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Reactivity of $[\mathrm{M{=}O}]^{3+}$ (M = Tc, Re) core towards 2-mercapto-1,3-azole ligands. Formation of a new organometallic complex of Re(IV) and X-ray crystal structures

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Abstract

Imidazole-2-thiol derivatives H_2L^{1-3} (H_2L^1 = 1*H*-benzoimidazole-2-thiol, H_2L^2 = 5-methyl-1*H*-benzoimidazole-2-thiol, and H_2L^3 = 1*H*-imidazole-2-thiol) act as neutral monodentate ligands in a number of technetium and rhenium complexes. Disubstituted M(V) (M = Tc, Re) complexes of the type $[AsPh_4]\{[MOCl_2(H_2L^n)_2(H_2O)]Cl_2\}$ are formed when $[MOCl_4]^-$ react with H_2L^{1-3} in 1:2 stoichiometric ratio. Single crystal X-ray structure determinations were carried out on $[AsPh_4]\{[TcOCl_2(H_2L^1)_2(H_2O)]Cl_2\}$. The coordination sphere is pseudo-octahedral in which the sulfur atoms of two ligands sit in the equatorial plane and a water molecule is in *trans* to the Tc═O multiple bond. All the complexes react with an excess of the corresponding ligand to form tetrasubstituted cationic species $\{[MO(H_2L^n)_4]Cl_3\}$. These complexes can be also isolated by reaction of $[MOCl_4]^-$ with an excess of ligand. No complex is obtained with benzothiazole-2-thiol (HL^4) and benzoxazole-2-thiol (HL^5). Ligand exchange reactions of $[ReOCl_3(PPh_3)_2]$ with $HL^{4,5}$ have also been investigated. Treating the oxo-precursor with HL^4 no product is isolated, while with HL^5 the chelate oxo-compound $[ReOCl_2(L^5)(PPh_3)]$ is formed as two isomers. An interesting organometallic complex of Re(IV) $[ReCl_3(L^{5*})(PPh_3)_2]$ is obtained when a slight excess of HL^5 reacts with $[ReOCl_3(PPh_3)_2]$ in refluxing benzene solution and in air. Geometry about the Re atom is approximately octahedral in which the equatorial plane contains three Cl atoms and the carbon atom of the benzoxazole ligand anion, the apical positions are occupied by two PPh_3. The reaction with *O*-ethyl *S*-hydrogen *p*-tolyl carbonothioimidate HL^6 which contains the same heteroatoms of HL^5 does not form an organometallic species, but forms the chelate oxo-Re(V) complex $[ReOCl_2(L^6)(PPh_3)]$. The solid-state structure has been authenticated by X-ray crystallography.
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1. Introduction

It is well known that the interest in coordination chemistry of technetium derives from its applications in radiodiagnosis due to optimal nuclear properties of ^{99m}Tc radionuclide (γ-emitter, E_{max} = 140 keV, $t_{1/2}$ = 6 h) [1,2]. Moreover, its availability from ^{99}Mo/^{99m}Tc generator system [3] makes the technetium compounds ideal for imaging in nuclear medicine practice. Both isotopes of rhenium (^{186}Re, E_{max} = 1.1 MeV, $t_{1/2}$ = 90.64 h; ^{188}Re, E_{max} = 2.1 MeV, $t_{1/2}$ = 17 h) are β-emitters and are suitable candidates for therapeutic applications by means of β-irradiation in radiotherapy. In particular, availability of a ^{188}W/^{188}Re generator [4] makes

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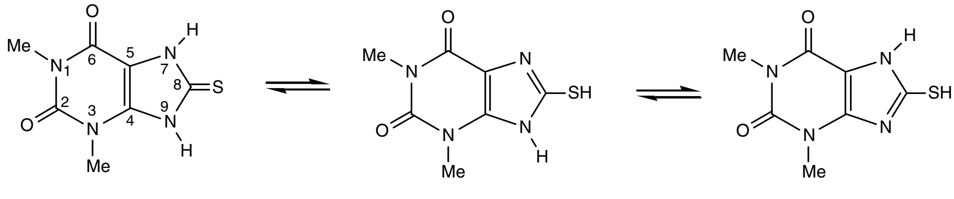
rhenium-188 the more promising choice for the development of radiopharmaceuticals for use in cancer therapy [5]. Technetium and rhenium possess a very rich chemistry because they display oxidation states ranging from −1 to + 7 and coordinate to a great variety of ligands showing various coordination geometries. This versatility is stressed in particular cores which have been studied for developing new potential radiopharmaceuticals. These are metal(V)-oxo $[M{=}O]^{3+}$ [1–3,6–13] and -nitrido $[M{=}N]^{2+}$[14–16], metal(III)-hydrazino $[MNNR]^{n+}$ [17,18] and more recently, metal(I)-carbonyl *fac*-$[M(CO)_3]^+$ [19–23] cores. Since the chemical species eluted from radionuclide generator is the $[MO_4]^-$ anion, the studies have been focused on oxo-metal(V) complexes containing the $[M{=}O]^{3+}$ fragment which is readily obtained by facile reduction of permetalate. In this oxidation state, the corresponding compounds are five- or six-coordinate species showing square pyramidal, trigonal bipyramidal and octahedral geometries. The majority of oxo-metal(V) complexes are represented by compounds which contain tetradentate ligands such as diaminedithiols or diamidedithiols (N_2S_2) [24–33], polydentate Schiff bases [34–36] which stabilize the $[M{=}O]^{3+}$ core. The so-called “3 + 1” system (a tridentate dithiol HSXSH, X=S, O, NR; and monodentate thiol ligands R-SH) was developed in order to prepare complexes of general formula [MO(SXS)(RS)] [37,38]. These compounds were found relatively unstable in vitro and in vivo. Recently, the “3 + 2” approach [39], which consists of a tridentate and bidentate ligand set, gives rise to more stable oxometal complexes because they are characterized by 18 electron structures compared to 16 electron structures of “3 + 1” oxo-compounds.



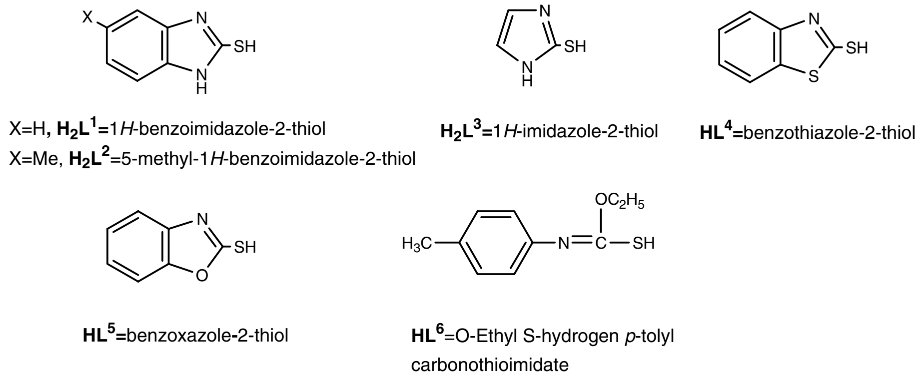
Purine bases are the principal constituents of nucleic acid derivatives. Natural purines such as caffeine and theophilline possess pharmacological activity (stimulant, cardiotonic, diuretic); some thiopurines (6-thioguanine, mercaptopurine) or more functionalized purines are employed and investigated for the treatment of leukemia and used for their antiviral activity [40,41]. Purine derivatives exhibit a variety of donor groups and consequently represent an interesting class of ligands towards a wide range of metal ions. Interaction among metal ions and purine bases is an important and continuous field of study in bioinorganic chemistry and many metal complexes containing this class of ligands have been reported [42–48]. Recently, Romerosa et al. [49–51] have reported a series of palladium and platinum complexes of several 8-thio-purine derivatives (8-TTH_2) in order to study their coordination chemistry. These thiopurines possess both N7H and SH groups, which may be deprotonated leading to potential bianionic bidentate ligands.

