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Rhenium(III) and technetium(III) complexes with 2-mercapto-1,3-azole ligands and X-ray crystal structures

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Abstract

Reactions of labile $[MCl_3(PPh_3)_2(NCMe)]$ (M = Tc, Re) precursors with 1*H*-benzoimidazole-2-thiol (H_2L^1) , 5-methyl-1*H*-benzoimidazole-2-thiol (H_2L^2) and 1*H*-imidazole-2-thiol (H_2L^3) , in the presence of PPh₃ and $[AsPh_4]Cl$ gave a new series of trigonal bipyramidal M(III) complexes $[AsPh_4]{[M(PPh_3)Cl(H_2L^{1-3})_3]Cl_3}$ (M = Re, 1–3; M = Tc, 4–6). The molecular structures of 1 and 3 were determined by X-ray diffraction. When the reactions were carried out with benzothiazole-2-thiol (HL^4) and benzoxazole-2-thiol (HL^5) , neutral paramagnetic monosubstituted M(III) complexes $[M(PPh_3)_2Cl_2(L^{4.5})]$ (M = Re, 8, 9; M = Tc, 10, 11) were obtained. In these compounds, the central metal ions adopt an octahedral coordination geometry as authenticated by single crystal X-ray diffraction analysis of 8 and 11. Rhenium and technetium complexes 1, 4 and rhenium chelate compounds 8, 9 have been also synthesized by reduction of $[MO_4]^-$ with PPh₃ and HCl in the presence of the appropriate ligand. All the complexes were characterized by elemental analyses, FTIR and NMR spectroscopy.

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1. Introduction

The coordination chemistry of rhenium and technetium is currently attracting much attention due to the radionuclide-based application in radiopharmaceuticals. ^{99m}Tc is the radionuclide of choice for use in diagnostic imaging due to its ideal physical properties ($t_{1/2} = 6.02$ h, γ -energy = 140 keV). Recently, ^{186/188}Re have been introduced in nuclear medicine as suitable β -emitting radionuclides for the therapy of malignant and degenerative diseases [1,2]. The ultimate goal of these investigations is to elucidate the molecular structures of

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^{99m}Tc- and ^{186/188}Re-based agents produced in very low concentrations at nanomolar scale. This may be achieved through the comparison of their chemical and physical properties with those of the corresponding compounds prepared at macroscopic scale with the long-lived isotope ⁹⁹Tc and with cold rhenium. In addition, rhenium and technetium belong to the same group of the periodic table and therefore they may show similar chemical properties and rhenium may be often used as a non-radioactive alternative to technetium. Chelates which contain nitrogen and sulfur donor atoms such as pyridine-2-thiolate ligands show an interesting coordination versatility and may give an important contribution as models for the development of diagnostic (^{99m}Tc) or therapeutic (^{186/188}Re) radiopharmaceuticals [3].

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Mercapto-1,3-azole ligands have an important role in industry and medicine [4–8] and an attractive feature is their acidity, which could influence their chemical properties towards transition metal ions determining the structure of the final complexes. These small molecules exist as two tautomeric conformations exhibiting thiol–thione isomerism involving –NH–C=S and – N=C–SH groups in a thione–thiol equilibrium.



Probably, only two atoms could act as bonding sites, the sulfur exocyclic atom and the cyclic nitrogen atom. Since the lone pairs on the oxygen or sulfur atoms in $HL^{4,5}$ are involved in the resonating structures of the molecules, we may expect that they should have no coordinating abilities.

At this regard and as part of our activity on rhenium and technetium chemistry, we decided to investigate the chemical behavior of ambidentate ligands such as 1Hbenzoimidazole-2-thiol (H₂L¹), 5-methyl-1*H*-benzoimidazole-2-thiol (H₂L²), 1*H*-imidazole-2-thiol (H₂L³), benzothiazole-2-thiol (HL⁴) and benzoxazole-2-thiol (HL⁵) (see Scheme 1) in order to compare their reactivity as a function of the different heteroatom in the fivemembered ring.

Accordingly, we have been examining the substitution reactions of Re(III) and Tc(III) precursors $[MCl_3(PPh_3)_2(NCMe)]$ as well as reduction reactions of $[MO_4]^-$ anions with this class of ligands. We report here the results of these reactions together with X-ray crystal structures of some representative complexes.



