

Synthesis, properties and spectroscopic studies of rhenium(v) complexes stabilized by tridentate Schiff bases derived from *S*-methyl dithiocarbazate

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Received 7th September 2001, Accepted 4th October 2001

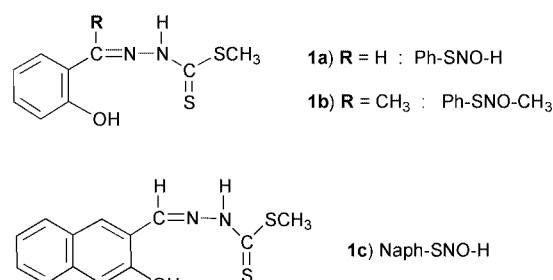
First published as an Advance Article on the web 27th November 2001

Neutral oxorhenium(v) complexes with tridentate SNO Schiff bases have been prepared by substitution reactions on the square pyramidal ionic complex $[\text{NBu}_4][\text{Re}^{\text{VOCl}}_4]$ and on the six-coordinate rhenium precursor $[\text{Re}^{\text{VOCl}}_3(\text{PPh}_3)_2]$. The chlororhenium intermediate species $[\text{Re}^{\text{VOCl}}(\text{Ph-SNO-CH}_3)]$ **1** allows the formation of the homologous iodo complex $[\text{Re}^{\text{VOI}}(\text{Ph-SNO-CH}_3)]$ **2** by a halogen exchange reaction with lithium iodide. The similar complexes $[\text{Re}^{\text{VOCl}}(\text{Ph-SNO-H})]$ **3** and $[\text{Re}^{\text{VOCl}}(\text{Naph-SNO-H})]$ **4** have been synthesised using *S*-methyl- β -*N*-(2-hydroxy-phenylmethylidene)dithiocarbazate (Ph-SNO-H) and *S*-methyl- β -*N*-(2-hydroxynaphthylmethylidene)dithiocarbazate (Naph-SNO-H). The ionic complex $[\text{NBu}_4][\text{ReOCl}_4]$ reacts with 4 equivalents of PPh_3 and Ph-SNO-H or Naph-SNO-H to give rise to the complexes $[\text{Re}^{\text{VOCl}}(\text{Ph-SNO-H})(\text{PPh}_3)]$ **5** and $[\text{Re}^{\text{VOCl}}(\text{Naph-SNO-H})(\text{PPh}_3)]$ **7** which are smoothly converted in ethanolic solution into $[\text{Re}^{\text{VOCl}}(\text{Ph-SNO-H})(\text{OPPh}_3)]$ **6** and $[\text{Re}^{\text{VOCl}}(\text{Naph-SNO-H})(\text{OPPh}_3)]$ **8**, respectively. Each compound was characterised by elemental analysis, IR, NMR spectra and FAB mass spectrometry. The crystallographic structures of $[\text{ReOI}(\text{Ph-SNO-CH}_3)]$ **2**, $[\text{ReOCl}(\text{Ph-SNO-H})(\text{PPh}_3)]$ **5** and $[\text{ReOCl}(\text{Ph-SNO-H})(\text{OPPh}_3)]$ **6** were determined by single crystal X-ray diffraction methods.

Introduction

Technetium and rhenium chemistry is an interesting field of research in inorganic chemistry due to the extensive use of γ -emitter $^{99\text{m}}\text{Tc}$ in diagnostic nuclear medicine and the advent of the β -emitters ^{186}Re and ^{188}Re for radiotherapeutic purposes.¹ Recently, the ^{186}Re -HEDP agent (HEDP = hydroxyethylidene-diphosphonate) has been proposed for the palliation (or relief) of pain in patients with metastatic bone cancer.² These applications have renewed the interest in exploring rhenium chemistry and Re/Tc chemical analogy. In this connection, a growing number of studies comparing properties of Tc and Re compounds have recently been published, especially involving Tc^{V} and Re^{V} complexes.³

Studies involving the $[\text{TcO}]^{3+}$ core have played a major role in Tc(v) chemistry. These compounds are generally diamagnetic five- or six-co-ordinate species adopting square pyramidal, octahedral or prismatic trigonal geometries.⁴ Polydentate Schiff base ligands have shown efficient coordination ability towards technetium cores such as TcO^{3+} , TcO_2^+ or TcN^{2+} ,^{4,5} and can act as stabilising groups in various oxidation states.⁶ Few technetium complexes bearing tridentate SNO Schiff bases (Scheme 1) have been studied⁷⁻⁹ and mainly in reactions involving the TcN^{2+} core.^{10,11}



Recently, we investigated the reactivity of several Schiff base ligands with rhenium to produce new stable model complexes suitable for the preparation of therapeutic radiopharmaceuticals labelled with ^{186}Re or ^{188}Re .¹² The present work extends our investigations to the reactivity of tridentate Schiff bases Ph-SNO-H, Naph-SNO-H and Ph-SNO-CH₃ towards usual rhenium precursors such as $[\text{NBu}_4][\text{ReOCl}_4]$ and $[\text{ReOCl}_3(\text{PPh}_3)_2]$.

Rhenium complexes synthesised herein are compared to similar technetium complexes bearing the tridentate Schiff base ligands shown in Scheme 1. Tc(v) complexes display square pyramidal geometries when tridentate Schiff bases are utilised.¹³ On the contrary, quasi-octahedral arrays are adopted if bidentate or tetradentate ligands are employed.¹⁴

In addition, we discuss and compare the X-ray crystal structures of some representative complexes: $[\text{ReOI}(\text{Ph-SNO-CH}_3)]$ **2**, $[\text{ReOCl}(\text{Ph-SNO-H})(\text{PPh}_3)]$ **5** and $[\text{ReOCl}(\text{Ph-SNO-H})(\text{OPPh}_3)]$ **6**.

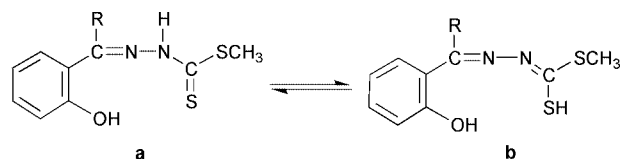
Results and discussion

The ligands

Three tridentate Schiff bases (Ph-SNO-H, Naph-SNO-H and Ph-SNO-CH₃, general abbreviation, SNO) have been used as chelating agents in the present work. The ligands employed undergo a tautomeric equilibrium in solution, as shown in Scheme 2. SNO ligands can act as tridentate dianionic S^-NO^- , as already described in the literature,^{9,10,12} by coordination *via* the neutral β -imine nitrogen, the charged phenolic oxygen and the charged thiolic sulfur atoms of the reactive form.