In view of all this and as a continuation of our studies on coordination chemistry of technetium and rhenium, it was useful to select simplified and commercially available model molecules which may mimic the reactivity of 8-TTH_2 towards these metal ions. Recently, we have investigated the reactivity of imidazole-2-thiol derivatives with Tc(III) and Re(III) precursors to produce new trigonal bipyramidal complexes in which ligands are bound through the neutral sulfur atom. Moreover, benzothiazole-2-thiol and benzoxazole-2-thiol ligands in which a nitrogen atom is replaced by an oxygen and sulfur showed a different reactivity giving octahedral chelate complexes [52]. Our aim was to study the chemical properties of these ligands (Scheme 1) towards the $[M{=}O]^{3+}$ core (M = Re, Tc). In this paper, we describe the synthesis and characterization of oxo-complexes of both metals. In addition, the X-ray crystal structures of some representative compounds are also discussed.

2. Experimental

2.1. Materials and instrumentations

Caution! ^{99}Tc is a weak β-emitter ($E_\beta = 0.292$ MeV, $t_{1/2} = 2.12 \times 10^5$ years). All manipulations were carried out in a laboratory approved for low-level radioactivity. Unless otherwise noted, all chemicals were of reagent grade and used without further purification. The starting compounds, $[AsPh_4][MOCl_4]$ (M = Re, Tc) [53–56] and $[ReOCl_3(PPh_3)_2]$ [57,58], were prepared according to the literature procedures. Ligands 1*H*-benzoimidazole-2-thiol (H_2L^1), 5-methyl-1*H*-benzoimidazole-2-thiol (H_2L^2), 1*H*-imidazole-2-thiol (H_2L^3), benzothiazole-2-thiol (HL^4), benzoxazole-2-thiol (HL^5) and 4-methyl-



Scheme 1.

phenylisothiocianate were purchased from Aldrich. Elemental analyses were performed using a Carlo Erba Instruments model EA 1110; FT-IR spectra were recorded in a range 4000–200 cm^{-1} on a Nicolet 510 P FT-IR instrument in KBr using a Spectra-Tech collector diffuse reflectance accessory. Proton spectra of $CDCl_3$, CD_2Cl_2, CD_3OD, and $(CD_3)_2CO$ solutions of the compounds were examined on a Bruker AM 200 spectrometer with $SiMe_4$ as internal standard, $^{31}P\{^1H\}$ NMR on the same instrument with a 85% H_3PO_4 solution as external standard. Conductivities were obtained at sample concentrations of ca. 1×10^{-4} M in CH_2Cl_2 solutions at room temperature with an Amel Model 134 conductivity meter.

2.2. Synthesis of [AsPh$_4$]{[MOCl$_2$(H$_2$L^n)$_2$(H$_2$O)]Cl$_2$} (n = 1–3) (M = Tc, 1–3; M = Re, 4–6)

The complexes **1–6** were prepared using the same synthetic procedure described, in detail, for **1**. The solid ligand H_2L^1 (34.2 mg; 0.228 mmol) was added to a stirred solution of [AsPh$_4$][TcOCl$_4$] (73 mg; 0.114 mmol) in acetone (30 ml) and the mixture was refluxed for 1 h. The resulting green solution was concentrated in vacuo, the crude solid was washed with acetone and dried with Et_2O. Conductivity measurements at sample concentrations of ca. 1×10^{-4} M in MeOH solutions gave values in the range 105–114 S cm^2 mol^{-1}. Yields were based on starting complexes. Recrystallization of **1** from hot Me_2CO and MeOH (3:1 v/v) gave suitable crystals for X-ray diffraction analysis.

[AsPh$_4$]{[TcOCl$_2$(H$_2$L^1)$_2$(H$_2$O)]Cl$_2$} (**1**). Yield 60%; Calc. for $C_{38}H_{34}N_4AsCl_4O_2S_2Tc$: C, 47.6; H, 3.6; N, 5.85; S, 6.7; Found: C, 47.5; H, 3.5; N, 5.8; S, 6.75%. FTIR (KBr, cm^{-1}): 3000–2500 ν(N–H ··· Cl); 1505–1356 ν(N–C–N); 1081 and 996 (AsPh$_4^+$); 997 ν(Tc=O); ^{1}H NMR [$(CD_3)_2CO$, ppm]: 7.25–7.35 (8H, m, Ph); 8.0–8.3 (20H, m, Ph).

[AsPh$_4$]{[TcOCl$_2$(H$_2$L^2)$_2$(H$_2$O)Cl$_2$]} (**2**). Yield 58%; Calc. for $C_{40}H_{38}N_4AsCl_4O_2S_2Tc$: C, 48.7; H, 3.9; N, 5.7; S, 6.5; Found: C, 48.65; H, 4.0; N, 5.7; S, 6.45%. FTIR (KBr, cm^{-1}): 3000–2500 ν(N–H ··· Cl); 1518–1441 ν(N–C–N); 1081 and 997 (AsPh$_4^+$); 997 ν(Tc=O); ^{1}H NMR [$(CD_3)_2CO$, ppm]: 2.4 (6H, s, CH$_3$); 7.0–7.4 (6H, m, Ph); 7.7–8.1 (20H m, Ph).

[AsPh$_4$]{[TcOCl$_2$(H$_2$L^3)$_2$(H$_2$O)]Cl$_2$} (**3**). Yield 55%; Calc. for $C_{30}H_{30}N_4AsCl_4O_2S_2Tc$: C, 42.0; H, 3.5; N, 6.5; S, 7.5; Found: C, 41.9; H, 3.55; N, 6.5; S, 7.4%. FTIR (KBr, cm^{-1}): 3000–2500 (N–H · Cl); 1775–1430 ν(N–C–N); 1081 and 997 ν(AsPh$_4^+$); 997 ν(Tc=O); ^{1}H NMR [$(CD_3)_2CO$, ppm]: 7.6 (4H, s, CH=CH); 8.1–8.3 (20H, m, Ph).

[AsPh$_4$]{[ReOCl $_2$(H$_2$L^1) $_2$(H$_2$O)]Cl$_2$} (**4**). Yield 70%; Calc. for $C_{38}H_{34}N_4$ $AsCl_4O_2ReS_2$: C, 43.6; H, 3.2; N, 5.35; S, 6.7%; Found: C, 43.5; H, 3.15; N, 5.3; S, 6.75%. FTIR (KBr, cm^{-1}): 3000–2500 ν(N–H · Cl); 1508–1450 ν(N–C–N); 1081 and 998 ν(AsPh$_4^+$); 998 (Re=O); ^{1}H NMR [$(CD_3)_2CO$, ppm]: 7.2–7.3 (8H, m, Ph); 7.9–8.1 (20H, m, Ph).

[AsPh$_4$]{[ReOCl$_2$(H$_2$L^2)$_2$(H$_2$O)]Cl$_2$} (**5**). Yield 60%; Calc. for $C_{40}H_{38}N_4$ $AsCl_4O_2ReS_2$: C, 44.7;H, 3.6; N, 5.2; S, 6.0; Found: C, 44.65; H, 3.5; N, 5.15; S, 5.9%. FTIR (KBr, cm^{-1}): 3000–2500 ν(N–H ··· Cl); 1518–1441 ν(N–C–N); 1081 and 998 (AsPh$_4^+$); 998 ν(Re=O); ^{1}H NMR [$(CD_3)_2CO$, ppm]: 2.4 (6H, s, CH$_3$); 7.1–7.3 (6H, m, Ph); 7.9–8.1 (20H, m, Ph).

[AsPh$_4$]{[ReOCl$_2$(H$_2$L^3)$_2$(H$_2$O)]Cl$_2$} (**6**). Yield 65%; Calc. for $C_{30}H_{30}N_4$ $AsCl_4O_2ReS_2$: C, 38.1; H, 3.2; N, 5.9; S, 6.7; Found: C, 38.0; H, 3.15; N, 5.8; S, 6.75%. FTIR (KBr, cm^{-1}): 3000–2500 ν(N–H · Cl); 1776–1430 ν(N–C–N); 1081 and 998 ν(AsPh$_4^+$); 999 ν(Re=O); ^{1}H NMR [$(CD_3)_2CO$, ppm]: 7.6 (4H, s, CH=CH); 8.1–8.3 (20H, m, Ph).