2.1. Materials and instrumentation

Caution! ⁹⁹Tc 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 $[MCl_3(PPh_3)_2(NCMe)]$ [9,10] (M = Re, Tc) 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) and benzoxazole-2-thiol (HL⁵) 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 CDCl₃ solutions of the compounds were examined on a Bruker AM 200 spectrometer with SiMe₄ as internal standard, ${}^{31}P{}^{1}H$ NMR on the same instrument with a 85% H₃PO₄ solution as external standard. Conductivities were obtained at sample concentrations of ca. 1×10^{-4} M in CH₂Cl₂ solutions at room temperature with an Amel Model 134 conductivity meter.

2.2. Synthesis of complexes $[AsPh_4] \{ [M(PPh_3)Cl (H_2L^n)_3]Cl_3 \}$ (n = 1 to 3), (M = Re, 1-3; M = Tc, 4-6) and $[Ph_3PC(Me)_2CH_2COMe] [ReCl_5(PPh_3)]$ (7)

The synthetic procedure for the preparation of complexes 1–6 was very similar. Complexes were prepared by a substitution route from $[MCl_3(PPh_3)_2(NCMe)]$ (*Method A*) and as an example, 1 and 4 by reduction reaction from $[MO_4]^-$ (*Method B*). Here, we describe the synthesis of 1 and 4 in detail.



 $H_2L^1 = 1$ *H*-benzoimidazole-2-thiol, X=H $H_2L^2 = 5$ -methyl-1*H*-benzoimidazole-2-thiol, X=Me



HL⁴= benzothiazole-2-thiol



 $H_2L^3 = 1H$ -imidazole-2-thiol



HL⁵= benzoxazole-2-thiol

Method A. A solution of H_2L^1 (0.42 mmol) in MeOH (2 ml), PPh₃ (0.56 mmol) as a solid and [AsPh₄]Cl (0.14 mmol) dissolved in 3 ml of MeOH were added to a stirred orange suspension of [MCl₃(PPh₃)₂(NCMe)] (0.14 mmol) in C_6H_6 (30 ml) kept under a nitrogen stream. Addition of triphenylphosphine as well as nitrogen atmosphere is required in order to minimise decomposition or oxidation of the labile M(III) precursors. The mixture was refluxed for 30 min. Within 20 min of reflux, the solution became transparent giving a violet color. The solvent was removed on a rotary evaporator and the residue treated with CH_2Cl_2 and C_6H_6 to separate 1 and 4 as dark violet solids. The crude solid was washed with hot benzene, acetone and finally dried with Et₂O. Conductivity measurements at sample concentrations of ca. 1×10^{-4} M in CH₂Cl₂ solutions gave values in the range 99–105 S cm² mol⁻¹. Yields were determined on starting materials.

Recrystallization of 1 and 3 from $CH_2Cl_2-C_6H_6$ (2:1 v/v) gave good quality crystals suitable for X-ray analysis.

Method B. 356.7 mg (1.36 mmol) of PPh₃, 71.2 mg (0.17 mmol) of [AsPh₄]Cl and 77.6 mg (0.51 mmol) of H_2L^1 were dissolved in 3 ml of acetone. This solution was added to a solution of KReO₄ (50 mg, 0.17 mmol) and 0.35 ml of HCl (37%) in 50 ml of acetone. Upon mixing the solutions, the color became bright green. The reaction mixture was stirred and refluxed for 2 h. Solvents were stripped in vacuo until a violet solid precipitated. The complex 1 was separated by filtration, washed three times with acetone and dried with Et₂O (yield 40%). An identical procedure was employed for the preparation of 4 (yield 35%). In a second experiment, in order to improve the yield of 1, the reaction mixture was refluxed for 10 h. During this time the color changed from green to brown. The volume of the reaction mixture was reduced in vacuo and after few minutes complex 1 precipitated in very poor yield (10%). It was separated by filtration. The mother solution was allowed to stand overnight at room temperature affording yellow-green suitable crystals for diffraction studies of [Ph₃PC(Me)₂CH₂COMe][ReCl₅(PPh₃)] (7). Yield 30%.

2.2.1. $[AsPh_4] \{ [Re(PPh_3)Cl(H_2L^1)_3]Cl_3 \}$ (1)

Yield: 80%. Anal. Calc. for $C_{63}H_{53}N_6AsCl_4PReS_3$: C, 53.0; H, 3.7; N, 5.9; S, 6.7. Found: C, 52.9; H, 3.6; N, 5.85; S, 6.6%. FTIR (KBr, cm⁻¹): 3000–2500 v(N–H···Cl), 1505–1436 v(N–C–N), 1095 v(PPh₃); ¹H NMR (CDCl₃, ppm): 14.45 (6H, s, NH), 7.86–7.08 (47H, m, Ph, C_6H_4); ³¹P NMR (CDCl₃, ppm): -0.72 (s).