Synthesis and characterisation of complexes

$[\text{ReOCl}(\text{SNO})]$ **1**, **3**, **4** and $[\text{ReOI}(\text{Ph-SNO-CH}_3)]$ **2**. Our first aim was to study the reactivity of these SNO ligands



Scheme 2 Tautomeric form of SNO ligands.

towards usual oxorhenium precursors. Thus, we carried out the reaction with $[\text{ReOCl}_4]^-$ in a 1 : 1 molar ratio in dichloromethane to obtain the rhenium(v) complexes $[\text{ReOCl}(\text{SNO})]$ **1**, **3** and **4** ($\text{SNO} = \text{Ph-SNO-CH}_3$, Ph-SNO-H and Naph-SNO-H , respectively). The crude compounds were purified by recrystallisation from a mixture of dichloromethane–petroleum ether (bp 30–60 °C). Classically, the ligand acts as a dianionic tridentate chelate S^-NO^- .^{9,10,12} As for similar technetium compounds,⁹ the oxorhenium(v) complexes $[\text{ReOCl}(\text{SNO})]$ are diamagnetic in solution. The ^1H NMR spectra of **1–4** show the SCH_3 signals at *ca.* 2.90 ppm downfield shifted with respect to the corresponding signals in the ligands (2.50 ppm). In addition, ^{13}C NMR spectra of complexes **1–4** exhibit the characteristic CS_2 signals at lower fields (189–196 ppm) compared to those of the ligands (196–201 ppm) indicating that coordination *via* the charged thiolic sulfur atom has occurred. The OH signals of each ligand disappear upon coordination and the associated C–O carbon signals are strongly deshielded: 175.0 ppm *vs.* 155.0 ppm in the ligands, confirming that coordination through the charged phenolic oxygen has occurred as well.

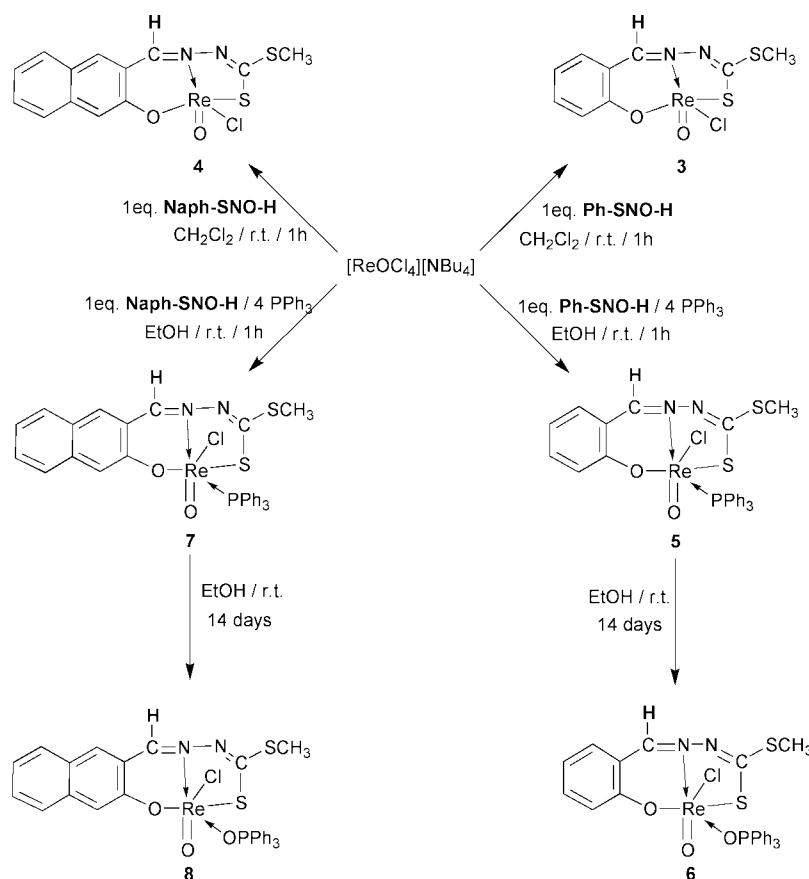
Each complex exhibits the distinctive $\text{Re}=\text{O}$ stretching vibration at 993–999 cm^{-1} , at the higher end of the range observed for mono-oxo Re species.¹⁵ Additional observations suggest that the ligand coordinates to the rhenium in the thiol form and behaves as a tridentate, dianionic donor according to the disappearance of the $\nu(\text{N-H})$ bands and the shift to lower energy (1000–1010 cm^{-1}) of the $\nu(\text{CS}_2)$ by *ca.* 30–50 cm^{-1} .

The mass spectra of complexes **1**, **2**, **3** and **4** show typical $[\text{ReO}(\text{SNO})\text{X}]^{++}$ parent ions ($\text{X} = \text{Cl}$ or I) at $m/z = 474.9$, 567.9, 459.9 and 512.2, respectively, with some fragmentations but no loss of halogen.

Thus, rhenium and technetium complexes of the type $[\text{MOCl}(\text{SNO})]$ are of similar structures.^{9,12} It is interesting that the ligand must be used in stoichiometric amount in the case of rhenium, otherwise the “3 + 2 mixed-ligand” complex $[\text{ReO}(\text{SNO})(\text{SN})]$, where one ligand behaves as tridentate (S^-NO^-) and the second as bidentate (S^-N) is obtained.¹⁶ This peculiar reactivity of rhenium compared to technetium might be useful in the development of molecules containing biofragments by using a *bifunctional* approach.

$[\text{ReOCl}(\text{SNO})(\text{PPh}_3)]$ **5, **7** and $[\text{ReOCl}(\text{SNO})(\text{OPPh}_3)]$ **6**, **8**.**

In the presence of an excess of triphenylphosphine, the precursor $[\text{NBu}_4][\text{ReOCl}_4]$ reacts with one equivalent of SNO ligand in ethanol to give the products $[\text{ReOCl}(\text{SNO})(\text{PPh}_3)]$ **5** and **7**, in which a triphenylphosphine molecule is bound to the metal to afford a six coordinate complex (Scheme 3). This reaction was conducted only with the ligands derived from salicylaldehyde and 2-hydroxynaphthaldehyde ($\text{SNO} = \text{Ph-SNO-H}$ and Naph-SNO-H). Complex **5** could be also obtained in good yield (69%) from $[\text{ReOCl}_3(\text{PPh}_3)_2]$ using the same experimental conditions. The violet complexes **5** and **7** were air stable but undergo conversion with oxidation of PPh_3 in ethanolic solution after two weeks to the red complexes $[\text{ReOCl}(\text{SNO})(\text{OPPh}_3)]$ **6** and **8**. In complexes **5–8** the Schiff base acts as dianionic tridentate chelate⁹ as mentioned above. On the other hand, for **6** and **8**, catalytic oxidation of tertiary phosphines by oxygen transfer *via* oxorhenium complexes has been already reported.¹⁷ However, few examples containing one molecule of ternary phosphine oxide OPR_3 in the coordination sphere of rhenium, have been described in the literature.¹⁸ In this context, the presence both of the oxorhenium core $\text{Re}^{\text{V}}=\text{O}$ and a molecule of OPR_3 in **6** and **8** is unexpected. Indeed, usually,



