradentate ligands produced unique and highly stable  $[\text{M}^{3+}\text{TcO}]^{3+}$  species,<sup>7</sup> in accordance to a recent contribution of Papachristou *et al.*<sup>8</sup> Moreover, our new tetraanionic chelating ligands can be functionalized through the aromatic ring (by amine or acid function) to obtain bifunctional chelating agents (BCAs) for targeting purposes.

The structural identity of the corresponding Re,  $^{99\text{m}}\text{Tc}$  and  $^{99\text{m}}\text{Tc}$  compounds was assessed by means of HPLC studies.

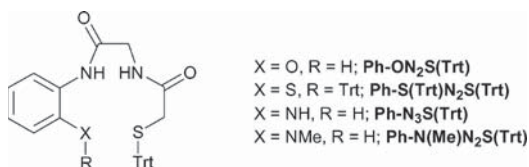
## Results and discussion

### The ligands

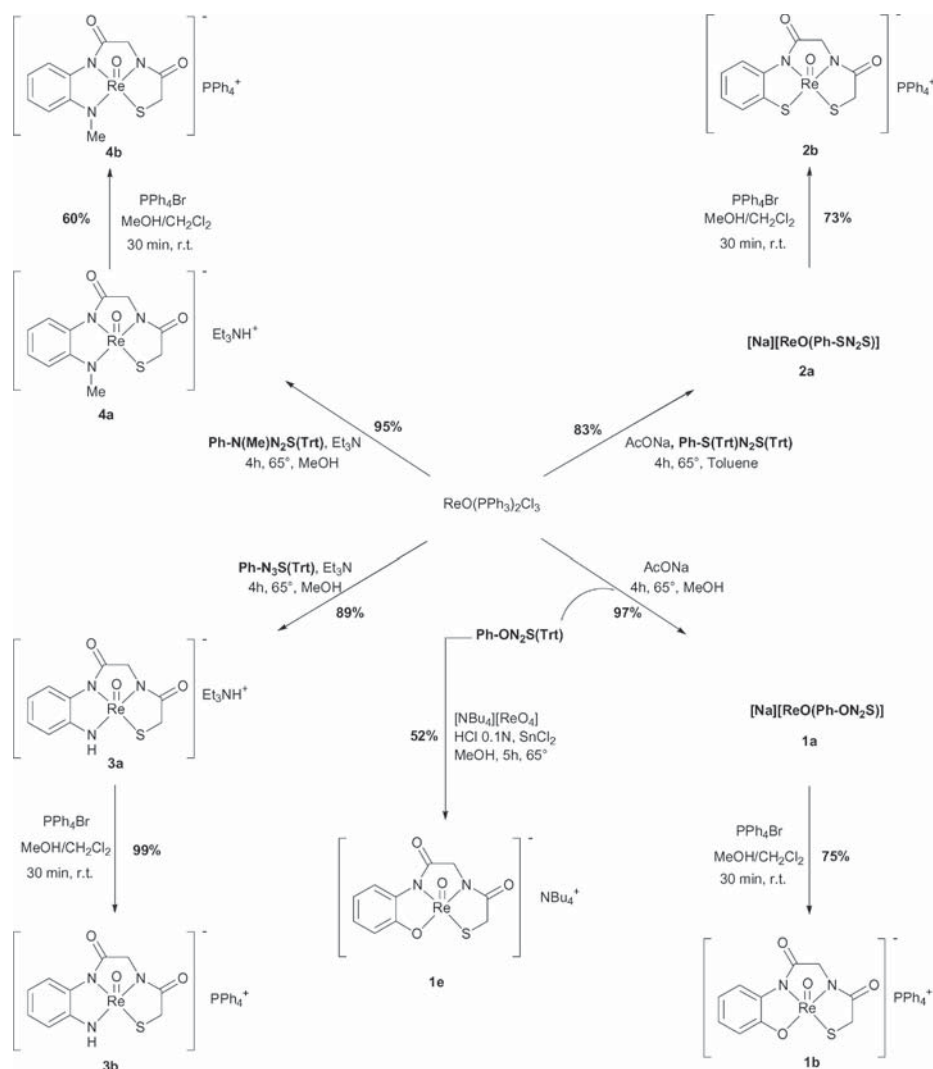
Four tetradentate semi-rigid ligands ( $\text{Ph}-\text{ON}_2\text{S}(\text{Trt})$ ,  $\text{Ph}-\text{S}(\text{Trt})\text{N}_2\text{S}(\text{Trt})$ ,  $\text{Ph}-\text{N}_3\text{S}(\text{Trt})$ ,  $\text{Ph}-\text{N}(\text{Me})\text{N}_2\text{S}(\text{Trt})$ , general abbreviation,  $\text{Ph}-\text{XN}_2\text{S}$ ; Trt = trityl) have been used as chelating agents in the present work. They were synthesised in good yield *via* multistep reactions as previously described.<sup>7</sup>  $\text{Ph}-\text{XN}_2\text{S}$  ligands act as tetraanionic ligands  $\text{X}^- \text{N}^- \text{N}^- \text{S}^-$ , by coordination *via* the charged X aromatic function, the two amide nitrogens and the sulfur atoms. Very preliminary studies on radiolabelling of these ligands showed that they form stable  $^{99\text{m}}\text{Tc}$  complexes **1d–4d** at tracer level.<sup>7</sup>

### Preparation of rhenium(v) complexes

Ligand-exchange reactions of labile  $\text{ReOCl}_3(\text{PPh}_3)_2$ <sup>9</sup> with a slight excess of the relevant tetradentate ligand (1 : 1.3 metal : ligand ratio) in the presence of a deprotonating agent (Scheme 2)



Scheme 1 Ph-XN<sub>2</sub>S Ligands.



Scheme 2 Preparation of the rhenium complexes.

gave  $[\text{MO}(\text{Ph-XN}_2\text{S})]^-$  compounds in high yield. In more detail, reactions of  $\text{Ph-ON}_2\text{S}(\text{Trt})$  or  $\text{Ph-S}(\text{Trt})\text{N}_2\text{S}(\text{Trt})$  with  $\text{ReOCl}_3(\text{PPh}_3)_2$  in the presence of sodium acetate in methanol or toluene resulted in oxorhenium complexes **1a** or **2a** as the sodium salts in 97 and 83% yield, respectively. The cleavage of trityl group was accomplished during the coordination of the ligand to the  $\text{ReO}^{3+}$  core and this is in agreement with the acidic contribution of the metal in the mechanism of sulfur detritylation.<sup>10</sup>

By using the above detailed conditions with  $\text{Ph-N}_3\text{S}(\text{Trt})$  or  $\text{Ph-N}(\text{Me})\text{N}_2\text{S}(\text{Trt})$ , only a mixture of several rhenium complexes were obtained. However, use of triethylamine instead of sodium acetate as deprotonating agent determined a quite rapid change of the methanol solution colour from greenish-yellow to the final reddish-brown. The coordination took place in 4 h at reflux and led, for each ligand, to a unique oxorhenium complex (**3a**, **4a**) as the triethylammonium salt, in good yield (>85%). The presence of triethylammonium chloride as a persistent contaminant, even after column chromatography purification, suggested the replacement of the counter-cation with larger  $\text{PPh}_4^+$ . Metathesis reactions were performed in dichloromethane/methanol solutions at room temperature. Under these conditions, analytically pure complexes **1b-4b** were obtained in high yield. Complex **1b** gave red crystals suitable for X-ray analysis from dichloromethane-methanol solution. This compound, as well as all other complexes prepared in this

study, contains a metal-monooxo core with no additional group coordinated *trans* to the yl-oxygen. This behaviour is typical of anionic five-coordinated complexes in which the ligand contains good  $\pi$  donor atoms.<sup>11,12</sup>

Rhenium complexation of the trityl protected  $\text{Ph-ON}_2\text{S}(\text{Trt})$  ligand was also performed in refluxing methanol by direct reduction of tetrabutylammonium perrhenate in the presence of an excess of tin chloride,<sup>13</sup> giving  $[\text{NBu}_4][\text{Ph-ON}_2\text{S}]$ , **1e**.