2.2.2. $[AsPh_4] \{ [Re(PPh_3)Cl(H_2L^2)_3]Cl_3 \}$ (2)

Yield 70%. *Anal.* Calc. for $C_{66}H_{59}N_6AsCl_4PReS_3$: C, 53.9; H, 4.2; N 5.7; S, 6.5. Found: C, 53.8; H, 4.1; N, 5.65; S, 6.45%. FTIR (KBr, cm⁻¹): 3000–2500 ν (N–H···Cl), 1481–1434 ν (N–C–N), 1092 ν (PPh₃); ¹H

NMR (CDCl₃, ppm): 14.3 (6H, s, NH), 7.9–6.9 (51H, m, Ph, C₆H₃), 2.2 (9H, s, CH₃); ³¹P NMR (CDCl₃, ppm): -3.0 (s).

2.2.3. $[AsPh_4] \{ [Re(PPh_3)Cl(H_2L^3)_3] Cl_3 \cdot 2H_2O \} (3)$

Yield 70%. *Anal.* Calc. for $C_{51}H_{55}N_6AsCl_4O_2PReS_3$: C, 46.6; H, 4.2; N, 6.4; S, 7.3. Found: C, 46.55; H, 4.15; N, 6.5; S, 7.35%. FTIR (KBr, cm⁻¹): 3000–2500 ν (N–H···Cl); 1580–1435 ν (N–C–N), 1092 ν (PPh₃); ¹H NMR (CDCl₃, ppm): 13.9 (6H, s, NH), 7.9–6.9 (41H, m, Ph, C₂H₂), 1.7 (4H, s, H₂O); ³¹P NMR (CDCl₃, ppm): -1.2 (s).

2.2.4. $[AsPh_4] \{ [Tc(PPh_3)Cl(H_2L^1)_3 | Cl_3 \} (4) \}$

Yield 73%. *Anal.* Calc. for $C_{63}H_{53}N_6AsCl_4PS_3Tc: C$, 56.6; H, 4.0; N, 6.3; S, 7.2. Found: C, 56.8; H, 4.1; N, 6.25; S, 7.3%. FTIR (KBr, cm⁻¹): 3000–2500 v(N–H···Cl); 1500–1440 v(N–C–N), 1081 v(PPh₃); ¹H NMR (CDCl₃, ppm): 14.3 (6H, s, N–H), 8.0–7.1 (47H, m, Ph, C_6H_4).

2.2.5. $[AsPh_4] \{ [Tc(PPh_3)Cl(H_2L^2)_3]Cl_3 \}$ (5)

Yield 68%. *Anal.* Calc. for $C_{66}H_{59}N_6AsCl_4PS_3Tc: C$, 57.5; H, 4.3; N, 6.1; S, 7.0. Found: C, 57.3; H, 4.3; N, 6.15; S, 7.1%. FTIR (KBr, cm⁻¹): 3000–2500 v(N–H···Cl), 1520–1470 v(N–C–N), 1085 v(PPh₃); ¹H NMR (CDCl₃, ppm): 14.1 (6H, s, N–H), 8.2–7.3 (44H, m, Ph, C_6H_3); 2.9 (9H, s, CH₃).

2.2.6. $[AsPh_4] \{ [Tc(PPh_3)Cl(H_2L^3)_3]Cl_3 \cdot 2H_2O \}$ (6)

Yield 70%. Anal. Calc. for $C_{51}H_{55}N_6AsCl_4O_2PS_3Tc:$ C, 50.0; H, 4.5; N, 6.8; S, 7.8. Found: C, 49.8; H, 4.45; N, 6.8; S, 7.75%. FTIR (KBr, cm⁻¹): 3000–2500 ν (N–H···Cl), 1576–1472 ν (N–C–N), 1087 ν (PPh₃); ¹H NMR (CDCl₃, ppm): 13.9 (6H, s, N–H), 7.1–6.9 (45H, m, Ph, C₂H₂), 1.8 (4H, br s, H₂O).