Scheme 3 Synthesis of $[\text{ReOCl}(\text{R-SNO-H})]$ **3**, **4**; $[\text{ReOCl}(\text{R-SNO-H})(\text{PPh}_3)]$ **5**, **7** and $[\text{ReOCl}(\text{R-SNO-H})(\text{OPPh}_3)]$ **6**, **8** ($\text{R} = \text{Ph}$ or Naph).

oxo-complexes might react with ternary phosphines to give rise to the corresponding ternary phosphine oxide OPR_3 in accordance with the catalytic and redox properties of the rhenium complex used. In that case, this potential ligand OPR_3 usually has a weak affinity for rhenium complexes reduced to the +III oxidation state.¹⁷ To our knowledge, some complexes such as $[\text{ReOCl}_3(\text{Me}_2\text{S})(\text{OPPh}_3)]$, $[\text{ReOCl}_3(\text{PPhEt}_2)(\text{OPPhEt}_2)]$ or more recently $[\text{ReOCl}_3(\text{PPh}_3)(\text{OPPh}_3)]$ and $[\text{NBu}_4][\text{ReOBr}_4(\text{OPPh}_3)]$ having the OPR_3 ligand in *trans* position to the oxo core, have been synthesised and characterised. However, few crystal structure determinations have been reported in the literature.¹⁹ In conclusion, $[\text{ReOCl}(\text{SNO})(\text{OPPh}_3)]$ **6** and **8** represent the first examples of oxorhenium(V) complexes coordinated by both Schiff bases and a molecule of O=PPh_3 bound to the metal *via* the oxygen atom. The spectroscopic data reported for **5–8** are very similar to the IR and NMR data obtained above for **1–4**. Indeed, the ^1H NMR spectra of **5–8** show deshielded SCH_3 signals at 2.80–2.90 ppm. In addition, the imine proton (9.00–10.00 ppm) and the C–O–Re carbon (173–176 ppm) signals of each complex are comparable to the data obtained for **1–4**. Nevertheless, the imine carbon signals $\text{C}=\text{N}$ of **5** and **6** are shifted at 165.4 and 167.3 ppm while the chemical shifts corresponding to **7** and **8** are 159.5 and 155.6 ppm, respectively. Moreover, the ^{13}C and ^{31}P NMR spectra of rhenium complexes **5–7** also exhibit different CS_2 and phosphorus signals at 182–186 ppm and -2.80 , -6.35 ppm with respect to **6–8** [183–193 ppm (CS_2); 31.77 and 30.58 ppm (OPPh_3)].

The infrared spectroscopic data have revealed the presence of $\text{C}=\text{N}$ (1594 – 1601 cm^{-1}) and CS_2 (1007 cm^{-1}) bands in each complex **5–8**. Nevertheless, a modification in the $\nu(\text{Re}=\text{O})$ stretching vibration is observed between complexes **5** and **7** (960 cm^{-1}) and **6** and **8** (990 cm^{-1}). These observations indicate a modification of ligand in *trans* position to the $\text{Re}=\text{O}$ core. Indeed, the data for **5** and **7** are in accordance with six coordinate oxorhenium compounds with a phenolic oxygen or a chlorine atom *trans* to $\text{Re}=\text{O}$ multiple bond [$\nu(\text{Re}=\text{O})$ 950 – 980 cm^{-1}].^{20,21} On the other hand, the $\nu(\text{Re}=\text{O})$ at 990 cm^{-1} in **6** and **8** indicate the presence of a molecule of OPPh_3 in *trans* position to the $\text{Re}=\text{O}$ group as in the case of $[\text{ReOCl}_3(\text{OPPh}_3)(\text{PPh}_3)]$ ¹⁹ or in square pyramidal oxotechnetium(V) compounds.^{9–12} Finally, the $\nu(\text{P}=\text{O})$ frequencies of **6** and **8**, at 1119 and 1116 cm^{-1} , respectively, are in the range 1105 – 1220 cm^{-1} reported for homologous complexes in the literature.^{18–21}

Mass spectrometry of complexes **5** and **7** shows the fragments $[\text{ReO}(\text{SNO})(\text{PPh}_3)]^{+}$: $m/z = 689.2$, 705.0 and also ions with loss of Cl and PPh_3 fragments.

The complete reaction pathway is reported in Scheme 3. Technetium and rhenium show some differences.⁹ In particular, the $[\text{TcOCl}(\text{SNO})]$ moiety is stable enough to exist as a five coordinate species, while $[\text{ReOCl}(\text{SNO})]$ can interact with the site *trans* to the $\text{Re}=\text{O}$ bond with nucleophilic phosphine such as PPh_3 to give a six-co-ordinate compound. Nevertheless, the higher stability of $[\text{ReOCl}(\text{SNO})(\text{OPPh}_3)]$ complexes **6** and **8** compared to $[\text{ReOCl}(\text{SNO})(\text{PPh}_3)]$ complexes **5** and **7** appears to be consistent with the trend of the positive inductive effect on the oxygen atom: OPPh_3 displaces the chlorine atom to the equatorial plane and is located in a favoured position *trans* to the $\text{Re}=\text{O}$ multiple bond.

Several attempts using analogous ligands such as Ph-SNO-CH_3 , in order to obtain the homologous oxorhenium compounds $[\text{ReOCl}(\text{Ph-SNO-CH}_3)(\text{PPh}_3)]$ and $[\text{ReOCl}(\text{Ph-SNO-CH}_3)(\text{OPPh}_3)]$ failed even if ^1H , ^{13}C NMR and mass spectrometry revealed the presence of $[\text{ReOCl}(\text{Ph-SNO-CH}_3)(\text{PPh}_3)]$ in a mixture of different side products.

X-Ray structure of complexes **5** and **6**

[ReO(Ph-SNO-CH₃)I] 2. Crystallographic data of the penta-co-ordinated complex of Re^{V} have already been published.¹²

[ReOCl(Ph-SNO-H)(PPh₃)] 5. In the mononuclear neutral $[\text{ReOCl}(\text{Ph-SNO-H})(\text{PPh}_3)]$ complex, the coordination geometry around the Re is highly distorted octahedral; the S(1), N(1), O(2) atoms from the tridentate S^-NO^- ligand and the phosphorus atom lie on the equatorial plane, while the chloride is positioned *trans* to the O(1) oxo atom (Fig. 1). The Re–P

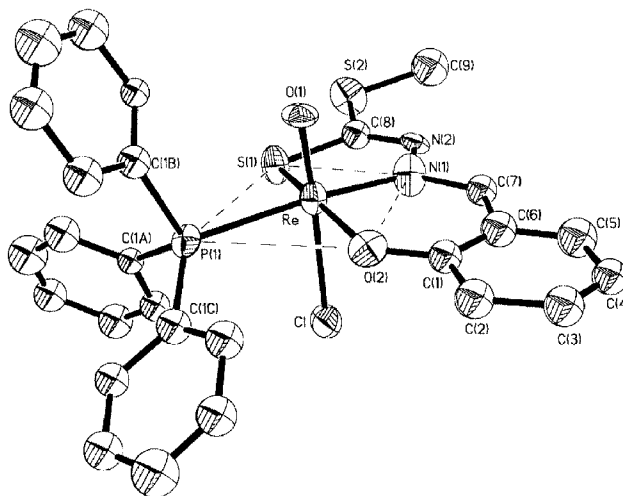


Fig. 1 A thermal ellipsoid plot of $[\text{ReOCl}(\text{Ph-SNO-H})(\text{PPh}_3)]$ **5**.