These oxo-rhenium compounds are soluble in dichloromethane, chloroform, methanol and insoluble in water. They are indefinitely stable in the solid state as well as in organic solvents (for a period of months) as shown by HPLC and NMR. The stability is not affected by the presence of air or moisture.

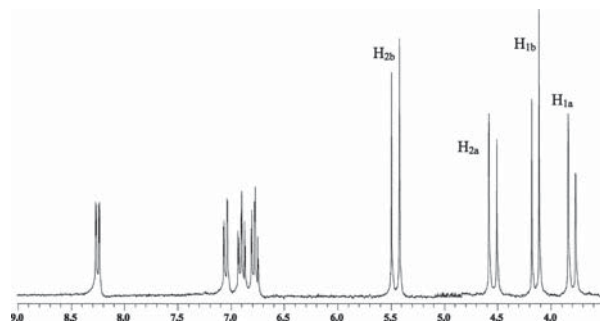
All the oxo-rhenium complexes were unambiguously identified by conventional analytical and spectroscopic techniques. In particular, IR spectra showed an intense band in the range 948–969  $\text{cm}^{-1}$  attributable to the  $\text{Re=O}$  stretching vibration,<sup>14</sup> and two strong bands in the range 1618–1667  $\text{cm}^{-1}$  assigned to  $\nu_{\text{C=O}}$  of both amides (Table 1). No multiple strong bands were detected in the ranges 1500–1560 and 3200–3400  $\text{cm}^{-1}$  of complexes **1a**, **1b**, **1e**, **2a** and **2b**, confirming that the amides were deprotonated.<sup>15</sup> Conversely, complexes **3a**, **4a** and **3b** exhibited vibrations in the 3200–3400  $\text{cm}^{-1}$  range, due to the presence of the triethylammonium counter-cation and/or of the aromatic amine N–H stretching vibrations, respectively. The IR spectra of complexes **1b-4b** exhibited five additional bands of the  $\text{PPh}_4^+$  moiety.

**Table 1** Selected  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and IR data of oxorhenium and oxotechnetium complexes **1–4**

	NMR			IR	
	$\text{CH}_2\text{S}$	$\text{CH}_2\text{N}$	$\text{C}=\text{O}$	$\text{C}=\text{O}$	$\text{M}=\text{O}$
	$\delta_{\text{H}}(\text{H}_{\text{exo}}/\text{H}_{\text{endo}})$ (ppm); $J_{\text{H-H}}/\text{Hz}$			$\delta_{\text{C}}$ (ppm)	$\nu/\text{cm}^{-1}$
<b>1a</b>	3.81/4.15; $J = 17.2$	4.54/5.46; $J = 18.3$	187.3/194.5	1661/1624	968
<b>2s</b>	3.71/3.90; $J = 17.4$	4.54/4.94; $J = 18.9$	190.5/194.8	1662/1620	964
<b>3a</b>	3.81/4.02; $J = 17.2$	4.55/5.12; $J = 18.7$	188.1/194.0	1635/1613	956
<b>4a</b>	3.83/3.99; $J = 17.1$	4.49/5.04; $J = 18.6$	187.6/193.4	1647/1622	953
<b>1e</b>	3.79/4.13; $J = 17.1$	4.57/5.53; $J = 18.4$	186.9/193.1	1664/1641	968
<b>1b</b>	3.71/4.01; $J = 16.8$	4.44/5.37; $J = 18.3$	187.5/193.9	1667/1638	969
<b>2b</b>	3.72/3.87; $J = 17.1$	4.56/4.88; $J = 18.9$	188.7/192.2	1665/1625	962
<b>3b</b>	3.77/3.93; $J = 16.8$	4.43/5.04; $J = 18.3$	187.7/192.8	1648/1618	948
<b>4b</b>	3.79/3.97; $J = 17.1$	4.39/5.01; $J = 18.6$	187.8/193.2	1649/1625	954
<b>1c</b>	3.85/4.04; $J = 16.9$	4.61/5.19; $J = 18.3$	182.5/185.9	1654/1634	953
<b>2c</b>	3.85/4.10; $J = 16.9$	4.72/4.82; $J = 18.9$	184.0/186.4	1655/1638	945
<b>3c</b>	3.72/4.07; $J = 16.7$	4.58/4.93; $J = 18.6$	183.3/186.2	<sup>a</sup>	<sup>a</sup>

<sup>a</sup> Not realised.

Proton NMR of Re-complexes revealed the loss of both amide and XR (XR = OH,  $\text{NH}_2$  or  $\text{NHMe}$ ) hydrogens indicating deprotonation and coordination. In complexes **3a,b** and **4a,b** the loss of aromatic amine nitrogen hydrogens, which is unusual in amines, may be attributed to the greater acidity imparted to the aniline-like amine hydrogens by conjugation with the aromatic ring.<sup>16</sup> Moreover, only a unique signal for hydrogen (**3a,b**) and the methyl group (**4a,b**) of the aromatic nitrogen, respectively, was detected indicating  $\text{sp}^2$  hybridization for the aromatic amine nitrogen. Methylene protons of the tetradentate ligand framework were found to be diastereotopic (AB pattern) with coupling constants in the range 17–19 Hz. *Exo* and *endo*  $\alpha$  protons of the glycine residue were detected at 4.54 ( $\text{H}_{2\text{a}}$ ) and 5.46 ppm ( $\text{H}_{2\text{b}}$ ) for **1a**, downfield shifted compared to the corresponding protons in the uncoordinated ligand (3.76 ppm). Similarly, the  $\alpha$  protons close to the thiolate group were deshielded from 3.21 ppm in the uncoordinated ligand to 3.81 ( $\text{H}_{1\text{a}}$ ) and 4.15 ppm ( $\text{H}_{1\text{b}}$ ) for **1a** (Fig. 1).

**Fig. 1** Proton NMR spectra for complex **1a** (MeOD, 25 °C).

Similar magnetic inequivalence of  $\text{CH}_2$  protons attached to amide donor atoms was observed in  $\text{MAG}_3\text{Re}$  type complexes.<sup>17</sup> According to the literature,<sup>10</sup> we assigned the downfield signal of both AB patterns to the *endo* protons (*syn* to the  $\text{Re}=\text{O}$

group) and the upfield signals to the *exo* ones (*anti* to the  $\text{Re}=\text{O}$  group).<sup>18</sup>  $^{13}\text{C}$  NMR spectra confirmed coordination of the ligands showing remarkable downfield shifts of the carbon signals nearby the ligating atom set compared to those of the corresponding carbons in the free ligand. For example, the amide carbons were downfield shifted by 20–25 ppm upon coordination,<sup>19</sup> and, analogously, the glycine  $\alpha$  carbons moved from 42–45 ppm in the free ligands to 60–62 ppm in the complexes.

Negative-ion ESI-MS spectra of each Re-complex showed the parent peak with the correct isotope distribution pattern consistent with the monomeric anion, without significant fragmentation. Conductivity measurements gave values in methanol consistent with a 1 : 1 electrolyte type.

### Synthesis of $^{99\text{g}}\text{Tc}$ complexes

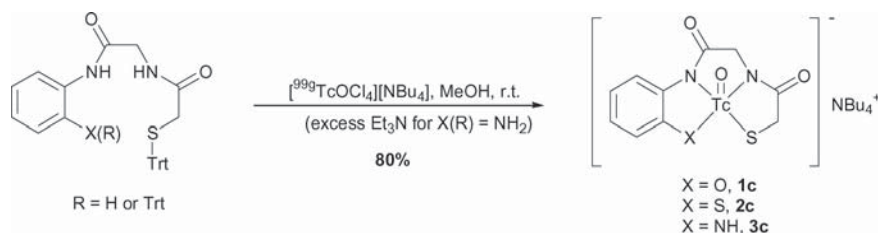
$^{99\text{g}}\text{Tc}$  complexes **1–3c** were synthesised by ligand-exchange reactions starting from  $[\text{NBu}_4][^{99\text{g}}\text{TcOCl}_4]$ <sup>20</sup> and the relevant ligand in methanol at room temperature. Addition of triethylamine was necessary to isolate pure **3c**. In contrast, complex **4c** was always collected as a mixture of two species (Scheme 3).