2.3. Synthesis of {[MO(H$_2$L^n)$_4$]Cl$_3$} · 3H$_2$O (n = 1–3) (M = Tc, 7–9; M = Re, 10–12)

These complexes were prepared by the same general procedure based on the reaction of [AsPh$_4$][MOCl$_4$] (*method A*), or [AsPh$_4$]{[MOCl$_2$(H$_2$L^n)$_2$(H$_2$O)]Cl$_2$} (n = 1–3) (M = Tc, **1–3**; M = Re, **4–6**) (*method B*), with an excess of H_2L^n. Details are given below for a representative case. The compound **7** has also been synthesized by reacting $[NH_4][TcO_4]$ with H_2L^1 (*method C*).

Method A. To a solution of $[AsPh_4][TcOCl_4]$ (50 mg; 0.078 mmol) in 30 ml of CH_2Cl_2, solid ligand H_2L^1 (70 mg; 0.47 mmol) was added and the resulting mixture was stirred magnetically for 15 min at room temperature. During this time **7** separated out as a red powder. The solution was filtered out and the solid was washed with CH_2Cl_2 and dried with Et_2O. For the synthesis of rhenium complexes **10–12**, the reactions were carried out in CH_2Cl_2–MeOH mixture (30 ml; 1:1 v/v). The solvent was removed under reduced pressure and the crude solid was recrystallized from MeOH–CH_2Cl_2 (1:2 v/v).

Method B. To a solution of $[AsPh_4]\{[TcOCl_2(H_2L^1)_2(H_2O)]Cl_2\}$ (60 mg; 0.062 mmol) in CH_2Cl_2–Me_2CO (1:1 v/v, 30 ml) solid ligand H_2L^1 (55.8 mg; 0.37 mmol) was added. Within 15 min at room temperature the mixture turned from yellow-green to red and a red precipitate of **7** formed. It was collected by filtration, washed with CH_2Cl_2 and dried with Et_2O. Also in this case for the synthesis of rhenium complexes the reactions were carried out in CH_2Cl_2–MeOH (30 ml; 1:1 v/v).

Method C. The $[NH_4][TcO_4]$ salt (50mg; 0.27 mmol) and solid H_2L^1 (2.2 mmol) were dissolved in acetone (30 ml). To the colorless solution, some drops of a mixture of HCl–acetone (1:1 v/v) were added under stirring until it became yellow-orange. The resulting solution was heated under reflux for 30 min. The solvent was removed on a rotary evaporator and the red-orange compound **7** was washed with CH_2Cl_2 and dried with Et_2O.

*$\{[TcO(H_2L^1)_4]Cl_3\}\cdot 3\ H_2O$ (**7**)*. Yield 88%; Calc. for $C_{28}H_{30}N_8Cl_3O_4S_4Tc$: C, 38.4; H, 3.45; N, 12.8; S, 14.6; Found: C, 38.2; H, 3.4; N, 12.75; S, 14.5%. FTIR (KBr, cm^{-1}): 3000–2500 ν(N–H $\cdots$ Cl); 1513–1468 ν(N–C–N); 974 ν(Tc=O); ^{1}H NMR (CD_3OD, ppm): 7.2–7.4 (16H, m, Ph).

*$\{[TcO(H_2L^2)_4]Cl_3\}\cdot 3H_2O$ (**8**)*. Yield 84%; Calc. for $C_{32}H_{38}N_8Cl_3O_4S_4Tc$: C, 41.2; H, 4.1; N, 12.0; S, 13.7; Found: C, 41.25; H, 4.05; N, 11.95; S, 13.6%. FTIR (KBr, cm^{-1}): 3000–2500 ν(N–H $\cdots$ Cl); 1615–1380 ν (N–C–N); 970 ν(Tc=O); ^{1}H NMR (CD_3OD, ppm): 2.6 (12H, s, CH_3); 7.2–7.6 (12H, m, Ph).

*$\{[TcO(H_2L^3)_4]Cl_3\}\cdot 3H_2O$ (**9**)*. Yield 87%; Calc. for $C_{12}H_{22}N_8Cl_3O_4S_4Tc$: C, 21.3; H, 3.3; N, 16.6; S, 18.95%; Found: C, 21.4; H, 3.25; N, 16.6; S, 18.9%. FTIR (KBr, cm^{-1}): 3000–2500 ν(N–H $\cdots$ Cl); 1585–1476 ν(N–C–N); 980 ν(Tc=O); ^{1}H NMR (CD_3OD, ppm): 7.1–7.3 (8H, m, Ph).

*$\{[ReO(H_2L^1)_4]Cl_3\}\cdot 3H_2O$ (**10**)*. Yield 80%; Calc. for $C_{28}H_{30}N_8Cl_3O_4ReS_4$: C, 34.9; H, 3.1; N, 11.6; S, 13.3; Found: C, 34.8; H, 3.0; N, 11.5; S, 13.4%. FTIR (KBr, cm^{-1}): 3000–2500 ν(N–H $\cdots$ Cl); 1499–1420 ν(N–C–N); 974 ν(Re=O); ^{1}H NMR (CD_3OD, ppm): 7.3–7.8 (16H, m, Ph).

*$\{[ReO(H_2L^2)_4]Cl_3\}\cdot 3\ H_2O$ (**11**)*. Yield 85%; Calc. for $C_{32}H_{38}N_8Cl_3O_4ReS_4$: C, 37.6; H, 3.7; N, 10.9; S, 12.5; Found: C, 37.5; H, 3.65; N, 10.8; S, 12.6%. FTIR (KBr, cm^{-1}): 3000–2500 ν(N–H $\cdots$ Cl); 1452–1430 ν(N–C–N); 970 ν(Re=O); ^{1}H NMR (CD_3OD, ppm): 3.3 (12H, s, CH_3); 7.5–7.9 (12H, m, Ph).

*$\{[ReO(H_2L^3)_4]Cl_3\}\cdot 3H_2O$ (**12**)*. Yield 89%; Calc. for $C_{12}H_{22}N_8Cl_3O_4ReS_4$: C, 18.85; H, 2.9; N, 14.7; S, 16.8; Found: C, 18.8; H, 2.85; N, 14.5; S, 16.9%. FTIR (KBr, cm^{-1}):3000–2500 ν(N–H $\cdots$ Cl); 1585–1480 ν(N–C–N); 980 ν(Re=O); ^{1}H NMR (CD_3OD, ppm): 6.9–7.4 (8H, m, Ph).

*2.4. Synthesis of $[ReOCl_2(L^5)(PPh_3)]$ (**13a**, **b**)*

To a solution of $[ReOCl_3(PPh_3)_2]$ (200 mg; 0.24 mmol) in C_6H_6 (50 ml) kept under a nitrogen stream, solid HL^5 (96.6 mg; 0.60 mmol) was added. The reaction mixture was stirred and refluxed for 3 h and it was accomplished by a color change from yellow-green to dark-green. The solvent was removed under reduced pressure and the residue rinsed several times with CH_2Cl_2 until an emerald green powder was obtained. The crude solid was recrystallized from CH_2Cl_2–MeOH (2:1 v/v, 10 ml) to give a mixture of green microcrystals of **13a, b**.

$[ReOCl_2(L^5)(PPh_3)]$ (**13a**, **b**). Yield 80%; Calc. for $C_{25}H_{19}NCl_2O_2PReS$: C, 43.0; H, 2.7; N, 2.0; S, 4.6%; Found: C, 42.8; H, 2.65; N, 1.95; S, 4.7%. FTIR (KBr, cm^{-1}): 1484–1405 ν(N–C–N); 1095 ν(PPh_3); 968, 942 (Re=O); ^{1}H NMR (CD_2Cl_2, ppm): 6.9–8.2 (19H, m, Ph); ^{31}P NMR (CD_2Cl_2, ppm): −3.0 (s); −11.0 (s).

*2.5. Synthesis of $[ReCl_3(L^{5*})(PPh_3)_2]$ (**14**)*

$[ReOCl_3(PPh_3)_2]$ (200 mg; 0.24 mmol) was dissolved in C_6H_6 (30 ml) and solid HL^5 (90 mg; 0.60 mmol) was added. The reaction mixture was stirred for 1 h in air. During this time the yellow-green solution rapidly changed to dark green and finally to dark red. The solution was evaporated under vacuum and the residue rinsed several times with CH_2Cl_2–EtOH until a red powder was obtained. The solid was washed repeatedly with Me_2CO until a lemon yellow powder was separated and dried with Et_2O. Recrystallization of the crude product **14** from CH_2Cl_2-1-butanol (1:1 v/v) gave suitable crystals for X-ray diffraction analysis. Yield was determined on starting compound.