[$2.450(6)\text{ \AA}$] and Re-N [$1.99(2)\text{ \AA}$] distances are in accordance with different lengths already reported in the literature for octahedral rhenium complexes.^{12,21} Moreover, the lengthening of the Re-Cl bond [$2.403(6)\text{ \AA}$] in *trans* position to the $\text{Re}=\text{O}$ core with respect to an equatorial coordination, is similar to the distances reported for homologous complexes such as $[\text{ReOCl}_2(\text{PPh}_3)\{p\text{-MeC}_6\text{H}_4\text{N}=\text{C}(\text{OEt})\text{-S}\}]$ ($\text{Re-Cl}_{\text{trans}}\text{ } 2.437\text{ \AA}$ vs. $\text{Re-Cl}_{\text{cis}}\text{ } 2.381\text{ \AA}$).²¹ In the crystal the molecules are packed individually and interact *via* normal Van der Waals contacts. The $\text{Re}=\text{O}$ distance is $1.70(1)\text{ \AA}$, indicating strong multiple bond character. The distance is quite similar to the $\text{Tc}=\text{O}$ bond distance found in $[\text{TcO}(\text{SNO})\text{Cl}]$ [$1.645(7)\text{ \AA}$]⁹ and to the $\text{Re}=\text{O}$ bond found in **2** [$1.660(7)\text{ \AA}$]. The $\text{O}(1)\text{-Re-Cl}$ axis is non-linear [$166.3(5)^\circ$] and the Re atom is displaced from the mean equatorial plane by 0.20 \AA towards the 'oxo' atom. In the ClSPNO_2 polyhedron, the Re is 1.02 \AA from the $\text{O}(1)\text{-S}(1)\text{-N}(1)$ plane and -1.38 \AA from the $\text{P}(1)\text{-Cl-O}(2)$ plane, the dihedral angle between these faces being 16.8° . In the mean equatorial plane, the four donor atoms deviate by $\pm 0.03\text{ \AA}$; the 'bite' distances $\text{O}(2) \cdots \text{N}(1)$ and $\text{N}(1) \cdots \text{S}(1)$ are comparable (2.788 and 2.815 \AA , respectively) and the major departure from the ideal value (90°) is represented by $\text{S}(1)\text{-P}(1)\text{-O}(2)$ (78.4°). The equatorial plane makes dihedral angles of 7.2 and 2.3° with the strictly planar six-membered $\text{Re-O}(2)\text{-C}(1)\text{-C}(6)\text{-C}(7)\text{-N}(1)$ ring and with the five-membered $\text{Re-N}(1)\text{-N}(2)\text{-C}(8)\text{-S}(1)$ ring, respectively. This latter ring is somewhat "twist-envelope" (C_2), torsion angles being from -8.1 to 10.9° .

Bond lengths and angles within the inner core show no unusual features, being within the range expected by comparison with other similar rhenium(V)-oxo complexes.²² All other bond distances and angles are comparable to **2** and do not require further discussion (Tables 1 and 2).

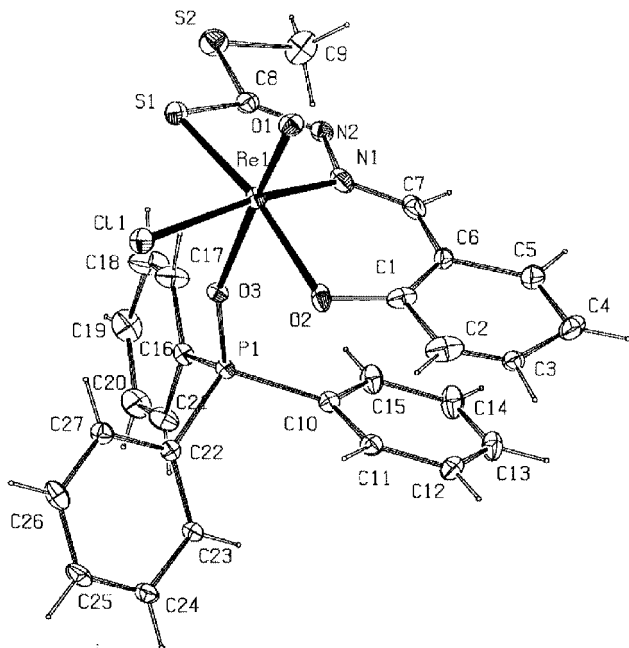
[ReOCl(Ph-SNO-H)(OPPh₃)] 6. The crystal consists of monomeric units packed together with no contact significantly shorter than the sum of the Van der Waals radii. The data and characterisation of the complex $[\text{ReOCl}(\text{Ph-SNO-H})(\text{OPPh}_3)]$ **6** together with the crystal structure determination indicate that the geometry of the molecule is pseudo-octahedral with the $\text{Re}=\text{O}$ group in axial position: the tridentate dianionic ligand S^-NO^- spans three positions in the plane normal to $\text{Re}=\text{O}$ through the neutral β nitrogen, the charged phenolic oxygen

Table 1 Selected bond lengths (Å) for complexes [TcOCl(Naph-SNO-H)] **2**, **5** and **6**

	2	5	6	[TcOCl(Naph-SNO-H)]
Re–O(1)	1.660(7)	1.70(1)	1.666(7)	Tc=O 1.645(7)
Re–O(2)	1.958(7)	1.99(1)	2.145(11)	Tc–O 1.961(6)
Re–O(3)	—	—	2.180(6)	—
Re–N(1)	2.062(7)	1.99(2)	2.051(10)	Tc–N 2.026(6)
Re–S(1)	2.256(2)	2.268(5)	2.372(4)	Tc–S 2.253(3)
Re–P(1)	—	2.450(6)	—	—
Re–Cl	2.6329(10) ^a	2.403(6)	2.355(3)	Tc–Cl 2.319(3)
N(1)–N(2)	1.412(11)	1.42(3)	1.500(15)	N–N 1.414(10)
C(1)–O(2)	1.331(12)	1.33(2)	1.348(17)	C–O 1.319(10)
S(1)–C(9)	1.778(10)	—	—	—
S(1)–C(8)	—	1.78(2)	1.689(12)	—
C(9)–N(2)	1.265(4)	—	—	—
C(8)–N(2)	—	1.27(2)	1.306(14)	C=N 1.259(10)
P(1)–O(3)	—	—	1.500(6)	—

^a Re–I bond length.**Table 2** Selected angles (°) for complexes [TcOCl(Naph-SNO-H)] **2**, **5** and **6**