The IR features of **1c–3c** were similar to those observed in oxorhenium analogues. The  $\text{Tc}=\text{O}$  stretching vibration appeared consistently at  $950\text{ cm}^{-1}$ , *ca.*  $15\text{--}20\text{ cm}^{-1}$  ipsochromic shifted compared to the vibrations observed in the corresponding oxorhenium compounds. This difference is common in series of isostructural mono-oxo Tc and Re species.<sup>21,22</sup>

Analogously,  $^1\text{H}$  and  $^{13}\text{C}$  NMR values do not change significantly on going from oxorhenium to oxotechnetium complexes, indicating structural similarity (Table 1) that was confirmed by the X-ray analysis of complex **1c**.

### X-Ray crystallography

The  $[\text{PPh}_4][\text{ReO}(\text{Ph}-\text{ON}_2\text{S})]$  **1b** and  $[\text{NBu}_4][^{99\text{g}}\text{TcO}(\text{Ph}-\text{ON}_2\text{S})]$  **1c** complexes were crystallised by slow evaporation of a dichloromethane–ethanol and a dichloromethane–isopropanol solution, respectively. Crystallographic data and structure

**Scheme 3** Synthesis of  $^{99\text{g}}\text{Tc}$  complexes **1c**, **2c**, **3c**.

refinement as well as selected bond distances and angles involving the atoms of the anions are summarised in Tables 2 and 3, respectively. Perspectives drawings of the two complexes are shown in Figs. 2 and 3.

Both compounds are monoanionic, the  $[\text{MO}]^{3+}$  core charge being balanced by the four hydrolysable functions of the tetradentate ligand. Each asymmetric unit cell contains only one metal complex, and the absolute configuration around the metal is clockwise. The stereochemical notation to describe this situation is  $(SP-5-24-C)-\mathbf{1b}$  and  $(SP-5-24-C)-\mathbf{1c}$ .<sup>23</sup> The acronym means that the complex assumes a square-pyramidal geometry with coordination number 5, 24 is the configuration

number according to the CIP (Cahn–Ingold–Prelog) rules,<sup>24</sup> and the symbol *C* is assigned to that configuration in which the CIP priority numbers of the ligating atoms in the equatorial plane increase proceeding in a clockwise manner when viewing the plane from the ligating atom on the  $C_4$  axis.

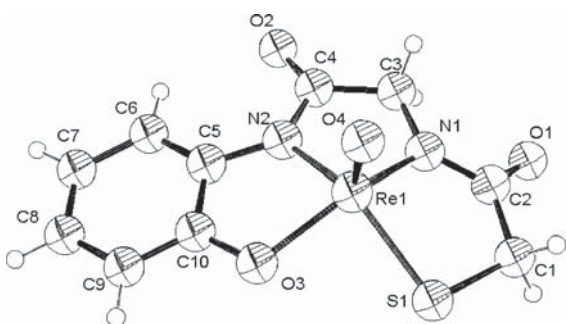
Thus,  $[\text{MO}(\text{Ph}-\text{ON}_2\text{S})]^-$  complexes exhibit a distorted square-pyramidal geometry with yl-oxygen in the apical position. The square planes defined by the combination of nitrogen, oxygen and sulfur atoms are little distorted, with the two amide nitrogens and the phenolate oxygen in the plane and the sulfur atom lying below the plane by about 0.28 and 0.30 Å in **1b** and **1c**, respectively. Re and Tc lie above the mean plane by 0.67 and

**Table 2** Crystal data and structure refinement for **1b** and **1c** complexes

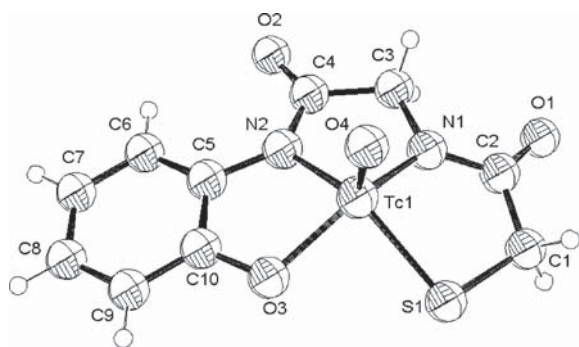
Complex	$[\text{PPh}_4][\text{ReO}(\text{Ph}-\text{ON}_2\text{S})] \mathbf{1b}$	$[\text{NBu}_4][^{99\text{m}}\text{TcO}(\text{Ph}-\text{ON}_2\text{S})] \mathbf{1c}$
Formula	$\text{C}_{34}\text{H}_{28}\text{N}_2\text{O}_4\text{PReS}$	$\text{C}_{26}\text{H}_{44}\text{N}_3\text{O}_4\text{STc}$
<i>M</i>	777.85	592.70
Crystal system	Orthorhombic	Monoclinic
Color	Dark red	Brown
Crystal size/mm	$0.21 \times 0.14 \times 0.64$	$0.20 \times 0.12 \times 0.06$
Space group	$P2_12_12_1$	$P2_1/n$
<i>a</i> /Å	9.600(4)	9.114(2)
<i>b</i> /Å	14.588(3)	18.383(4)
<i>c</i> /Å	21.525(9)	17.360(4)
$\beta/^\circ$	90	91.32(3)
<i>V</i> /Å <sup>3</sup>	3015(2)	2907.8(9)
<i>Z</i>	4	4
<i>T</i> /K	298	293
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.714	1.354
<i>F</i> (000)	1536	1248
Total reflections	35340	7250
Independent reflections	9963	7250
Observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	6195	3700
Data/restraints/parameters	6195/0/378	3700/0/315
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	$R_1 = 0.0505, wR_2 = 0.0962$	$R_1 = 0.0454, wR_2 = 0.1064$
<i>R</i> Indices (all data)	$R_1 = 0.1070, wR_2 = 0.1080$	$R_1 = 0.0900, wR_2 = 0.1286$
GOF	0.947	0.881

**Table 3** Selected bond lengths (Å) and angles (°) in complexes **1b** and **1c**

	$[\text{PPh}_4][\text{ReO}(\text{Ph}-\text{ON}_2\text{S})] \mathbf{1b}$	$[\text{NBu}_4][^{99\text{m}}\text{TcO}(\text{Ph}-\text{ON}_2\text{S})] \mathbf{1c}$
M(1)–O(4)	1.675(4)	1.653(2)
M(1)–O(3)	2.000(4)	1.986(2)
M(1)–N(2)	1.999(5)	1.984(3)
M(1)–N(1)	1.983(6)	1.960(3)
M(1)–S(1)	2.276(2)	2.276(1)
C(1)–S(1)	1.788(9)	1.822(4)
C(2)–O(1)	1.208(9)	1.219(4)
C(2)–N(1)	1.356(9)	1.365(5)
C(4)–O(2)	1.225(9)	1.216(5)
C(4)–N(2)	1.388(9)	1.375(5)
C(5)–N(2)	1.398(8)	1.414(5)
C(10)–O(3)	1.347(8)	1.359(4)
O(4)–M(1)–N(1)	110.9(3)	109.7(1)
O(4)–M(1)–O(3)	109.3(2)	110.8(1)
O(4)–M(1)–N(2)	114.1(2)	114.3(1)
O(4)–M(1)–S(1)	110.4(2)	110.9(1)
O(3)–M(1)–N(2)	78.6(2)	79.2(1)
N(2)–M(1)–N(1)	78.4(2)	78.9(1)
N(1)–M(1)–S(1)	83.2(2)	82.81(9)
O(3)–M(1)–S(1)	89.9(1)	88.64(8)
N(2)–M(1)–S(1)	135.4(2)	134.66(9)
O(3)–M(1)–N(1)	139.1(2)	139.0(1)
M(1)–S(1)–C(1)	100.4(3)	99.7(1)
M(1)–N(1)–C(2)	125.2(5)	125.9(3)
M(1)–N(2)–C(4)	117.6(5)	118.5(3)
M(1)–N(2)–C(5)	116.0(4)	115.7(3)
M(1)–O(3)–C(10)	113.9(4)	113.5(2)
N(2)–C(4)–O(2)	123.1(8)	126.0(4)
N(1)–C(2)–O(1)	123.5(9)	123.6(4)
C(3)–C(4)–O(2)	125.3(8)	122.9(4)
C(1)–C(2)–O(1)	122.4(8)	122.2(4)



**Fig. 2** An ORTEP drawing of the asymmetric anionic unit  $[\text{ReO}(\text{Ph-ON}_2\text{S})]^-$  of complex **1b** with its numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.