*$[ReCl_3(L^{5*})(PPh_3)_2]$ (**14**)*. Yield 60%; Calc. for $C_{43}H_{34}NCl_3OP_2Re$: C, 55.2; H, 3.65; N, 1.5; Found: C, 55.3; H, 3.7; N, 1.5%. FTIR (KBr, cm^{-1}): 1582–1405 ν(N–C–N); 1095 ν(PPh_3); ^{1}H NMR (CD_2Cl_2, ppm): 8.9 (18H, m, PPh_3); 10.2 (1H, t, $J = 12.2$, CH); 10.75 (1H, d, $J = 12.2$, CH); 11.1 (1H, d, $J = 12.2$, CH); 11.8 (1H, t, $J = 12.2$, CH); 15.8 (12H, m, PPh_3).

2.6. Synthesis of O-ethyl S-hydrogen p-tolyl carbonothioimidate, HL^6

A solution of 4-methyl-phenylisothiocianate (5 g; 33 mmol) in EtOH (95%) was refluxed under stirring for one week. The HL^6 ligand separated out as a white powder. The solution was filtered out and the solid was dried with *n*-hexane.

Yield 80%; Calc. for $C_{10}H_{13}NOS$: C, 61.5; H, 6.7; N, 7.2; S, 16.4; Found: C, 61.35; H, 6.6; N, 7.1; S, 16.55%. FTIR (KBr, cm^{-1}): 1595 ν(CN); ^{1}H NMR ($CDCl_3$, ppm): 1.4 (3H, t, $J = 6.9$, CH_3); 2.3 (3H, s, CH_3) 4.6 (2H, q, $J = 6.9$, CH_2); 7.2 (2H, d, $J = 7.6$, Ph); 7.3(2H, d, $J = 7.6$, Ph); 8.6 (1H, s, SH).

*2.7. Synthesis of [ReOCl$_2$(L^6)(PPh$_3$)] (**15**)*

Method A. A solution of [ReOCl$_3$(PPh$_3$)$_2$] (200 mg; 0.24 mmol) and HL^6 (93 mg; 0.48 mmol) was refluxed for 3 h in 50 ml of C_6H_6. The solution turned from yellow-green to bright green. The reaction mixture was concentrated under reduced pressure and the emerald green residue of **15** was washed with C_6H_6 and dried with Et_2O.

Method B. To a solution of [ReOCl$_3$(PPh$_3$)$_2$] (200 mg; 0.24 mmol) in C_6H_6 (50 ml), solid 4-methyl-phenylisothiocianate (0.48 mmol) and EtOH (10 ml) were added. The reaction mixture was heated under reflux and stirred for 3 h. During this time the yellow-green solution changed to bright green. The solution was evaporated under vacuum, the green microcrystals washed with C_6H_6 and dried with Et_2O. Recrystallization of the product **15** from CH_2Cl_2-Me_2CO (1:1 v/v) gave suitable crystals for X-ray diffraction analysis. Yield was determined on starting materials.

*[ReOCl$_2$(L^6)(PPh$_3$)] (**15**)*. Yield 80%; Calc. for $C_{28}H_{27}NCl_2O_2PReS$: C, 46.0; H, 3.7; N, 1.9; S, 4.3%; Found: C, 45.8; H, 3.65; N, 1.85; S, 4.35%. FTIR (KBr, cm^{-1}): 1514–1434 ν(N–C–N); 1095 ν(PPh$_3$); 985 ν(Re=O); ^{1}H NMR (CD_2Cl_2, ppm): 1.4 (3H, t, $J = 6.9$, CH_3); 2.3 (3H, s, CH_3); 4.6 (2H, q, $J = 6.9$, CH_2); 7.2 (2H, d, $J = 7.6$, Ph); 7.3 (2H, d, $J = 7.6$, Ph); 7.4–7.5 (9H, m, PPh$_3$); 7.7–7.9 (6H, m, PPh$_3$); ^{31}P NMR (CD_2Cl_2, ppm): −16.0 (s).

2.8. Crystal structure determinations

The crystal data for the three compounds **1**, **14** and **15** were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation. The data sets were integrated with the Denzo-SMN package [59] and corrected for Lorentz, polarization and absorption effects (SORTAV) [60]. The structures were solved by direct methods (SIR97) [61] and refined using full-matrix least-squares with all non-hydrogen atoms anisotropic and hydrogens included on calculated positions, riding on their carrier atoms. The crystal of compound **1** includes a tetraphenylarsonium ion and a benzene molecule which are disordered around mirror planes. The crystal of compound **14** contains a disordered solvent molecule of MeOH, per octahedral complex, which was refined over two independent positions with occupancy 0.5, and a disordered molecule of benzene.

All calculations were performed using SHELXL-97 [62] and PARST [63] implemented in WINGX [64] system of programs. The crystal data and refinement parameters are summarized in Table 1.

3. Results and discussion

3.1. Synthesis of O-ethyl S-hydrogen p-tolyl carbonothioimidate, HL^6

The ligand was synthesized by reaction of 4-methylphenylisothiocianate in EtOH under reflux for one week. It was characterized by elemental analysis and FTIR and ^{1}H NMR spectra. The ligand is stable in the solid state for several months.

3.2. Synthesis and characterization of complexes

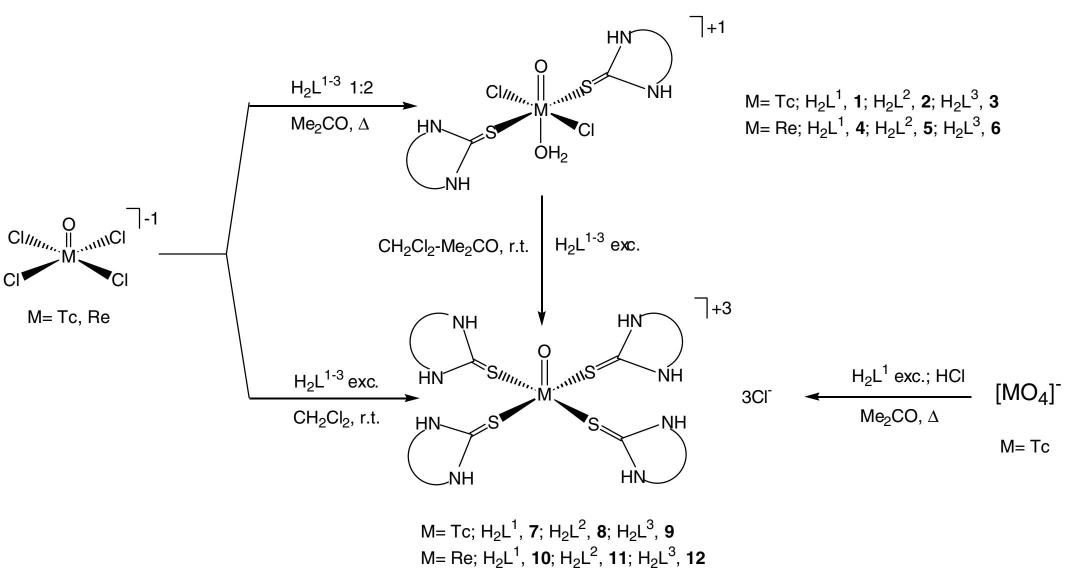
*3.2.1. Oxotechnetium(V) and oxorhenium(V) complexes [AsPh$_4$]{[MOCl$_2$(H$_2$L^n)$_2$(H$_2$O)]Cl$_2$} (n = 1–3) (M = Tc, **1–3**; M = Re, **4–6**)*