	2	5	6	[TcOCl(Naph-SNO-H)]
Cl–Re–P(1)	—	82.8(2)	—	—
Cl–Re–S(1)	87.98(7) ^a	90.1(2)	92.88(11)	Cl–Tc–S 87.9(1)
Cl–Re–O(1)	101.9(3) ^a	166.3(5)	99.7(3)	Cl–Tc=O 106.0(2)
Cl–Re–O(2)	84.5(2) ^a	78.4(4)	86.9(2)	Cl–Tc–O 83.0(2)
Cl–Re–O(3)	—	—	83.84(18)	—
Cl–Re–N(1)	154.8(2) ^a	89.4(6)	164.5(3)	Cl–Tc–N 150.4(2)
O(1)–Re–N(1)	103.2(3)	98.5(7)	95.6(4)	N–Tc=O 103.6(3)
O(2)–Re–N(1)	85.2(3)	88.8(7)	93.8(4)	N–Tc–O 85.0(3)
O(1)–Re–S(1)	109.6(3)	101.9(5)	97.5(3)	O=Tc–S 108.7(3)
O(2)–Re–S(1)	130.6(2)	165.6(4)	164.8(2)	O–Tc–S 134.5(2)
N(1)–Re–S(1)	81.5(2)	82.4(5)	82.4(4)	N–Tc–S 81.4(2)
O(1)–Re–P(1)	—	90.3(5)	—	—
N(1)–Re–P(1)	—	170.2(4)	—	—
S(1)–Re–P(1)	—	91.5(2)	—	—
C(9)–S(1)–Re	96.8(3)	—	—	C–S–Tc 97.0(3)
C(8)–S(1)–Re	—	96.4(7)	96.2(4)	—
N(2)–N(1)–Re	119.4(6)	124(1)	120.6(7)	N–N–Tc 119.8(5)
C(1)–O(2)–Re	122.0(6)	130(2)	112.9(8)	C–O–Tc 126.8(5)
P(1)–O(3)–Re	—	—	156.4(4)	—

^a Angles are calculated with respect to the iodide atom.**Fig. 2** A thermal ellipsoid plot of [ReOCl(Ph-SNO-H)(OPPh₃)] **6**.

and the charged thiolic sulfur atoms, the fourth site on the plane being occupied by a chlorine atom *trans* to N(1) (Fig. 2). As expected, the rhenium atom is displaced by 0.31 Å from the

mean equatorial plane of the equatorial SNOCl donor atom set, towards the oxo ligand and the O(1)–Re–O(3) angle is essentially linear (176.4°). The Re^v=O bond length of 1.666(7) Å falls in the range of similar distances found in the other oxo complexes of rhenium¹² and in **2** and **5**. The *trans* distance Re–OPPh₃ [2.180(6) Å] is longer than similar bond lengths usually reported in the literature.¹⁸ [ReOX₃(PR₃)(OPR₃)] (X = Cl, Br) complexes show shorter Re–OPR₃ bond lengths (2.053–2.082 Å) than **6**.¹⁹ However, the Re–O(3) distance is close to a bond length determined for single bond rhenium–oxygen [Re–O(2) 2.14(1) Å]. On the other hand, the distance Re–Cl_{cis} [2.355(3) Å] is shorter than a similar bond length reported for [ReOCl₃(PPh₃)(OPPh₃)] or [ReOCl₃(PPhEt₂)(OPPhEt₂)] (>2.361 Å).¹⁹ Moreover, the bond length of 1.500(6) Å in this complex between P(1) and O(3) is significantly shorter indicating a typical double bond between oxygen and phosphorus atoms and a weaker coordination to the rhenium metal. Moreover, this Re–OPPh₃ bond length seems to exclude considerable *trans* weakening, due to a strong π bonding of the oxo group, although a structural *trans* effect is present in **5**. An evaluation of the structure of Re(v) complexes available in the Cambridge Structural Data Base reveals that an oxo ligand in this system preferably coordinates *trans* to “hard” ligands such as aryl or alkoxy ligands, followed by nitrogen donor ligands and less preferably coordinates *trans* to “soft” ligands such as halides or phosphides. It is obvious that the system under investigation in general tries to avoid a *trans* arrangement of an oxo and a chloro ligand. As in the case of [ReOCl(Ph-SNO-H)(OPPh₃)] **6**, the relatively hard OPPh₃ donor ligand prefers the *trans* position to the Re=O

moiety for electronic reasons and probably also for steric reasons. This could explain the rearrangement of **5** into **6** or **7** into **8** in ethanolic solution, **5** and **7** are the kinetic products while **6** and **8** represents the thermodynamic compounds. The Re–N(1) [2.05(1) Å], Re–O(2) [2.14(1) Å] and Re–S(1) [2.372(4) Å] distances are longer than the corresponding distances found in compound **5** [1.99(2), 1.99(1) and 2.268(5) Å respectively], this is probably due to the smaller *trans* effect in compound **6**.

Thermal ellipsoid plots drawn by PLATON of each molecule are shown in Figs. 1 and 2. Selected bond lengths and angles for **2**, **5**, **6** and [TcOCl(Naph–SNO–H)] are given in Tables 1 and 2.

Thus the structure and properties of these rhenium complexes differ substantially from those described in literature for square pyramidal oxotechnetium(v) complexes with tridentate Schiff bases derived from *S*-methyl dithiocarbazate.⁹

Conclusion

Tc(v) complexes having a terminal Tc=O group, in which an oxo atom is multiply bonded to the Tc(v) centre, are usually characterised by a square pyramidal geometry where the terminal oxo group is in apical position. The remaining four sites of the basal plane of the square pyramid are available for coordination of some suitable ligand such as Schiff bases. In this paper, we continued the work already done with technetium by studying the reactivity of rhenium oxo complexes towards Schiff bases derived from *S*-methyl dithiocarbazate. It is well established that the knowledge of the geometrical features of a radiopharmaceutical is of fundamental importance for understanding of biological behaviour. Thus, molecular structures of original neutral rhenium complexes involving various geometries were performed by X-ray diffraction methods. Attachment of a bioactive species to these type of structures is in progress in order to determine the different physical, physicochemical and biological properties of these complexes. The simplicity of the preparation methods, the stability of some complexes under normal conditions and the versatility of the ligands are important in the design of ^{186/188}Re radiopharmaceuticals containing SNO donor atom sets.