**Fig. 3** Perspective view and atom-labelling scheme of the asymmetric anionic unit  $[\text{}^{99\text{m}}\text{TcO}(\text{Ph-ON}_2\text{S})]^-$  of complex **1c**. All non hydrogen atoms are represented by their 50% thermal probability ellipsoids.

0.70 Å, respectively. The angles between the opposite atoms of the equatorial plane deviate from the ideal value of 180°, N(2)–M–S(1) and N(1)–M–O(3) being 135.4(2) and 139.1(2)° for **1b** and 134.66(9) and 139.0(1)° for **1c**. In addition, the trigonality index  $\tau$ , defined by Addison *et al.*,<sup>25</sup> was 0.07 and 0.06 for **1b** and **1c**, respectively. The M–N(1) and M–N(2) bond distances, *ca.* 1.98 Å, are shorter than typical M–N single bonds, *ca.* 2.15 Å,<sup>26</sup> suggesting multiple bonding character. These bonds lengths are within the range observed for M–N<sub>amide</sub> bonds in M<sup>VO</sup> five-coordinate square-pyramidal complexes,<sup>10,21,22</sup> as well as M–S<sub>thiolate</sub> bond distances (both 2.276 Å).<sup>27</sup> For each complex, two of the three five-membered rings in the coordination sphere, *i.e.* those defined by MO(3)C(10)C(5)N(2) and MN(2)C(4)C(3)N(1) adopt the stable envelope conformation. The metal is 0.34 and 0.53 Å for **1b** and 0.39 Å and 0.53 Å for **1c** out of the mean plane of the remaining four atoms. On the contrary, the third five-membered ring defined by N(1)C(2)C(1)S(1)M tends to the envelope conformation, due to the sulfur atom having the largest displacement of 0.49 Å (**1b**) and 0.44 Å (**1c**) out of the best mean plane. Moreover, the O<sub>phenolate</sub>–M–N<sub>amide</sub> and N<sub>amide</sub>–M–N<sub>amide</sub> bond angles are all approximately 79° which is comparable with those found in analogous complexes. Then, the M=O bond distances (1.675(4) in **1b** and 1.653(2) Å in **1c**) are similar with those found for square-pyramidal M<sup>VO</sup> complexes such as the MAG<sub>3</sub> derivatives ( $d_{\text{Re=O}} = 1.653(2)^\circ$ )<sup>27a</sup> and analogous semi-rigid complexes recently developed by Papadopoulos *et al.*<sup>22</sup> ( $d_{\text{Re=O}} = 1.673(5)$  Å,  $d_{\text{Tc=O}} = 1.657(3)$  Å).

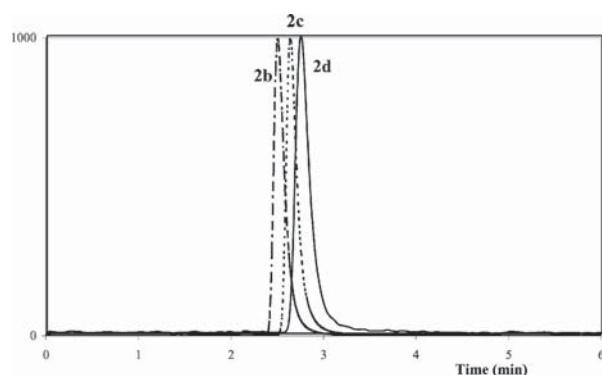
HPLC profiles of Re-, <sup>99g</sup>Tc- and <sup>99m</sup>Tc-complexes (Fig. 4), obtained by using a combination of UV-vis and radiometric detections, revealed that these three species possessed similar retention times (Table 4), thereby indicating identity of their molecular structures.<sup>7,28</sup>

The minor difference of retention times observed between Tc and Re complexes could be explained by the different polarities of the  $[\text{Tc=O}]^{3+}$  and  $[\text{Re=O}]^{3+}$  group.<sup>29</sup> These results indicate

**Table 4** HPLC retention times of the <sup>99m</sup>Tc, <sup>99g</sup>Tc and <sup>185/187</sup>Re complexes

Ligand	Metallic complexes		
	<sup>99m</sup> TcO	<sup>99g</sup> TcO	ReO
Ph–ON <sub>2</sub> S(Trt) <sup>a</sup>	4.31 ( <b>1d</b> )	4.21 ( <b>1c</b> )	3.89 ( <b>1b</b> )
Ph–S(Trt)N <sub>2</sub> S(Trt) <sup>b</sup>	2.74 ( <b>2d</b> )	2.64 ( <b>2c</b> )	2.51 ( <b>2b</b> )
Ph–N <sub>2</sub> S(Trt) <sup>a</sup>	3.59 ( <b>3d</b> )	3.50 ( <b>3c</b> )	3.87 ( <b>3b</b> )
Ph–N(SMe)N <sub>2</sub> S(Trt) <sup>b</sup>	2.98 ( <b>4d</b> )	—	2.87 ( <b>4b</b> )

<sup>a</sup> Eluent: MeOH–H<sub>2</sub>O–TFA (55 : 45 : 0.1). <sup>b</sup> Eluent: MeOH–H<sub>2</sub>O–TFA (70 : 30 : 0.1).



**Fig. 4** Comparative reverse-phase HPLC chromatograms: **2b** (rhenium complex, UV recording at 270 nm,  $t_r = 2.51$  min), **2c** (<sup>99g</sup>Tc complex, UV recording at 270 nm,  $t_r = 2.64$  min), **2d** (<sup>99m</sup>Tc complex, radiometric detection,  $t_r = 2.74$  min).

that our semi-rigid ligands form similar 1 : 1 complexes at macroscopic (Re/<sup>99g</sup>Tc) and at tracer level (<sup>99m</sup>Tc).

To conclude, in this paper we have shown that semi-rigid Ph–XN<sub>2</sub>S-type ligands allow stabilization of identical mono-oxo Re and Tc species both in the solid and in the solution states. The incorporation of an aromatic ring fused into the chelate backbone imparts rigidity to a portion of the ligand enhancing the formation and stability of the resulting complex by an entropy effect. The high *in vivo* stability of the corresponding <sup>99m</sup>Tc complexes established before<sup>7</sup> with the structural details and correlations reported here provide support for the potential development of agents as diagnostic (<sup>99m</sup>Tc)/therapeutic (<sup>188</sup>Re) matched pairs. Incorporation of biologically active fragments into this kind of chelate for the development of *in vivo* target-specific radiopharmaceuticals remains our main objective.

## Experimental

### Safety note

**CAUTION!**: <sup>99g</sup>Tc is a weak  $\beta$ -emitter ( $E_{\beta^-} = 0.292$  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, <sup>99g</sup>Tc does not present a serious health hazard because common laboratory glassware provides adequate shielding. *Bremsstrahlung* is not a significant problem due to the low energy of the  $\beta$ -particles. However, normal radiation safety procedures must be used at all times, especially with solid samples, to prevent contamination and inhalation.