The tetrachloro-oxometalate(V) anions [MOCl$_4$]$^-$ (M = Tc, Re) are good starting materials for the preparation of metal(V) complexes. They reacted rapidly and under mild conditions with H$_2$L^n ligands (*n* = 1–3) in a 1:2 molar ratio to form stable, light green complexes [AsPh$_4$]{[MOCl$_2$(H$_2$L^n)$_2$(H$_2$O)]Cl$_2$}(M = Tc, **1–3**; M = Re, **4–6**) Scheme 2. Appreciable differences in the reactivity of the two oxometal precursors were not observed. These oxo-metal(V) compounds were fully characterized by elemental analysis, NMR and FTIR spectroscopy which are in agreement with the proposed formulations. They are air stable in both the solid state and solution. The ^{1}H NMR spectra recorded in $(CD_3)_2CO$ at room temperature present, for the protons of tetraphenylarsonium cation and for those of ligands, patterns consistent with oxo-metal(V) diamagnetic species (details are reported in Section 2). The presence of the M=O fragment is confirmed by a strong adsorption band in IR spectra at ca. 1000 cm^{-1}, although it may be superimposed with that of [AsPh$_4$] moiety. This value is at high side of the range 900–1000 cm^{-1} usually observed for oxo-group in square-pyramidal complexes with ligands which possess σ- and π-donating properties [65–69]. In our previous study concerning the Tc=O$_{oxo}$ distances in complexes containing the O_{oxo}=Tc–O_{trans} fragment, we

Table 1
Crystal data

Compound	**1**	**14**	**15**
Formula	$(C_{14}H_{14}Cl_2N_4O_2S_2Tc)^+ \cdot (C_{24}H_{20}As)^+ \cdot 2Cl^- \cdot C_6H_6$	$C_{43}H_{34}Cl_3NOP_2Re \cdot CH_3OH \cdot C_6H_6$	$C_{28}H_{27}Cl_2N_2OPReS$
Molecular weight	1035.64	1045.35	729.64
System	orthorhombic	orthorhombic	triclinic
Space group	$Cmc2_1$	$P2_12_12_1$	$P\bar{1}$
a (Å)	13.1769(2)	15.0478(1)	10.0298(2)
b (Å)	28.4984(4)	17.3614(2)	11.4029(3)
c (Å)	13.8973(2)	18.2735(2)	13.0002(4)
α (°)	90	90	77.757(1)
β (°)	90	90	79.684(1)
γ (°)	90	90	86.521(1)
U (Å^3)	5218.7(1)	4473.97(8)	1429.12(6)
Z	4	4	2
D_{calc} (g cm^{-3})	1.318	1.454	1.696
μ (cm^{-1})	12.26	28.19	45.93
θ_{min}–θ_{max} (°)	4.2–28.0	2.9–28.0	3.2–28.0
Unique reflections	6226	11486	6610
R_{int}	0.044	0.051	0.062
Observed reflections [$I > 2\sigma(I)$]	5715	10224	5768
R (observed reflections)	0.0543	0.0407	0.0438
wR (all reflections)	0.1547	0.1230	0.1115
S	1.09	1.20	1.04
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (e Å^{-3})	0.76; −0.59	0.92; −1.14	1.88; −0.93

demonstrated that when the *trans* ligand is alcoholate RO^- anion, a very strong Lewis base, the $Tc{=}O_{oxo}$ distance is long and the $Tc{-}O_{trans}$ distance is very short [70]. Coordination of a weaker donor in *trans* to $Tc{=}O_{oxo}$ causes a decreasing of the $Tc{=}O_{oxo}$ distance which assumes a triple bond character. The short bond distance is reflected in a high value of the $\nu(Tc{=}O_{oxo})$ stretching. On the basis of analytical data together with spectroscopic measurements, we may consider these species as octahedral complexes $[AsPh_4]\{[MOCl_2(H_2L^n)_2(H_2O)]Cl_2\}$, where a water molecule is in *trans* position to the M=O group. These observations suggest that the ligand coordinates to the metal through the neutral sulfur atom and behaves as a monodentate donor according to the presence of $\nu(N{-}H \cdots Cl)$ bands in IR spectra. In the case of $[AsPh_4]\{[TcOCl_2(H_2L^1)_2(H_2O)]Cl_2\}$ (**1**), suitable crystals for X-ray diffraction study were grown from methanol–acetone mixture. As expected, the Tc=O distance is very short (1.639 Å) and the $Tc{-}OH_2$ distance is relatively long (1.321 Å).



Scheme 2.

Table 2
Selected bond distances and angles (Å and degree) and hydrogen bond parameters for compound **1**

Tc1–Cl1	2.355(2)	C1–N1	1.328(6)
Tc1–Cl2	2.367(2)	C1–N2	1.337(6)
Tc1–S1	2.381(1)	N1–C2	1.391(6)
Tc1–O1	1.635(5)	N2–C7	1.385(6)
Tc1–O2	2.323(4)	C2–C7	1.381(7)
S1–C1	1.729(4)		
Cl1–Tc1–Cl2	162.33(6)	S1–Tc1–O1	99.60(3)
Cl1–Tc1–S1	93.39(3)	S1–Tc1–O2	80.40(3)
Cl1–Tc1–O1	98.6(2)	O1–Tc1–O2	180
Cl1–Tc1–O2	81.4(1)	Tc1–S1–C1	106.5(1)
Cl2–Tc1–S1	83.67(3)	N1–C1–N2	108.7(4)
Cl2–Tc1–O1	99.1(2)	C1–N1–C2	109.3(4)
Cl2–Tc1–O2	80.9(1)	C1–N2–C7	109.1(4)
S1–Tc1–S1′	158.43(4)		
Hydrogen bonds			
D–H	D···A	H···A	D–H···A
O2–H	O2···Cl3	H···Cl3	O2–H···Cl3
0.82	3.258(3)	2.49	157
N2–H	N2···Cl3	H···Cl3	N2–H···Cl3
0.86	3.059(4)	2.21	169
N1–H	N1···Cl3 (1/2 − *x*, 1/2 − *y*,1/2 + z)	H···Cl3	N1–H···Cl3
0.86	3.087(4)	2.27	157

A selected list of bond distances and angles is given in Table 2 and ORTEP drawing is shown in Figs. 1(a) and (b).

3.2.2. Oxotechnetium(V) and oxorhenium(V) complexes $\{[MO(H_2L^n)_4]Cl_3\}\cdot 3H_2O$ (n = 1–3) (M = Tc, **7–9**; M = Re, **10–12**)

The formation of red complexes $\{[TcO(H_2L^n)_4]Cl_3\}\cdot 3H_2O$ **7–9** from $[AsPh_4][TcOCl_4]$ and an excess of ligand H_2L^{1-3} occurs quickly, in high yield and at room temperature. The corresponding oxo-rhenium analogs **10–12** required the presence of methanol in the reaction mixture. The complexes **7–9** and **10–12** could also be obtained from reaction of **1–6** with an excess of the appropriate ligand. It was observed that the formation of the corresponding rhenium compounds occurred only if assisted by alcohol. Moreover, in order to evaluate the possibility to form oxo-technetium compounds starting from pertechnetate ion, a reaction in acetone with HCl as reducing agent was performed with H_2L^1 (Scheme 2). The red product was identified by a comparison of analytical and spectroscopic data with those of **7**. In similar reaction conditions, no product was recovered starting from perrhenate anion, because