Experimental

Starting materials

Ethanol was distilled twice under nitrogen over magnesium turnings. Dichloromethane and petroleum ether (bp 30–60 °C) were distilled over calcium chloride. Carbon disulfide, hydrazine dihydrochloride, methyl iodide, lithium iodide, triphenylphosphine, salicylaldehyde, 2-hydroxy-1-naphthaldehyde and 2-hydroxyacetophenone are commercially available from Aldrich (Saint Quentin Fallavier, France). [NBu₄][ReOCl₄] **A**, [ReOCl₃(PPh₃)₂] **B** and *S*-methyl-β-*N*-(2-hydroxyphenylmethylidene)dithiocarbazate (Ph–SNO–H), *S*-methyl-β-*N*-(2-hydroxynaphthylmethylidene)dithiocarbazate (Naph–SNO–H) and *S*-methyl-β-*N*-(2-hydroxyphenylethylidene)dithiocarbazate (Ph–SNO–CH₃) were prepared according to literature methods.^{15,23}

Analysis and physical measurements

Carbon, hydrogen and sulfur analyses were performed by I.C.S.N. (91198 Gif sur Yvette, France) on a Carlo Erba elemental analyser Model-1106. IR spectra were obtained by a Nicolet 205 instrument in KBr pellets (4000–500 cm^{−1}). Mass spectrometry was carried out by C.R.M.P.O. (37500 Rennes, France) on a Zabspect TOF (Micromass) spectrometer (FAB+, NBA matrix). All prepared compounds were characterised by ¹H, ¹³C and ³¹P NMR spectroscopy recorded with a BRUKER ARX 400 at 400.13, 100.62 and 161.98 MHz, respectively. Chemical shift values are referred to CHCl₃ (7.26 ppm: ¹H NMR and 77.1 ppm: ¹³C NMR). Spin-spin structures are

abbreviated as: s, singlet; d, doublet; t, triplet and m, multiplet. IR abbreviations are s: strong; w: weak; m: medium and sb: strong and broad.

Synthesis of complexes

[ReO(Ph–SNO–CH₃)Cl] 1 and **[ReO(Ph–SNO–CH₃)I] 2**. The synthesis and characterisation of chloro complex **1** and iodo complex **2** have been reported previously.¹²

[ReO(Ph–SNO–H)Cl] 3. To a dichloromethane solution (5 mL) of [NBu₄][ReOCl₄] (0.100 g, 0.17 mmol), *S*-methyl-β-*N*-(2-hydroxyphenylmethylidene)dithiocarbazate (0.038 g, 0.17 mmol) in dichloromethane (20 mL) was added dropwise and the solution was stirred at room temperature for 2 hours. The solvent was removed by evaporation under vacuum and the residue was dissolved in a mixture of dichloromethane–petroleum ether (bp 30–60 °C) (30/70; 20–30 mL). After 5 days at room temperature, red crystals of [ReO(Ph–SNO–H)Cl] were collected, washed with petroleum ether and dried under reduced pressure. Recrystallisation was carried out to remove the residual salts (NBu₄Cl and HCl) (0.066 g, yield = 84%).

Found: C, 23.47; H, 1.73; S, 13.88%. C₉H₈O₂ClN₂ReS₂ requires: C, 23.40; H, 1.70; S, 13.90%. Selected IR bands (cm^{−1}): 1598 [m, ν(C=N)], 1561 (m), 1527 (s), 1491 (m), 1421 (w), 1407 (w), 1311 (m), 1224 (m), 1007 [s, ν(CS₂)], 993 [s, ν(Re=O)], 755 (s). Mass spectrometry (FAB): *m/z* 459.9246: [ReO(Ph–SNO–H)Cl]⁺; 424.9575: {[ReO(Ph–SNO–H)Cl] – Cl}⁺. ¹H NMR (CDCl₃), δ 2.83 (s, SCH₃), aromatic protons: 7.00 (t, *J* = 7.5 Hz), 7.39 (d, *J* = 7.5 Hz), 7.56 (d, *J* = 7.5 Hz), 7.64 (t, *J* = 7.5 Hz), 9.43 (s, CH=N). ¹³C NMR (CDCl₃), δ 19.1 (SCH₃), 120.9, 122.1, 136.3 and 139.2 (4 CH aromatics), 119.2 (C–CH=N), 168.1 (CH=N), 172.9 (C–O), 192.3 (CS₂).

[ReO(Naph–SNO–H)Cl] 4. To a dichloromethane solution (5 mL) of [NBu₄][ReOCl₄] (0.100 g, 0.17 mmol), *S*-methyl-β-*N*-(2-hydroxynaphthylmethylidene)dithiocarbazate (0.049 g, 0.17 mmol) in dichloromethane (20 mL) was added dropwise and the solution was stirred at room temperature for 2 hours. The solvent was removed by evaporation under vacuum and the residue was dissolved in a mixture of dichloromethane–petroleum ether (bp 30–60 °C) (30/70; 20–30 mL). After 5 days at room temperature, yellow–green crystals of [ReO(Naph–SNO–H)Cl] were collected, washed with petroleum ether and dried under reduced pressure. Recrystallisation was carried out to remove the residual salts (NBu₄Cl and HCl) (0.08 g, yield = 92%).

Found: C, 30.31; H, 1.94; S, 12.79. C₁₃H₁₀O₂ClN₂ReS₂ requires: C, 30.50; H, 2.00; S, 12.50%. Selected IR bands (cm^{−1}): 1615 (w), 1594 [s, ν(C=N)], 1570 (m), 1542 (s), 1451 (w), 1411 (w), 1361 (m), 1349 (m), 1328 (m), 1316 (m), 1282 (w), 1237 (w), 1205 (m), 1142 (w), 1007 [s, ν(CS₂)], 999 [s, ν(Re=O)], 964 (w), 832 (m), 755 (m). Mass spectrometry (FAB): *m/z* = 512.2: [ReO(Naph–SNO–H)Cl]⁺. ¹H NMR (CDCl₃), δ 2.92 (s, SCH₃), aromatic protons: 7.60 (t, *J* = 7.6 Hz), 7.70 (d, *J* = 9.1 Hz), 7.79 (t, *J* = 7.1 Hz), 7.93 (d, *J* = 7.6 Hz), 8.19 (d, *J* = 9.1 Hz), 8.36 (d, *J* = 8.7 Hz), 10.30 (s, CH=N). ¹³C NMR (CDCl₃), δ 19.2 (SCH₃), 120.8, 122.4, 126.6, 130.0, 130.1 and 142.0 (6 CH aromatics), 113.0 129.2 and 132.6 (3 C aromatics), 162.2 (CH=N), 174.5 (C–O aromatic), 188.7 (CS₂).

[ReOCl(Ph–SNO–H)(PPh₃)] 5. *Method A*. To an ethanol solution (20 mL) of [NBu₄][ReOCl₄] (0.100 g, 0.17 mmol), *S*-methyl-β-*N*-(2-hydroxyphenylmethylidene)dithiocarbazate (0.038 g, 0.17 mmol) in ethanol (10 mL) was added dropwise and the solution stirred under nitrogen atmosphere for 30 min. Triphenylphosphine (0.180 g, 0.68 mmol) in hot ethanol (10 mL) was added dropwise to the resulting red mixture. A dark violet precipitate appeared and after 30 min stirring at room temperature, the crude product was filtered off, washed

rapidly with ethanol and dried under reduced pressure. The dark violet powder was recrystallised from a minimum mixture of petroleum ether–dichloromethane (bp 30–60 °C) (70/30). After one night at room temperature under nitrogen atmosphere, dark crystals of [ReOCl(Ph–SNO–H)(PPh₃)] were collected, washed with petroleum ether and dried under reduced pressure (0.078 g, yield = 63%).