### General

All chemicals were of the highest purity commercially available. Solvents were purified by standard methods before use and stored over 0.3 nm molecular sieves. Technetium as  $[\text{NH}_4][\text{}^{99\text{g}}\text{TcO}_4]$  was obtained from Oak Ridge National Laboratory. Samples were dissolved in water and treated with

an excess of aqueous ammonia and H<sub>2</sub>O<sub>2</sub> (30%) at 80 °C prior to use to oxidise residual TcO<sub>2</sub>. Slow evaporation of the solvent with heating at 40 °C afforded [NH<sub>4</sub>]<sup>99m</sup>TcO<sub>4</sub> as a white powder which was converted to the [NBu<sub>4</sub>][TcOCl<sub>4</sub>] precursor following a literature method.<sup>20</sup> Rhenium(VII) oxide was purchased from Aldrich Chem. Co. It was converted to ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> according to published protocols.<sup>9</sup> The ligands *N*-(2-hydroxyphenyl)-2-[(triphenylmethylthio)methylcarbonylamino]ethanamide, Ph-ON<sub>2</sub>S(Trt); *N*-[2-(triphenylmethylthio)phenyl]-2-[(triphenylmethylthio)methylcarbonylamino]ethanamide, Ph-S(Trt)N<sub>2</sub>S(Trt); *N*-(2-aminophenyl)-2-[(triphenylmethylthio)methylcarbonylamino]ethanamide, Ph-N<sub>3</sub>S(Trt); *N*-[2-(*N*-methylamino)phenyl]-2-[(triphenylmethylthio)methylcarbonylamino]ethanamide, Ph-N(Me)N<sub>2</sub>S(Trt) and the corresponding <sup>99m</sup>Tc complexes have been prepared as described previously.<sup>7</sup>

### Instrumentation

For rhenium compounds, NMR spectra were recorded on a Bruker AC 200 (50.323 MHz for <sup>13</sup>C and 200.133 MHz for <sup>1</sup>H) or 250 apparatus (62.896 MHz for <sup>13</sup>C and 250.133 MHz for <sup>1</sup>H). Chemical shifts are indicated in  $\delta$  values (ppm) downfield from internal TMS. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of each complex were recorded at room temperature in CDCl<sub>3</sub> except for **1a**, **2a** which were performed in MeOD. Unambiguous assignments, were established by two-dimensional [<sup>1</sup>H, <sup>1</sup>H] COSY and [<sup>1</sup>H, <sup>13</sup>C] HMQC and HMBC experiments (Table 1).

IR spectra were recorded as KBr pellets on a Bruker Vector 22 spectrophotometer in the range 4000–400 cm<sup>-1</sup>. Negative electrospray mass spectra were obtained on a NERMAG R 10–10 mass spectrometer. Microanalysis was performed by the microanalytical department of the Ecole Nationale Supérieure de Chimie de Toulouse. TLC was performed using precoated Kieselgel 60 plates F<sub>254</sub> (TLC plates, Merck) and was visualised by UV. Column chromatography was carried out using “gravity” silica (SDS silica gel).

For technetium compounds, NMR spectra were collected on a Bruker AC-300 apparatus (75.467 MHz for <sup>13</sup>C and 300.13 MHz for <sup>1</sup>H) using SiMe<sub>4</sub> as internal reference (<sup>1</sup>H). FT IR spectra were recorded on a Nicolet 510P Fourier transform spectrometer in the range 4000–400 cm<sup>-1</sup> in KBr pellets using a Spectra-Tech diffuse-reflectance collector accessory. Mass spectra of selected technetium compounds (*ca.* 10<sup>-6</sup> M solutions) were recorded on a LCQ instrument (Finnigan, Palo Alto, CA). The complexes have been directly injected by a syringe pump at a flow of 5  $\mu$ L min<sup>-1</sup>. Thin-layer chromatography (TLC) was performed using sheets from Riedel de Haen (Silica gel 60 F<sub>254</sub>).

HPLC comparison was achieved on a waters 600E gradient chromatography with a Waters Lambda Max UV detector, a SAIP radioactivity detector and an ICS dual integrator for effluent monitoring and a Satisfaction RP18AB column using MeOH–H<sub>2</sub>O–TFA (55 : 45 : 0.1 or 70 : 30 : 0.1) as eluent (flow rate of 1 mL min<sup>-1</sup>). The eluate was monitored by UV absorbance at 270 nm for Re and <sup>99m</sup>Tc complexes, or  $\gamma$ -ray detection for <sup>99m</sup>Tc complexes.

### X-Ray crystal structure determination for compounds **1b** and **1c**

Diffraction measurements for **1b** were performed on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) while, for **1c**, diffraction data were collected on a Nicolet R3m/V diffractometer (Mo-K $\alpha$  radiation;  $\lambda = 0.71073$  Å). The structures were solved by direct methods for **1b** and by heavy-atom methods for **1c**. Both were refined with full-matrix least-squares procedure based on  $F^2$ . Structure determination and refinement were performed using the SIR97,<sup>30</sup> Maxus<sup>31</sup> and SHELX-97<sup>32</sup> programs. 7350 and 3700 independent reflections with  $I \geq 2\sigma(I)$  were used for refinement of the unit cell for **1b** and **1c**, respectively. Hydrogens for the disordered chain of the tBu molecule in compound **1c** were not located. The most significant details of the crystallography study

are reported in Table 2. A collection of selected bond distance and angles are shown in Table 3.

CCDC reference numbers 275918 and 275919.

See <http://dx.doi.org/10.1039/b508661b> for crystallographic data in CIF or other electronic format.

### Synthesis of complexes

[Na][ReO(Ph-ON<sub>2</sub>S)] **1a** and [Na][ReO(Ph-SN<sub>2</sub>S)] **2a**. The synthesis and characterisation of the two complexes **1a** and **2a** have been reported previously.<sup>7</sup>

[PPh<sub>4</sub>][ReO(Ph-ON<sub>2</sub>S)] **1b**. **1a** (100.0 mg, 0.22 mmol) and tetraphenylphosphonium chloride (89.2 mg, 0.24 mmol) were dissolved in a mixture of MeOH (15 mL) and CH<sub>2</sub>Cl<sub>2</sub> (15 mL). The solution was stirred for 30 min at room temperature and then allowed to precipitate during 2 days. A red solid was filtered and washed with cold water and dried under vacuum (126.3 mg, yield = 75%).

Found: C, 52.23; H, 3.63; N, 3.46. C<sub>34</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>PreS requires C, 52.50; H, 3.63; N, 3.60%; IR:  $\nu_{\max}/\text{cm}^{-1}$  1667, 1638 (CO); 969 (ReO); <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  3.71 (d, <sup>2</sup> $J_{\text{HH}} = 16.8$  Hz, 1 H, CH<sub>2</sub>S), 4.01 (d, <sup>2</sup> $J_{\text{HH}} = 16.8$  Hz, 1 H, CH<sub>2</sub>S), 4.44 (d, <sup>2</sup> $J_{\text{HH}} = 18.3$  Hz, 1 H, CH<sub>2</sub>N), 5.37 (d, <sup>2</sup> $J_{\text{HH}} = 18.3$  Hz, 1 H, CH<sub>2</sub>N), 6.63 (dt, <sup>3</sup> $J_{\text{HH}} = 7.6$  Hz, <sup>4</sup> $J_{\text{HH}} = 1.2$  Hz, 1 H, CH<sub>Ar</sub>), 6.75 (dt, <sup>3</sup> $J_{\text{HH}} = 7.6$  Hz, <sup>4</sup> $J_{\text{HH}} = 1.5$  Hz, 1 H, CH<sub>Ar</sub>), 6.99 (dd, <sup>3</sup> $J_{\text{HH}} = 7.6$  Hz, <sup>4</sup> $J_{\text{HH}} = 1.2$  Hz, 1 H, CH<sub>Ar</sub>), 7.52 (m, 8 H, CH<sub>Ar</sub> PPh<sub>4</sub>), 7.69 (m, 8 H, CH<sub>Ar</sub> PPh<sub>4</sub>), 7.83 (m, 4 H, CH<sub>Ar</sub> PPh<sub>4</sub>), 8.22 (dd, <sup>3</sup> $J_{\text{HH}} = 7.6$  Hz, <sup>4</sup> $J_{\text{HH}} = 1.5$  Hz, 1 H, CH<sub>Ar</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (62.5 MHz, CDCl<sub>3</sub>):  $\delta_{\text{C}}$  40.9 (CH<sub>2</sub>S), 61.8 (CH<sub>2</sub>N), 116.1, 118.7, 119.5, 123.4 (4 CH<sub>Ar</sub>), 117.3 (4 C<sub>Ar</sub> PPh<sub>4</sub>), 131.2, 131.4, 134.9, 135.0, 136.3, 136.4 (20 CH<sub>Ar</sub> PPh<sub>4</sub>), 141.4, 171.1 (2 C<sub>Ar</sub>), 187.5, 193.9 (2 CO); MS (ES<sup>-</sup>):  $m/z$  (%) 437 (60), 439 (100) [M<sup>-</sup>].