2.2.7. $[Ph_3PC(Me)_2CH_2COMe][ReCl_5(PPh_3)]$ (7)

Yield 30%; *Anal.* Calc. for $C_{42}H_{41}Cl_5OP_2Re: C, 51.0;$ H, 4.2. Found: C, 50.95; H, 4.2%. FTIR (KBr, cm⁻¹): 1720 v(C=O), 1096 $v(PPh_3)$; ¹H NMR (CDCl₃, ppm): 19.7 (2H, s, PPh₃), 10.9 (1H, t, PPh₃), 8.77 (2H, s, PPh₃), 8.18 (1H, s, PPh₃⁺), 7.9 (2H, s, PPh₃⁺), 7.4 (2H, m, PPh₃⁺), 3.15 (3H, s, CH₃), 2.15 (3H, s, CH₃), 2.0 (3H, s, CH₃), 1.8 (2H, d, CH₂); ³¹P NMR (CDCl₃, ppm): 59.0 (br, s).

2.3. Synthesis of $[M(PPh_3)_2Cl_2(L^{4,5})]$ (M = Re, 8, 9; M = Tc, 10, 11)

All rhenium(III) and technetium(III) chelate complexes 8–11 were prepared using a common procedure and very similar to that reported for 1–6.

Method A. For the synthesis of these compounds, the more convenient stoichiometric ratio was 1:2 and addition of [AsPh₄]Cl salt was not required. Within 1 h of

reflux the solution turned from yellow-orange to red for **8–10** and magenta for **11**. The reaction mixture was concentrated in vacuo and the residue treated with CH_2Cl_2 and MeOH. Slow evaporation of solvent provided crystals of desired products. They were washed with MeOH and dried with Et_2O . Recrystallization from CH_2Cl_2 –MeOH (2:3 v/v) of **8** and **11** gave suitable crystal for X-ray diffraction analysis. Yields were determined on starting compounds.

Method B. For the synthesis of 8 and 9 starting from KReO₄, the procedure described for 1 was employed. After a few minutes of mixing the two solutions, the [Re-OCl₃(PPh₃)₂] complex precipitated. Benzene (50 ml) was added to the mixture and the solution was stirred and refluxed for 2 h. During the first hour the yellow-green color of the solution turned to orange-red. Solvents were removed and the residue was dissolved in 2 ml of dichloromethane. Addition of 3 ml of ethanol led to the formation of microcrystals of 8 in 70% yield and 9 (50%), respectively. Similar reactions carried out with pertechnetate gave a dark green powder. Repeated elemental analyses of these compounds gave unacceptable results.

2.3.1. $[Re(PPh_3)_2Cl_2(L^4)]$ (8)

Yield 70%. *Anal.* Calc. for $C_{43}H_{34}NCl_2P_2ReS_2$: C, 54.4; H, 3.6; N, 1.5; S, 6.75. Found: C, 54.3; H, 3.65; N, 1.55; S, 6.7%. FTIR (KBr, cm⁻¹): 1482–1370 v(C–N–C), 1090 v(PPh₃); ¹H NMR (CDCl₃, ppm): 13.9–13.7 (12H, m, Ph), 8.7–8.3 (18H, m, Ph), 7.1 (1H, t, J = 7.6), 5.2 (1H, d, J = 7.6), 3.8 (1H, d, J = 7.6), 2.4 (1H, t, J = 7.6).

2.3.2. $[Re(PPh_3)_2Cl_2(L^5)]$ (9)

Yield 70%. *Anal.* Calc. for $C_{43}H_{34}NCl_2OP_2ReS: C, 55.4; H, 3.7; N, 1.5; S, 3.4. Found: C, 55.5; H, 3.75; N, 1.6; S, 3.5%. FTIR (KBr, cm⁻¹): 1481–1430 v(C–N–C), 1091 v(PPh₃); ¹H NMR (CDCl₃, ppm): 13.6–13.3 (12H, m, Ph), 8.5–8.1 (18H, m, Ph), 6.8 (1H, t, <math>J = 7.8$), 3.45 (1H, d, J = 7.8), 1.3 (1H, d, J = 7.8), 0.2 (1H, t, J = 7.8).

2.3.3. $[Tc(PPh_3)_2Cl_2(L^4)]$ (10)

Yield 70%. Anal. Calc. for $C_{43}H_{34}NCl_2P_2S_2Tc: C$, 59.8; H, 4.0; N, 1.6; S, 7.4. Found: C, 59.65; H, 3.9; N, 1.65; S, 7.35%. FTIR (KBr, cm⁻¹): 1482–1434 v(C–N–C); 1091 v(PPh₃); ¹H NMR (CDCl₃, ppm): 16.8–16.5 (12H, m, Ph) 11.8 (1H, t), 10.3 (1H, d); 9.8–9.6 (6H, m, Ph), 8.1–7.6 (12H, m, Ph), 2.1 (1H, d), -11.6 (1H, t).