Method B. To an ethanol solution (20 mL) of [ReOCl₃(PPh₃)₂] (1.00 g, 1.2 mmol), *S*-methyl-β-*N*-(2-hydroxyphenyl)methylidene)dithiocarbazate (0.27 g, 1.2 mmol) in ethanol (10 mL) was added dropwise. After 30 min stirring at room temperature under nitrogen atmosphere, the dark violet precipitate was filtered off, washed rapidly with ethanol and dried under reduced pressure (0.60 g, yield = 69%).

Found: C, 44.88; H, 3.22; S, 8.89%. C₂₇H₂₃O₂ClN₂PrReS₂ requires: C, 44.80; H, 3.20; S, 8.90%. Selected IR bands (cm⁻¹): 1598 [s, ν(C=N)], 1579 (s), 1534 (s), 1480 (w), 1432 (s), 1366 (m), 1291 (m), 1093 (m), 1007 [s, ν(C=S)], 966 [sb, ν(Re=O)], 950 (s), 750 (s), 691 (s), 525 (s). Mass spectrometry (FAB): *m/z* 689.2 {[ReOCl(Ph–SNO–H)(PPh₃) – Cl]⁺}, 427.0: [M⁺⁺ – Cl – PPh₃]. ¹H NMR (CDCl₃), δ 2.79 (s, SCH₃), aromatic protons: 6.69 (t, *J* = 7.0 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.5 Hz, 1H), 7.48 (m, 10H), 7.80 (m, 5H), 9.02 (s, CH=N). ¹³C NMR (CDCl₃), δ 18.9 (SCH₃), 119.2, 123.0, 136.8 and 138.8 (4 CH_{ar}), 128.4 (d, *J* = 10 Hz, C_{metalortho} PPh₃), 131.4 (d, *J* = 2 Hz, C_{para} PPh₃), 132.1 (d, *J* = 50 Hz, C_{quaternary} PPh₃), 135.0 (d, *J* = 10 Hz, C_{metalortho} PPh₃), 139.6 (C=C=N aromatic), 165.4 (CH=N), 172.2 (C–O), 185.7 (CS₂). ³¹P NMR (CDCl₃), δ –6.35 (Re–PPh₃).

[ReOCl(Ph–SNO–H)(OPPh₃)] 6. An ethanolic suspension (5 mL) of [ReOCl(Ph–SNO–H)(PPh₃)] (0.050 g, 0.070 mmol) was stirred at room temperature for 14 days during which the violet solution turned dark red. The solvent was removed by evaporation under vacuum and the residue was dissolved in a mixture of dichloromethane–petroleum ether (50/50; 10 mL). On standing at room temperature for 5 days, dark red crystals of [ReOCl(Ph–SNO–H)(OPPh₃)] were collected, washed with petroleum ether and dried under reduced pressure (0.025 g, yield = 48%).

Found: C, 43.91; H, 3.14; S, 8.68. C₂₇H₂₃O₃ClN₂PrReS₂ requires: C, 43.80; H, 3.10; S, 8.60%. Selected IR bands (cm⁻¹): 1594 [s, ν(C=N)], 1584 (s), 1535 (s), 1487 (w), 1462 (w), 1435 (s), 1364 (w), 1283 (m), 1193 (w), 1140 (s), 1119 (s), 1085 (s), 1007 [s, ν(C=S)], 991 [sb, ν(Re=O)], 754 (s), 725 (s), 692 (s), 536 (s). Mass spectrometry (FAB): *m/z* 705.0 {[ReOCl(Ph–SNO–H)(OPPh₃) – Cl]⁺}, 443.0 {[ReOCl(Ph–SNO–H)(OPPh₃) – Cl – OPPh₃]⁺⁺}. ¹H NMR (CDCl₃), δ 2.78 (s, SCH₃), aromatic protons: 6.95 (t, *J* = 7.6 Hz, 1H), 7.48 (m, 7H), 7.81 (m, 10H), 7.62 (t, *J* = 8.6 Hz, 1H), 9.16 (s, CH=N). ¹³C NMR (CDCl₃), δ 19.0 (SCH₃), 119.0, 120.7, 122.3 and 136.1 (4 CH aromatics), 128.6 (d, *J* = 10 Hz, C_{metalortho} PPh₃), 129.9 (d, *J* = 50 Hz, C_{quaternary} PPh₃), 132.4 (d, *J* = 2 Hz, C_{para} PPh₃), 132.5 (d, *J* = 10 Hz, C_{metalortho} PPh₃), 139.3 (C=C=N aromatic), 167.3 (CH=N), 172.7 (C–O aromatic), 192.6 (CS₂). ³¹P NMR (CDCl₃), δ 31.77 (Re–OPPh₃).

[ReOCl(Naph–SNO–H)(PPh₃)] 7. To an ethanolic solution (20 mL) of [NBu₄][ReOCl₄] (0.100 g, 0.17 mmol), *S*-methyl-β-*N*-(2-hydroxynaphthyl)methylidene)dithiocarbazate (0.049 g, 0.17 mmol) in ethanol (10 mL) was added dropwise and the solution stirred under nitrogen atmosphere for 30 min. Triphenylphosphine (0.180 g, 0.68 mmol) in hot ethanol (10 mL) was added dropwise to the resulting red mixture and after 10 min, a dark violet precipitate appeared. After 30 min, stirring at room temperature, the crude product was filtered off, washed rapidly with ethanol and dried under reduced pressure. The resulting dark violet powder was recrystallised from a minimum volume of petroleum ether–dichloromethane (bp 30–60 °C)

(70/30). On standing at room temperature under nitrogen atmosphere for one night, dark crystals of [ReOCl(Naph–SNO–H)(PPh₃)] were collected, washed with petroleum ether and dried under reduced pressure (0.130 g, yield = 99%).

Found: C, 43.89; H, 3.12; S, 8.75. C₃₁H₂₅O₂ClN₂PrReS₂ requires: C, 48.10; H, 3.25; S, 8.30%. Selected IR bands (cm⁻¹): 1615 (w), 1599 [m, ν(C=N)], 1568 (s), 1536 (s), 1482 (m), 1434 (s), 1387 (w), 1352 (s), 1331 (s), 1318 (s), 1295 (w), 1190 (m), 1112 (m), 1095 (m), 1073 (w), 1042 (w), 1030 (w), 1007 [s, ν(CS₂)], 958 [s, ν(Re=O)], 949 (m), 909 (s), 744 (s), 706 (s), 693 (s), 522 (s), 509 (m). ¹H NMR (CDCl₃), δ 2.84 (s, SCH₃), 6.95 (t, *J* = 8.9 Hz, 1H), 7.32 (s, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.49 (s, 10H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.80 (m, 6H), 8.09 (d, *J* = 8.4 Hz, 1H), 9.90 (s, CH=N). ¹³C NMR (CDCl₃), δ 18.9 (SCH₃), 111.3, 120.1, 124.7, 128.7, 129.3, 130.7, 131.7 and 132.3 (8 C aromatics), 128.4 (d, *J* = 10 Hz, C_{metalortho} PPh₃), 131.3 (d, *J* = 2 Hz, C_{para} PPh₃), 133.9 (d, *J* = 50 Hz, C_{quaternary} PPh₃), 135.0 (d, *J* = 10 Hz, C_{metalortho} PPh₃), 140.4 (C=C=N), 159.5 (CH=N), 173.2 (C–O), 182.1 (CS₂). ³¹P NMR (CDCl₃), δ –2.80 (Re–PPh₃).