[NBu<sub>4</sub>][ReO(Ph-ON<sub>2</sub>S)] **1e**. To a boiling solution of Ph-ON<sub>2</sub>S(Trt) (148.8 mg, 0.30 mmol) in 40 mL of MeOH was added a solution of tin(II) chloride (143.5 mg, 0.63 mmol, in 1 mL of 0.1 M HCl), followed immediately by a solution of tetrabutylammonium perrhenate (310.6 mg, 0.63 mmol, in 1 mL of MeOH). Refluxing was continued for 5 h, the solution cooled at room temperature and washed with 20 mL of hexane. MeOH was removed and the crude solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL), then washed with water (20 mL). The organic layer was dried with solid Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. The crude material was purified by column chromatography on silica gel (eluent CH<sub>2</sub>Cl<sub>2</sub>–MeOH (95 : 5)) followed by two crystallisations in methanol–ether mixture (3 : 1 v/v). Under these conditions, [Bu<sub>4</sub>N]Cl remained in solution and the complex was obtained as a red–orange powder (105 mg, 52%).

Found: C, 45.75; H, 6.60; N, 5.72. C<sub>27</sub>H<sub>48</sub>N<sub>3</sub>O<sub>4</sub>ReS requires C, 46.53; H, 6.94; N, 6.03%; IR:  $\nu_{\max}/\text{cm}^{-1}$  1641 (CO), 968 (ReO); <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  0.99 (m, 12 H, CH<sub>3</sub>), 1.49 (m, 16 H, CH<sub>2</sub>), 3.07 (m, 8 H, CH<sub>2</sub>), 3.79 (d, <sup>2</sup> $J_{\text{HH}} = 17.1$  Hz, 1 H, CH<sub>2</sub>S), 4.13 (d, <sup>2</sup> $J_{\text{HH}} = 17.1$  Hz, 1 H, CH<sub>2</sub>S), 4.57 (d, <sup>2</sup> $J_{\text{HH}} = 18.4$  Hz, 1 H, CH<sub>2</sub>N), 5.53 (d, <sup>2</sup> $J_{\text{HH}} = 18.4$  Hz, 1 H, CH<sub>2</sub>N), 6.75 (dt, <sup>3</sup> $J_{\text{HH}} = 7.8$  Hz, <sup>4</sup> $J_{\text{HH}} = 1.2$  Hz, 1 H, CH<sub>Ar</sub>), 6.86 (dt, <sup>3</sup> $J_{\text{HH}} = 7.8$  Hz, <sup>4</sup> $J_{\text{HH}} = 1.5$  Hz, 1 H, CH<sub>Ar</sub>), 7.05 (dd, <sup>3</sup> $J_{\text{HH}} = 7.8$  Hz, <sup>4</sup> $J_{\text{HH}} = 1.2$  Hz, 1 H, CH<sub>Ar</sub>), 8.33 (dd, <sup>3</sup> $J_{\text{HH}} = 7.8$  Hz, <sup>4</sup> $J_{\text{HH}} = 1.5$  Hz, 1 H, CH<sub>Ar</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta_{\text{C}}$  13.6 (4 CH<sub>3</sub>), 19.7, 23.8 (8 CH<sub>2</sub>), 40.0 (CH<sub>2</sub>S), 58.6 (4 CH<sub>2</sub>), 61.2 (1 CH<sub>2</sub>N), 115.5, 118.3, 119.3, 123.0 (4 CH<sub>Ar</sub>), 140.9, 170.5 (2 C<sub>Ar</sub>), 186.9, 193.1 (2 CO);  $m/z$  (%) 437 (60), 439 (100) [M<sup>-</sup>].

[PPh<sub>4</sub>][ReO(Ph-SN<sub>2</sub>S)] **2b**. **2a** (105.0 mg, 0.22 mmol) and tetraphenylphosphonium chloride (89.2 mg, 0.24 mmol) were dissolved in a mixture of MeOH (15 mL) and CH<sub>2</sub>Cl<sub>2</sub> (15 mL). After 30 min under stirring, the solvent was removed and the crude was purified by column chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>–MeOH (95 : 5 then 90 : 10)) to yield the complex **2b** as an orange powder (121.0 mg, yield = 73%).

Found: C, 50.86; H, 3.48; N, 3.17. C<sub>34</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub>PreS<sub>2</sub> requires C, 51.44; H, 3.55; N, 3.53; IR:  $\nu_{\max}/\text{cm}^{-1}$  1665, 1625 (CO); 962



(ReO);  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  3.72 (d,  $^2J_{\text{HH}} = 17.1$  Hz, 1 H,  $\text{CH}_2\text{S}$ ), 3.87 (d,  $^2J_{\text{HH}} = 17.1$  Hz, 1 H,  $\text{CH}_2\text{S}$ ), 4.56 (d,  $^2J_{\text{HH}} = 18.9$  Hz, 1 H,  $\text{CH}_2\text{N}$ ), 4.88 (d,  $^2J_{\text{HH}} = 18.9$  Hz, 1 H,  $\text{CH}_2\text{N}$ ), 6.85 (m, 2 H,  $\text{CH}_{\text{Ar}}$ ), 7.49 (m, 9 H, 1  $\text{CH}_{\text{Ar}} + 8 \text{CH}_{\text{Ar PPh}_4}$ ), 7.65 (m, 8 H,  $\text{CH}_{\text{Ar PPh}_4}$ ), 7.80 (m, 4 H,  $\text{CH}_{\text{Ar PPh}_4}$ ), 8.75 (m, 1 H,  $\text{CH}_{\text{Ar}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  39.3 ( $\text{CH}_2\text{S}$ ), 60.3 ( $\text{CH}_2\text{N}$ ), 116.8, 118.0 (4  $\text{C}_{\text{Ar PPh}_4}$ ), 120.6, 122.9, 124.1, 128.1 (4  $\text{C}_{\text{Ar}}$ ), 130.6, 130.7, 134.3, 134.4, 135.7, 135.8 (20  $\text{CH}_{\text{Ar PPh}_4}$ ), 147.3, 152.2 (2  $\text{C}_{\text{Ar}}$ ), 188.7, 192.2 (2 CO); MS ( $\text{ES}^-$ ):  $m/z$  (%) 453 (60), 455 (100) [ $\text{M}^-$ ].

**[Et<sub>3</sub>NH][ReO(Ph–N<sub>3</sub>S)] 3a.** To a stirred suspension of Ph–N<sub>3</sub>S(Trt) (144.3 mg, 0.30 mmol) and  $\text{ReOCl}_3(\text{PPh}_3)_2$  (324.5 mg, 0.39 mmol) in MeOH (40 mL) neat Et<sub>3</sub>N (148.1  $\mu\text{L}$ , 1.20 mmol) was added. The mixture was refluxed for 4 h and then cooled to room temperature. The solvent was removed and the crude purified by column chromatography on silica gel (eluent:  $\text{CHCl}_3$ –MeOH (95 : 5 then 90 : 10)) to afford the complex **3a** as a red–orange powder (114.2 mg, yield = 89%).

Found: C, 35.16; H, 4.52; N, 10.68.  $\text{C}_{16}\text{H}_{25}\text{N}_4\text{O}_3\text{ReS}$  requires C, 35.61; H, 4.67; N, 10.38%; IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  1635, 1613 (CO); 956 (ReO);  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  1.23 (t,  $^3J_{\text{HH}} = 7.4$  Hz, 9 H,  $\text{CH}_3$ ), 3.09 (q,  $^3J_{\text{HH}} = 7.4$  Hz, 6 H,  $\text{NCH}_2$ ), 3.81 (d,  $^2J_{\text{HH}} = 17.2$  Hz, 1 H,  $\text{CH}_2\text{S}$ ), 4.02 (d,  $^2J_{\text{HH}} = 17.2$  Hz, 1 H,  $\text{CH}_2\text{S}$ ), 4.55 (d,  $^2J_{\text{HH}} = 18.7$  Hz, 1 H,  $\text{CH}_2\text{N}$ ), 5.12 (d,  $^2J_{\text{HH}} = 18.7$  Hz, 1 H,  $\text{CH}_2\text{N}$ ), 6.62 (m, 1 H,  $\text{CH}_{\text{Ar}}$ ), 6.88 (m, 2 H,  $\text{CH}_{\text{Ar}}$ ), 8.21 (m, 1 H,  $\text{CH}_{\text{Ar}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  7.8 (3  $\text{CH}_3$ ), 40.4 ( $\text{CH}_2\text{S}$ ), 46.5 (3  $\text{CH}_2$ ), 60.0 (1  $\text{CH}_2\text{N}$ ), 114.2, 117.5, 117.8, 123.1 (4  $\text{CH}_{\text{Ar}}$ ), 140.9, 158.9 (2  $\text{C}_{\text{Ar}}$ ), 188.1, 194.0 (2 CO); MS ( $\text{ES}^-$ ):  $m/z$  (%) 436 (60), 438 (100) [ $\text{M}^-$ ].