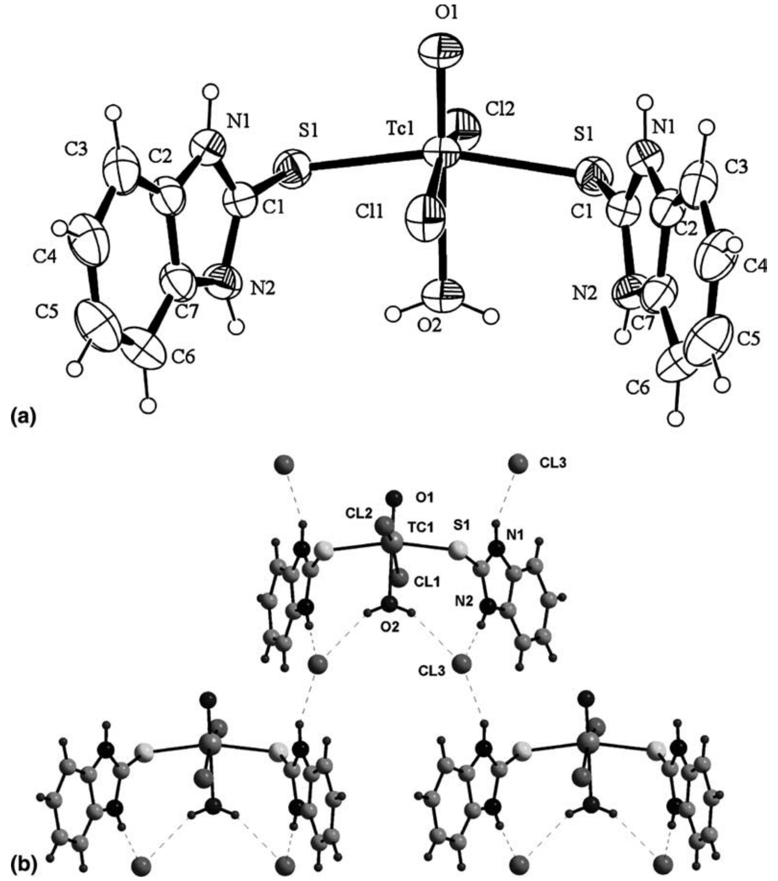


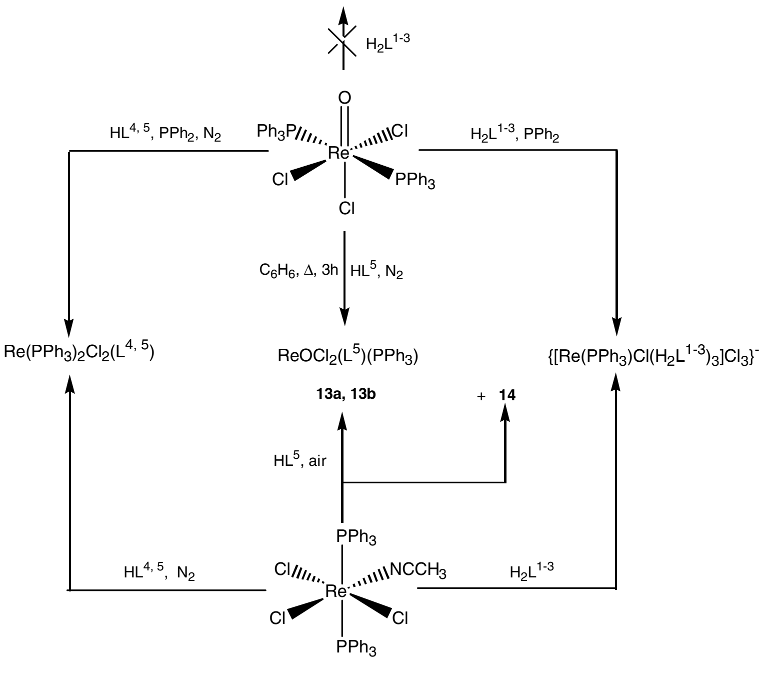
Fig. 1. (a) An ORTEP view of complex **1** showing thermal ellipsoids at 30% probability. (b) Hydrogen bond network in crystal of compound **1**.

rhenium is more difficult to reduce than is its technetium analog. A complete reaction pathway is reported in Scheme 2.

All of these new oxo-complexes are stable in the solid state but they slowly decompose in solution. Repeated attempts to obtain crystals suitable for X-ray analysis always failed. Elemental analyses (see Section 2) are in good agreement with the proposed formulations. In the IR spectra, all of the oxo-M(V) complexes exhibit an absorption typical of the [M=O] multiple bond at ca. 970–980 cm^{-1}. These M=O stretching values are comparable with those observed for other square pyramidal oxo-species of technetium and rhenium [65–69]. The ^1H NMR spectra in CD_3OD of complexes **7-12** are comparable and present a pattern characteristic of diamagnetic species in solution. In fact, they display multiplets of the aromatic protons of the ligands at δ 7.0–7.8. An additional resonance at δ 2.6 and at δ 3.3 in the spectrum of **8** and **11**, respectively, is attributed to methyl protons of H_2L^2. Finally, NMR spectra reveal the absence of aromatic protons of the $[AsPh_4]^+$ group. Although X-ray structure could not be determined, we can hypothesize from the experimental data that these compounds possess a "umbrella-shaped" square pyramidal geometry in which four neutral monodentate ligands are on the basal plane and the oxo-oxygen atom at the apical position. Oxo-technetium(V) and rhenium(V) complexes with monothiolate ligands such as $[MO(ArS)_4]^-$ have been reported [71,72]. In all these complexes, ligands are coordinated in monoanionic manner through the sulfur atom. Although technetium and rhenium complexes with aromatic thiols have been described, studies with heterocyclic thiols are rare [73,74]. Moreover, mononuclear and dinuclear oxorhenium(V) complexes such as $[ReOLCl_3(OH_2)]$, $[ReOL_2Cl(OH_2)_3]Cl_3$, $[ReOLCl(OH_2)_3]Cl_2$, $[Re_2O_3L_2Cl_4]\cdot 2H_2O$ and $[Re_2O_2L_3Cl_6]\cdot 2H_2O$ obtained from the reaction of 1*H*-benzoimidazole-2-thiol (H_2L^1) with $H_2[ReOCl_5]$ were reported by Mashaly [75,76]. These compounds were characterized on the basis of molar conductivity, IR and electronic spectroscopies and magnetic measurements.

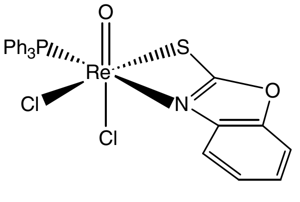
3.2.3. Reactivity of $[ReOCl_3(PPh_3)_2]$. Synthesis and characterization of $[ReOCl_2(L^5)(PPh_3)]$ (**13a, b**)

Since our aim was to study the reactivity of the ligands mentioned above towards oxo-rhenium precursors, we performed some experiments with $[ReOCl_3(PPh_3)_2]$. Reactions carried out with H_2L^{1-3} ligands did not lead to products which could be characterized because a decomposition process occurred. In the presence of an excess of triphenylphosphine, the oxo-precursor reacted to give diamagnetic, violet compounds which were identified as trigonal bipyramidal Re(III) complexes $\{[Re(PPh_3)Cl(H_2 L^{1-3})_3]Cl_3\}^-$. When the same reactions were carried out with $HL^{4,5}$ under a nitrogen atmosphere, paramagnetic chelate complexes $[Re^{III}(PPh_3)_2Cl_2(L^{4,5})]$ were formed (Scheme 3). These complexes were obtained from the Re(III) precursor $[ReCl_3(PPh_3)_2(NCMe)]$ and have been previously reported [52]. Treating $[ReOCl_3(PPh_3)_2]$ with an excess of HL^5 in refluxing benzene and under a nitrogen stream, a green oxo-derivative $[ReOCl_2(L^5)(PPh_3)]$ **13** was obtained. It is air stable in both solution and solid

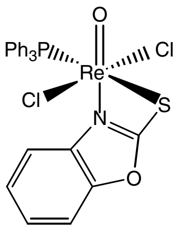


Scheme 3.

state. In this complex, the ligand classically acts as a monoanionic bidentate chelate NS^- replacing a Cl^- anion and a PPh_3 group. The proposed formulation is in accord with elemental analysis and spectroscopic measurements. The infrared spectrum showed two medium absorption bands at 968 and 942 cm^{-1} attributed to ν(Re=O) stretching vibration. These values are in the usual range observed in six coordinate oxo-Re(V) complexes but they are indicative of the presence of two species **13a**, **13b** in which a different heteroatom is in *trans* position to Re=O multiple bond. The ^1H and ^{31}P NMR spectra were consistent with diamagnetic monosubstituted compounds. Proton NMR spectrum showed multiplets of aromatic protons of PPh_3 and ligand at δ 8.2–6.9. Moreover, ^{31}P NMR spectrum displayed two singlets at δ −3.0 and −11.0 for the coordinate PPh_3 moiety (arbitrarily: **13a** major, **13b** minor; molar ratio, based on ^{31}P NMR integration, ca. 3:2). Formation of **13a** and **13b** was monitored by ^{31}P NMR spectroscopy. At first, there was a singlet of coordinated PPh_3 of [$ReOCl_3(PPh_3)_2$] at δ −18.6. After 15 min, this signal decreased and three singlets at δ −4.8 (uncoordinated PPh_3), δ −3.0 and δ −11.0 (**13a** and **13b**) began to appear. Finally, the signal of the oxo-precursor completely disappeared. Furthermore, in order to verify the presence of two different complexes, we collected ^{31}P NMR spectrum over a range of temperatures from 25 to 55 °C, but the two signals remained unchanged. From these observations, it is reasonable to assume as the most likely structures for **13** that are reported below:



13a



13b

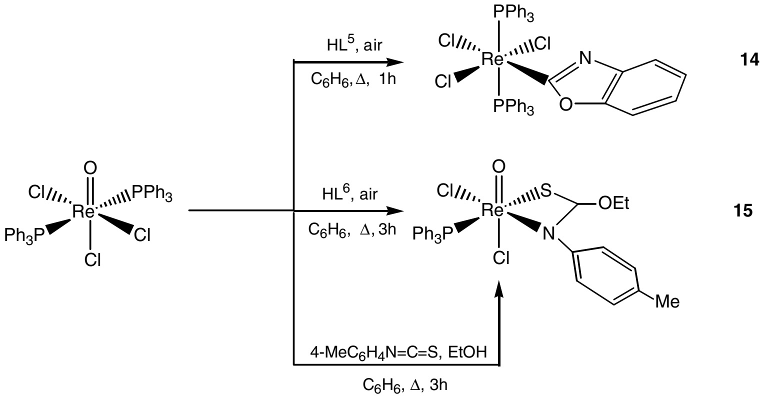
All attempts to obtain only one of the two complexes or alternatively to separate them have been useless. Alternatively and following a similar procedure, complexes **13a**, **13b** could be also obtained in good yields from [$ReCl_3(PPh_3)_2(NCMe)$] when the reaction was conducted in air. Moreover, the formation of a new yellow product **14** in very low amount (ca. 10%) was observed. Afterwards, this complex was synthesized and fully characterized (see below). Finally, we were unable to isolate and characterize analogous complexes with HL^4 ligand. All these reactions are depicted in Scheme 3.

3.2.4. Synthesis and characterization of [$ReCl_3(L^{5*})(PPh_3)_2$] (14) and [$ReOCl_2(L^6)(PPh_3)$] (15)

In order to provide a more convenient route to obtain this new yellow product **14**, some reactions were performed with HL^5. When a slight excess of ligand reacted with [$ReOCl_3(PPh_3)_2$] in refluxing benzene solution and in air, only the yellow complex could be recovered in good yield (Scheme 4).

Surprisingly, elemental analysis indicated the absence of sulfur in the complex and in IR spectrum the typical absorption band of Re=O multiple bond was absent. Furthermore, proton MNR spectrum displayed a characteristic pattern of a paramagnetic compound. In fact, it exhibited two sets of aromatic signals arising from the six phenyl groups of PPh_3 at δ 15.8 and 8.9 and a further set of two doublets and two triplets at δ 11.8 (t), 11.1 (d), 10.75 (d) and 10.2 (t) of the aromatic protons of ligand. All of these resonances were unequivocally attributed on the basis of 2D ^1H COSY experiment (Fig. 2).

On the basis of analytical data together with spectroscopic measurements, we hypothesized this compound as a neutral octahedral complex containing two PPh_3 moieties and a fragment derived from HL^5, (HL^{5*}), as a result of a desulfurization process and the central metal ion in a different oxidation state. In any case, we were unable to give an appropriate formulation. Fortunately, crystals grew from dichloromethane and 1-butanol and



Scheme 4.

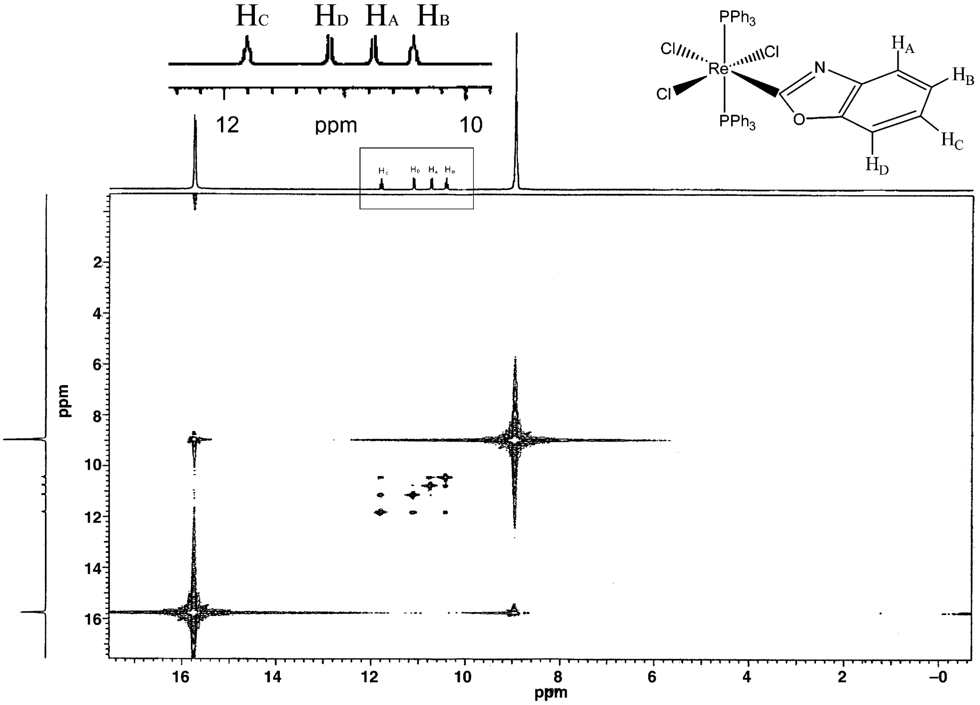


Fig. 2. Section of ^{1}H COSY spectrum of **14** (CD_2Cl_2).

the solid-state structure could be determined by X-ray diffraction methods (Fig. 3). This analysis confirmed the identity of **14** as a Re(IV)-carbene complex [$ReCl_3(L^{5*})(PPh_3)_2$].

To our knowledge, formation of carbene complexes by a desulfurization process induced by an oxo-complex of rhenium is not documented, although oxo-rhenium complexes have been studied as catalysts in desulfurization of thiiranes and in oxidation of thiols [77,78]. Formation of carbene complexes of rhenium in high oxidation states is rare and is reported by Hahn [79]. In these reactions, 2-(trimethylsiloxy)phenyl isocyanide ligand underwent a nucleophilic attack and a dicarbene complex [$ReOCl_3$(NH–C–O)$_2$] (NH–C–O = 1,2-dihydrobenzoxazol-2-ylidene) was identified and structurally characterized. It is worthy to note that with HL^4, formation of organometallic species was never observed. In the reaction reported here, a redox process took place; probably, the oxidation of S^{2-} is accomplished by reduction of rhenium from +5 to +4 oxidation state. Ligand HL^6 was synthesized in order to hypothesize a plausible mechanism of this process. It contains the same heteroatoms of HL^5 but in a linear structure. The reaction between ligand and oxo-Re(V) precursor was carried out in the same reaction conditions for the synthesis of **14**. To our disappointment, a green chelate NS^- oxo-complex [$ReOCl_2(L^6)(PPh_3)$] (**15**) was recovered. It is interesting to note that **15** could be formed from the reaction between [$ReOCl_3(PPh_3)_2$] and 4-methyl-phenylisothiocianate in the presence of EtOH. Probably, ligand is formed in situ, thus the synthesis of ligand is not required (Scheme 4).

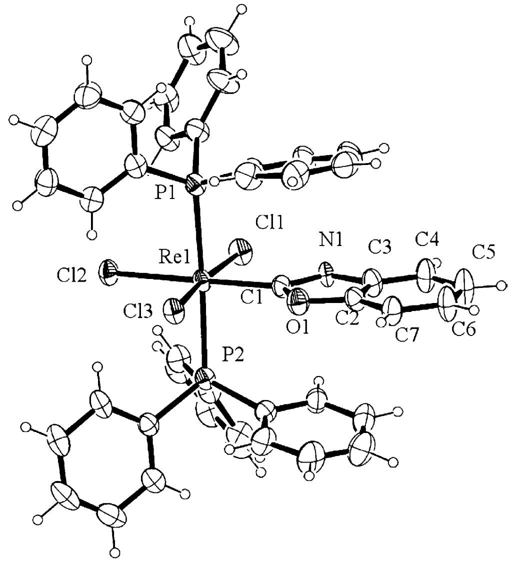


Fig. 3. An ORTEP view of complex **14** showing thermal ellipsoids at 30% probability.