[ReOCl(Naph–SNO–H)(OPPh₃)] 8. An ethanolic suspension (5 mL) of [ReOCl(Naph–SNO–H)(PPh₃)] (0.020 g, 0.025 mmol) was stirred at room temperature for 14 days during which the violet solution turned dark red. The solvent was removed by evaporation under vacuum and the residue was dissolved in a mixture of dichloromethane–petroleum ether (50/50; 10 mL). On standing at room temperature for 5 days, dark red crystals of [ReOCl(Naph–SNO–H)(OPPh₃)] were collected, washed with petroleum ether and dried under reduced pressure (0.016 g, yield = 87%).

Found: C, 47.00; H, 3.20; S, 8.23. C₃₁H₂₅O₃ClN₂PrReS₂ requires: C, 47.10; H, 3.20; S, 8.10%. Selected IR bands (cm⁻¹): 1601 [s, ν(C=N)], 1584 (s), 1535 (s), 1487 (w), 1462 (w), 1435 (s), 1364 (w), 1283 (m), 1193 (w), 1140 (s), 1119 (s), 1085 (s), 1008 [s, ν(CS₂)], 992 [sb, ν(Re=O)], 959 (m), 948 (m), 830 (m), 754 (m), 725 (s), 692 (s), 524 (s). Mass spectrometry (FAB): *m/z* 705.0 [ReO(Naph–SNO–H)(OPPh₃)⁺]. ¹H NMR (CDCl₃), δ 2.78 (s, SCH₃), aromatic protons: 6.95 (t, *J* = 7.6 Hz, 1H), 7.48 (m, 7H), 7.81 (m, 10H), 7.62 (t, *J* = 8.6 Hz, 1H), 9.85 (s, CH=N). ¹³C NMR (CDCl₃), δ 18.5 (SCH₃), 119.0, 120.7, 122.3 and 136.1 (4 CH aromatics), 128.6 (d, *J* = 10 Hz, C_{metalortho} PPh₃), 129.9 (d, *J* = 50 Hz, C_{quaternary} PPh₃), 132.4 (d, *J* = 2 Hz, C_{para} PPh₃), 132.5 (d, *J* = 10 Hz, C_{metalortho} PPh₃), 139.3 (C=C=N aromatic), 155.6 (CH=N), 171.4 (C–O aromatic), 182.8 (CS₂). ³¹P NMR (CDCl₃), δ 30.58 (Re–OPPh₃).

Crystallography

Single crystals of complexes **5** and **6** were grown by slow evaporation of a petroleum ether–dichloromethane solution of the respective complexes. Pertinent crystallographic data and structure refinement for compounds **5** and **6** are summarised in Table 3 as well as bond lengths and angles (Tables 1 and 2 respectively).

Data for **6** were collected on an automatic CAD4 NONIUS diffractometer with graphite monochromatised Mo-Kα radiation.²⁴ The cell parameters were obtained by fitting a set of 25 high theta reflections. After Lorentz and polarisation corrections and absorption corrections with ψ scans²⁵ the structure was solved with SIR-97,²⁶ which revealed the non-hydrogen atoms of the structure. After anisotropic refinement, all the hydrogen atoms were found by Fourier difference. We observed two peaks around the centre of symmetry of the cell: these peaks may be assumed to non-stoichiometric C and O atoms. The whole structure was refined with SHELXL97²⁷ by full matrix least-squares techniques. Atomic scattering factors were obtained from *International Tables for X-Ray Crystallography*.²⁸ Thermal ellipsoid diagrams were realised with PLATON98.²⁹ All the calculations were performed on a Silicon Graphics Indy Computer.

Table 3 Crystallographic data for compounds **5** and **6**

Compound ^a	5	6
Formula	C ₂₇ H ₂₃ O ₂ ClN ₂ PrESe ₂ ·H ₂ O	C ₂₇ H ₂₃ O ₃ ClN ₂ PrESe ₂
<i>M</i>	742.21	740.21
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>T</i> /K	293(2)	293(2)
<i>a</i> /Å	17.395(6)	9.603(7)
<i>b</i> /Å	9.861(5)	30.375(8)
<i>c</i> /Å	16.911(9)	11.142(4)
β /°	102.28(3)	114.995(5)
<i>V</i> /Å ³	2835(2)	2946(3)
<i>Z</i>	4	4
μ (Mo-K α)/cm ⁻¹	46.20	45.36
<i>F</i> (000)	1460	1448
Total reflections	6373	6331
Independent reflections	3315	5960
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	2251	4709
<i>R</i> _{int}	0.0621	0.0513
<i>R</i> 1/ <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0881, 0.2312	0.0625, 0.1727
<i>R</i> 1/ <i>wR</i> 2 (all data)	0.0108, 0.2500	0.0833, 0.1852

^a Crystallographic data for [ReOCl(SNO)I]¹² and [TcOCl(Naph-SNO-H)]⁹ have already been reported.

Crystals of [ReOCl(Ph-SNO-H)(PPh₃)] **5** were of low quality and repeated attempts to obtain higher quality crystals were unsuccessful due to the fast conversion of **5** into **6** in solution; as a consequence, refinement of the crystal structure was not satisfactory and was severely hampered by two factors. In the first instance, the crystals appear cracked and accompanied by very small gem-like blocks and the only remotely suitable sample for a single-crystal determination was substandard. Secondly, the peaks were broad and the crystal was a weak diffractor, the diffracting ability falling rapidly with increasing Bragg angle. Data for **5** were collected on an automatic Nicolet R3m/V diffractometer with graphite monochromatised Mo-K α radiation.²⁴ The structure was solved by the heavy atom method and refined anisotropically for non-carbon atoms by full matrix least-squares calculations based on *F*². During the refinement it became apparent that a water molecule was trapped in the lattice, without any significant interaction. The maximum residual peak in the final difference map corresponded to 1.51 e Å⁻³, 1.14 Å from rhenium. Programs in the Siemens X-ray package were used for data collection and for structure solution and refinement.^{26,27} Bond distances and angles are affected by relatively high e.s.d.s. However, the structural analysis did attain the objective by providing proof of the stereochemistry of the complex [ReOCl(Ph-SNO-H)(PPh₃)] **5**.

CCDC reference numbers 172245 and 140024.

See <http://www.rsc.org/suppdata/dt/b1/b109020h/> for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank Region Bretagne for financial support. We also acknowledge G. Bandoli (University of Padova Italy) and L. Toupet (University of Rennes I) for crystallographic experiments and data collection.

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