**[PPh<sub>4</sub>][ReO(Ph–N<sub>3</sub>S)] 3b.** To a stirred solution of **3a** (118.8 mg, 0.22 mmol) in 10 mL of MeOH and 10 mL of  $\text{CH}_2\text{Cl}_2$  was added tetraphenylphosphonium chloride (71.2 mg, 0.19 mmol). The mixture was stirred for 15 min and then treated with  $\text{H}_2\text{O}$  (20 mL). The solution was extracted twice with  $\text{CH}_2\text{Cl}_2$  (20 mL). The organic layers were dried with  $\text{MgSO}_4$ , filtered and dried under vacuum to give a red powder (170.9 mg, yield = 99%).

Found: C, 52.14; H, 3.66; N, 4.89.  $\text{C}_{34}\text{H}_{29}\text{N}_3\text{O}_3\text{PReS}$  requires C, 52.57; H, 3.76; N, 5.41%; IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  1648, 1618 (CO); 948 (ReO);  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  3.77 (d,  $^2J_{\text{HH}} = 16.8$  Hz, 1 H,  $\text{CH}_2\text{S}$ ), 3.93 (d,  $^2J_{\text{HH}} = 16.8$  Hz, 1 H,  $\text{CH}_2\text{S}$ ), 4.43 (d,  $^2J_{\text{HH}} = 18.3$  Hz, 1 H,  $\text{CH}_2\text{N}$ ), 5.04 (d,  $^2J_{\text{HH}} = 18.3$  Hz, 1 H,  $\text{CH}_2\text{N}$ ), 6.50 (m, 1 H,  $\text{CH}_{\text{Ar}}$ ), 6.71 (m, 2 H,  $\text{CH}_{\text{Ar}}$ ), 7.57 (m, 8 H,  $\text{CH}_{\text{Ar PPh}_4}$ ), 7.71 (m, 8 H,  $\text{CH}_{\text{Ar PPh}_4}$ ), 7.83 (m, 4 H,  $\text{CH}_{\text{Ar PPh}_4}$ ), 8.22 (m, 1 H,  $\text{CH}_{\text{Ar}}$ ), 8.79 (s, 1 H, NH);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  40.2 ( $\text{CH}_2\text{S}$ ), 60.4 ( $\text{CH}_2\text{N}$ ), 116.9, 118.0 (4  $\text{C}_{\text{Ar PPh}_4}$ ), 114.2, 117.6, 118.2, 122.4 (4  $\text{CH}_{\text{Ar}}$ ), 130.6, 130.8, 134.3, 134.4, 135.7, 135.8 (20  $\text{CH}_{\text{Ar PPh}_4}$ ), 140.1, 158.3 (2  $\text{C}_{\text{Ar}}$ ), 187.7, 192.8 (2 CO); MS ( $\text{ES}^-$ ):  $m/z$  (%) 436 (60), 438 (100) [ $\text{M}^-$ ].

**[Et<sub>3</sub>NH][ReO(Ph–N(Me)N<sub>2</sub>S)] 4a.** Using the same procedure adopted for **3a**, Ph–N(Me)N<sub>2</sub>S(Trt) (148.5 mg, 0.30 mmol) gave the complex as a red solid (157.5 mg, yield = 95%) which was contaminated by traces of residual Et<sub>3</sub>NHCl salt.

IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  1647, 1622 (CO); 953 (ReO);  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  1.25 (t, 9 H,  $^3J_{\text{HH}} = 7.3$  Hz,  $\text{CH}_3$ ), 3.01 (q,  $^3J_{\text{HH}} = 7.3$  Hz, 6 H,  $\text{CH}_2$ ), 3.83 (d,  $^2J_{\text{HH}} = 17.1$  Hz, 1 H,  $\text{CH}_2\text{S}$ ), 3.99 (d,  $^2J_{\text{HH}} = 17.1$  Hz, 1 H,  $\text{CH}_2\text{S}$ ), 4.14 (s, 3 H,  $\text{CH}_3$ ), 4.49 (d,  $^2J_{\text{HH}} = 18.6$  Hz, 1 H,  $\text{CH}_2\text{N}$ ), 5.04 (d,  $^2J_{\text{HH}} = 18.6$  Hz, 1 H,  $\text{CH}_2\text{N}$ ), 6.66 (m, 1 H,  $\text{CH}_{\text{Ar}}$ ), 6.87 (m, 2 H,  $\text{CH}_{\text{Ar}}$ ), 8.28 (m, 1 H,  $\text{CH}_{\text{Ar}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  9.1 (3  $\text{CH}_3$ ), 40.8 (1  $\text{CH}_2\text{S}$ ), 47.3 (3  $\text{CH}_2$ ), 49.9 ( $\text{CH}_3$ ), 60.3 ( $\text{CH}_2\text{N}$ ), 110.9, 117.7, 118.2, 123.3 (4  $\text{CH}_{\text{Ar}}$ ), 142.9, 160.0 (2  $\text{C}_{\text{Ar}}$ ), 187.6, 193.4 (2 CO); MS ( $\text{ES}^-$ ):  $m/z$  (%) 450 (60), 452 (100) [ $\text{M}^-$ ].

**[PPh<sub>4</sub>][ReO(Ph–N(Me)N<sub>2</sub>S)] 4b.** This complex was prepared analogously to **2b** in 60% yield using  $\text{CH}_2\text{Cl}_2$ –MeOH (98 : 2) as eluent for column chromatography purification.

Found: C, 52.27; H, 3.89; N, 4.93.  $\text{C}_{35}\text{H}_{31}\text{N}_3\text{O}_3\text{PReS}$  requires C, 53.15; H, 3.95; N, 5.31%; IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  1649, 1625 (CO); 954

(ReO);  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ): 3.79 (d,  $^2J_{\text{HH}} = 17.1$  Hz, 1 H,  $\text{CH}_2\text{S}$ ), 3.97 (d,  $^2J_{\text{HH}} = 17.1$  Hz, 1 H,  $\text{CH}_2\text{S}$ ), 4.14 (s, 3 H,  $\text{NCH}_3$ ), 4.39 (d,  $^2J_{\text{HH}} = 18.6$  Hz, 1 H,  $\text{CH}_2\text{N}$ ), 5.01 (d,  $^2J_{\text{HH}} = 18.6$  Hz, 1 H,  $\text{CH}_2\text{N}$ ), 6.53 (m, 1 H,  $\text{CH}_{\text{Ar}}$ ), 6.80 (m, 2 H,  $\text{CH}_{\text{Ar}}$ ), 7.53 (m, 8 H,  $\text{CH}_{\text{Ar PPh}_4}$ ), 7.67 (m, 8 H,  $\text{CH}_{\text{Ar PPh}_4}$ ), 7.82 (m, 4 H,  $\text{CH}_{\text{Ar PPh}_4}$ ), 8.28 (m, 1 H,  $\text{CH}_{\text{Ar}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ): 40.2 ( $\text{CH}_2\text{S}$ ), 49.8 ( $\text{CH}_3$ ), 60.3 ( $\text{CH}_2\text{N}$ ), 110.4 ( $\text{CH}_{\text{Ar}}$ ), 116.8, 118.0 (4  $\text{C}_{\text{Ar PPh}_4}$ ), 110.4, 117.4, 117.7, 122.4 (4  $\text{CH}_{\text{Ar}}$ ), 130.6, 130.8, 134.2, 134.4, 135.8, 135.9 (20  $\text{CH}_{\text{Ar PPh}_4}$ ), 143.4, 160.2 (2  $\text{C}_{\text{Ar}}$ ), 187.8, 193.2 (2 CO); MS ( $\text{ES}^-$ ):  $m/z$  (%) 450 (60), 452 (100) [ $\text{M}^-$ ].