Complex **15** was characterized by elemental analysis, and IR and NMR spectroscopy which were in good agreement with the proposed formulation. The complex exhibits the distinctive Re=O stretching vibration at 985 cm^{-1} and ^{31}P NMR spectrum showed a singlet at δ −16.0. Details are reported in Section 2. These results are in agreement with an octahedral, diamagnetic compound as confirmed by X-ray crystallographic analysis (Fig. 4).

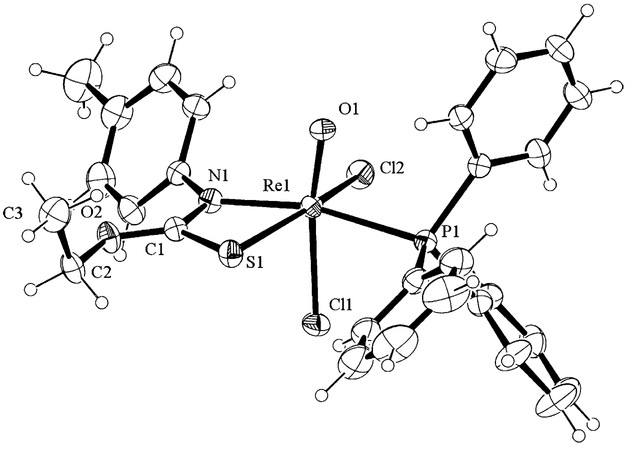


Fig. 4. An ORTEP view of complex **15** showing thermal ellipsoids at 30% probability.

In conclusion, we are unable to give an explanation of this desulfurization process, but it only occurs when the reaction between the oxo-Re(V) precursor and HL^5 is carried out in air.

3.3. Crystal structures

ORTEP [80] views of complexes **1**, **14** and **15** are shown in Figs. 1, 3 and 4. Selected interatomic distances and angles are given in Tables 2–4.

Compound **1** is a Tc(V)-oxo cationic complex where the coordination environment around Tc can be described as a distorted octahedron. The Tc1, O1, O2, Cl1 and Cl2 atoms are situated on a mirror *m* crystallographic plane. If the axial positions are defined to be those of the Tc-*oxo* and the *trans* water molecule, the equatorial positions are occupied by two Cl atoms and two sulfur atoms belonging to two 1*H*-benzoimidazole-2-thiol ligands. As observed in all Tc(V)-*oxo* complexes, the oxo group induces an octahedral distortion where Tc1 is displayed by 0.3626(4) Å, toward the oxygen atoms, from the mean plane passing through the Cl1, Cl2 and S1 atoms. The multiple Tc1=O1 bond length of 1.635(5) Å is slightly shorter than Re=O multiple bond in **15** (see below) and is in accordance with many other structural determinations. The Tc–O2(water) lengthening of 2.323(4) Å can be ascribed to the strong *trans* influence exerted by the oxo group [70]. The neutral 1H-benzoimidazole-2-thiol ligands, in mutual *trans* position, are in *cisoid* orientation and are linked to the Tc(V) atom in a tautomeric zwitterionic form with the negative charge on the sulfur atom and the positive charge delocalized on the H–N1–C1–N2–H moiety. The cationic complexes and Cl3 anions form a network of hydrogen bonds (Fig. 1(b)), where each chloride anion accepts three hydrogen bonds donated by both N–H groups of imidazole ring and by water molecule.

Table 3
Selected bond distances and angles (Å and degree) for compound **14**

Re1–Cl1	2.328(2)	C1–N1	1.344(8)
Re1–Cl2	2.469(2)	C1–O1	1.358(8)
Re1–Cl3	2.364(2)	N1–C3	1.381(8)
Re1–P1	2.484(2)	C2–O1	1.392(8)
Re1–P2	2.484(2)	C2–C3	1.372(9)
Re1–C1	2.080(6)		
Cl1–Re1–Cl2	91.13(6)	Cl3–Re1–P1	89.01(6)
Cl1–Re1–Cl3	173.24(6)	Cl3–Re1–P2	87.79(6)
Cl1–Re1–P1	91.50(6)	Cl3–Re1–C1	86.0(2)
Cl1–Re1–P2	91.83(6)	P1–Re1–P2	176.54(5)
Cl1–Re1–C1	87.2(2)	P1–Re1–C1	90.9(2)
Cl2–Re1–Cl3	95.62(6)	P2–Re1–C1	90.2(2)
Cl2–Re1–P1	89.15(6)	Re1–C1–N1	123.4(5)
Cl2–Re1–P2	89.83(6)	Re1–C1–O1	128.1(4)
Cl2–Re1–C1	178.4(2)	N1–C1–O1	108.5(5)

Table 4
Selected bond distances and angles (Å and degree) for compound **15**

Re1–Cl1	2.439(2)	Re1–N1	2.079(5)
Re1–Cl2	2.384(2)	C1–S1	1.743(6)
Re1–S1	2.406(2)	C1–O2	1.299(8)
Re1–P1	2.493(1)	C1–N1	1.318(9)
Re1–O1	1.676(4)	N1–C4	1.430(7)
Cl1–Re1–Cl2	85.17(6)	S1–Re1–P1	102.49(5)
Cl1–Re1–S1	84.38(6)	S1–Re1–O1	97.3(2)
Cl1–Re1–P1	81.51(6)	S1–Re1–N1	68.3(1)
Cl1–Re1–O1	169.1(2)	P1–Re1–O1	87.6(2)
Cl1–Re1–N1	87.9(1)	P1–Re1–N1	166.8(1)
Cl2–Re1–S1	159.25(6)	O1–Re1–N1	102.7(2)
Cl2–Re1–P1	93.62(5)	Re1–S1–C1	78.8(2)
Cl2–Re1–O1	96.3(2)	Re1–N1–C1	101.9(4)
Cl2–Re1–N1	93.4(1)		

In compound **14**, the overall geometry about the Re atom of the Re(IV) complex is approximately octahedral with the equatorial plane comprising three Cl atoms and the carbon atom of the benzoxazole ligand anion and the apical positions occupied by two triphenylphosphines. The organic ligand is planar and is situated on the equatorial plane forming an angle of only 0.6(1) Å with the mean plane passing through Cl1, Cl2, Cl3 and C1 atoms. The Re–Cl2 bond distance of 2.469(2) Å is much longer than those of Re–Cl1 and Re–Cl3 of 2.328(2) and 2.364(2) Å, which are typical for Re–Cl bonds in *trans* position to each other [81], because of strong *trans* effect exerted by Re1–C1 bond which displays the distance of 2.080(6) Å in accordance with Re–C simple bond distance [82].

Compound **15** is a Re(V)-oxo complex whose structure exhibits distorted geometry about the Re center. The equatorial basal plane contains a Cl atom, a triphenylphosphine molecule, and a S-thiolate and N-imido atoms belonging to a bidentate imido thiocarbonate anion. The Re1=O1 multiple bond of 1.676(4) Å is in agreement with many other Re(V)-oxo complexes giving rise to a distortion of the octahedral geometry produced by the steric requirements of the oxo-group shown by the displacement of 0.2339(2) Å towards O1 of the Re1 from the mean plane passing through N1, P1, Cl1 and Cl2. The lengthening of Re1–Cl1 bond of 2.438(2) Å can be accounted in terms of *trans* influence exerted by the *oxo* group. The Re-S(thiolate) distance of 2.406(2) Å is in agreement with that of 2.389(4) Å observed in a Re-oxo octahedral complex, where the sulfur is in *trans* position to a Cl atom [83].

4. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 245657–245659. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or on application to CCDC, Union Road, Cambridge CB2 1EZ, UK [fax: (+44)1223 336033, mailto:e-mail: deposit@ccdc.cam.ac.uk].

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