**[NBu<sub>4</sub>][TcO(Ph–ON<sub>2</sub>S)] 1c.** To a stirred green solution of  $[\text{NBu}_4][\text{TcOCl}_4]$  (31 mg, 0.062 mmol) in MeOH (3 mL) Ph–ON<sub>2</sub>S(Trt) (30 mg, 0.062 mmol) was added. The solution turned orange suddenly. After 1 h stirring at room temperature, the solvent was removed by a gentle stream of N<sub>2</sub> and the crude was purified by column chromatography on silica gel (eluent:  $\text{CH}_2\text{Cl}_2$ –MeOH (95 : 5)) to afford a yellow powder (29.4 mg, 80%).

IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  1654, 1634 (CO); 953 (TcO);  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  0.98 (m, 12 H,  $\text{CH}_3$ ), 1.36 (m, 16 H,  $\text{CH}_2$ ), 2.95 (m, 8 H,  $\text{CH}_2$ ), 3.85 (d,  $^2J_{\text{HH}} = 16.9$  Hz, 1 H,  $\text{CH}_2\text{S}$ ), 4.04 (d,  $^2J_{\text{HH}} = 16.9$  Hz, 1 H,  $\text{CH}_2\text{S}$ ), 4.61 (d,  $^2J_{\text{HH}} = 18.3$  Hz, 1 H,  $\text{CH}_2\text{N}$ ), 5.19 (d,  $^2J_{\text{HH}} = 18.3$  Hz, 1 H,  $\text{CH}_2\text{N}$ ), 6.75 (dt,  $^3J_{\text{HH}} = 7.8$  Hz,  $^4J_{\text{HH}} = 1.1$  Hz, 1 H,  $\text{CH}_{\text{Ar}}$ ), 6.89 (dt,  $^3J_{\text{HH}} = 7.8$  Hz,  $^4J_{\text{HH}} = 1.4$  Hz, 1 H,  $\text{CH}_{\text{Ar}}$ ), 7.23 (dd,  $^3J_{\text{HH}} = 7.8$  Hz,  $^4J_{\text{HH}} = 1.1$  Hz, 1 H,  $\text{CH}_{\text{Ar}}$ ), 8.24 (dd,  $^3J_{\text{HH}} = 7.8$  Hz,  $^4J_{\text{HH}} = 1.4$  Hz, 1 H,  $\text{CH}_{\text{Ar}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  13.6 (4  $\text{CH}_3$ ), 19.6 (4  $\text{CH}_2$ ), 23.8 (4  $\text{CH}_2$ ), 36.9 ( $\text{CH}_2\text{S}$ ), 58.6 (4  $\text{CH}_2$ ), 59.9 ( $\text{CH}_2\text{N}$ ), 114.7, 118.3, 118.6, 122.9 (4  $\text{CH}_{\text{Ar}}$ ), 139.5, 165.2 (2  $\text{C}_{\text{Ar}}$ ), 182.5, 185.9 (2 CO); MS ( $\text{ES}^-$ ):  $m/z$  (%) 351 (100) [ $\text{M}^-$ ].

**[NBu<sub>4</sub>][TcO(Ph–SN<sub>2</sub>S)] 2c.** As for **1c**, 25 mg (0.05 mmol) of Ph–S(Trt)N<sub>2</sub>S(Trt) gave the complex as a yellow–brown oil.

IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  1655, 1638 (CO); 945 (TcO);  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  0.94 (m, 12 H,  $\text{CH}_3$ ), 1.33 (m, 16 H,  $\text{CH}_2$ ), 2.86 (m, 8 H,  $\text{CH}_2$ ), 3.85 (d,  $^2J_{\text{HH}} = 16.9$  Hz, 1 H,  $\text{CH}_2\text{S}$ ), 4.10 (d,  $^2J_{\text{HH}} = 16.9$  Hz, 1 H,  $\text{CH}_2\text{S}$ ), 4.72 (d,  $^2J_{\text{HH}} = 18.9$  Hz, 1 H,  $\text{CH}_2\text{N}$ ), 4.82 (d,  $^2J_{\text{HH}} = 18.9$  Hz, 1 H,  $\text{CH}_2\text{N}$ ), 6.96 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 1 H,  $\text{CH}_{\text{Ar}}$ ), 7.06 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 1 H,  $\text{CH}_{\text{Ar}}$ ), 7.48 (d,  $^3J_{\text{HH}} = 7.6$  Hz, 1 H,  $\text{CH}_{\text{Ar}}$ ), 8.75 (d,  $^3J_{\text{HH}} = 7.6$  Hz, 1 H,  $\text{CH}_{\text{Ar}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  13.6 (4  $\text{CH}_3$ ), 19.6 (4  $\text{CH}_2$ ), 23.7 (4  $\text{CH}_2$ ), 37.3 ( $\text{CH}_2\text{S}$ ), 58.5 (4  $\text{CH}_2$ ), 59.3 ( $\text{CH}_2\text{N}$ ), 120.6, 122.8, 124.3, 127.0 (4  $\text{CH}_{\text{Ar}}$ ), 140.3, 150.1 (2  $\text{C}_{\text{Ar}}$ ), 184.0, 186.4 (2 CO); MS ( $\text{ES}^-$ ):  $m/z$  (%) 367 (100) [ $\text{M}^-$ ].

**[NBu<sub>4</sub>][TcO(Ph–N<sub>3</sub>S)] 3c.** To a stirred green solution of  $[\text{NBu}_4][\text{TcOCl}_4]$  (16.0 mg, 0.032 mmol) in MeOH (3 mL) was added Ph–N<sub>3</sub>S(Trt) (15.4 mg, 0.032 mmol) and an excess of triethylamine (22.5  $\mu\text{L}$ , 0.160 mmol). The reaction was stirred for 30 min and the solution turned dark orange. The crude solution was then treated twice with hexane (2  $\times$  3 mL) and then the solvents were removed. The solid was dissolved in  $\text{CH}_2\text{Cl}_2$  (5 mL), treated with water (5 mL), and the organic layers were separated, dried and concentrated to dryness. The title compound was obtained as a yellow–orange solid (15 mg, 79%).

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  0.95 (m, 12 H,  $\text{CH}_3$ ), 1.30 (m, 16 H,  $\text{CH}_2$ ), 2.84 (m, 8 H,  $\text{CH}_2$ ), 3.72 (d,  $^2J_{\text{HH}} = 16.7$  Hz, 1 H,  $\text{CH}_2\text{S}$ ), 4.07 (d,  $^2J_{\text{HH}} = 16.7$  Hz, 1 H,  $\text{CH}_2\text{S}$ ), 4.58 (d,  $^2J_{\text{HH}} = 18.6$  Hz, 1 H,  $\text{CH}_2\text{N}$ ), 4.93 (d,  $^2J_{\text{HH}} = 18.6$  Hz, 1 H,  $\text{CH}_2\text{N}$ ), 6.65 (t,  $^3J_{\text{HH}} = 7.2$  Hz, 1 H,  $\text{CH}_{\text{Ar}}$ ), 6.80 (m, 2 H,  $\text{CH}_{\text{Ar}}$ ), 8.03 (s, 1 H, NH), 8.28 (d,  $^3J_{\text{HH}} = 7.2$  Hz, 1 H,  $\text{CH}_{\text{Ar}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  13.6 (4  $\text{CH}_3$ ), 19.6 (4  $\text{CH}_2$ ), 23.6 (4  $\text{CH}_2$ ), 37.3 ( $\text{CH}_2\text{S}$ ), 58.3 (4  $\text{CH}_2$ ), 59.4 ( $\text{CH}_2\text{N}$ ), 113.6, 117.8, 118.1, 122.8 (4  $\text{CH}_{\text{Ar}}$ ), 139.9, 153.8 (2  $\text{C}_{\text{Ar}}$ ), 183.3, 186.2 (2 CO); MS ( $\text{ES}^-$ ):  $m/z$  (%) 350 (100) [ $\text{M}^-$ ].

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