2.3.4. $[Tc(PPh_3)_2Cl_2(L^5)]$ (11)

Yield 73%. Anal. Calc. for $C_{43}H_{34}Cl_2NOP_2STc: C$, 61.0; H, 4.1; N, 1.7; S, 3.8. Found: C, 61.15; H, 4.0; N, 1.75; S, 3.85%. FTIR (KBr, cm⁻¹): 1481–1434 v(C– N–C); 1092 v(PPh₃); ¹H NMR (CDCl₃, ppm): 16.8– 16.6 (12H, m, Ph). 13.1 (1H, t), 9.8–9.5 (6H, m, Ph), 8.1–7.8 (12H, m, Ph), 7.5 (1H, d), 6.8 (1H, d), -4.1 (1H, t).

2.4. Crystal structure determinations

The crystal data for the five compounds 1, 3, 7, 8 and 11 were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite monochromated Mo Ka radiation. The data sets were integrated with the DENZO-SMN package [11] and corrected for Lorentz, polarization and absorption effects (SORTAV) [12]. The structures were solved by direct methods (SIR97) [13] and refined using full-matrix least-squares with all non-hydrogen atoms anisotropic and hydrogens included on calculated positions, riding on their carrier atoms. In compound 1, the tetraphenylarsonium ion is disordered around a threefold axis and a phenyl group was refined with three independent orientations. In compound 3, a molecule of ethylic alcohol was found disordered an around a twofold axis and their atoms were refined with the occupancy of 0.5. In compound 11, the ligand 1,3benzoxazole-2-thiol and the Cl2 atom are disordered around the Cl1–Tc1 \cdots C2 axis. Accordingly, S1, N1, C1, C2, O1 and Cl2 atoms were refined with two orientations with the occupancy of 0.5. Furthemore, the asymmetric unit includes also a molecule of triphenylphosphine.

All calculations were performed using SHELXL-97 [14] and PARST [15] implemented in WINGX [16] system of programs. The crystal data and refinement parameters are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and characterization of $[AsPh_4] \{ [M (PPh_3)Cl(H_2L^{1-3})_3]Cl_3 \}$ (M = Re, 1-3; M = Tc, 4-6) and $[Ph_3PC(Me)_2CH_2COMe] [ReCl_5(PPh_3)]$ (7)

Reactions of the labile precursors $[MCl_3(PPh_3)_2(NCMe)]$ (M = Re, Tc) with three equivalents of H_2L^{1-3} in refluxing C_6H_6 -MeOH mixture in the presence of an excess of PPh₃ and $[AsPh_4]Cl$ salt under a nitrogen atmosphere yielded violet products $[AsPh_4]{[M(PPh_3)Cl(H_2L^{1-3})_3]Cl_3\}}$ (M = Re, 1–3; M = Tc, 4–6) in high yields and with a reaction time of 30 min (Scheme 2a).

The violet rhenium and technetium complexes 1 and 4 could be synthesized from $[MO_4]^-$ anions (M = Re, Tc) in acetone, in the presence of triphenylphosphine as reducing agent, in an acidified solution with a reaction time of 2 h according to Scheme 2b. Yields (ca. 40%) were slightly lower than in the synthesis of 1 and 4 from the corresponding M(III) precursors. If the reaction with KReO₄ and H₂L¹ was refluxed for 10 h, yield

Table 1	
Crystal	data

Compound	1	3	7	8	11
Formula	$\begin{array}{c} (C_{39}H_{33}ClN_6PReS_3)^{2+} \cdot \\ (C_{24}H_{20}As)^+ \cdot 3Cl^- \end{array}$	$\frac{(C_{27}H_{27}CIN_6PReS_3)^{2+}}{(C_{24}H_{20}As)^+3Cl^-} \cdot \\ 2H_2O1/2(C_2H_5OH)$	$\begin{array}{c} (C_{18}H_{15}Cl_5PRe)^- \cdot \\ (C_{24}H_{26}OP)^+ \end{array}$	$C_{43}H_{34}Cl_2NP_2ReS_2$	$\begin{array}{c} C_{43}H_{34}Cl_2NOP_2STc \cdot \\ C_{18}H_{15}P \end{array}$
M	1424.18	1333.08	987.14	947.90	1106.80
System	cubic	monoclinic	monoclinic	monoclinic	tsriclinic
Space group	<i>Pa</i> -3	C2/c	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	23.3819(2)	21.6655(3)	9.9681(2)	11.8451(2)	11.2324(1)
b (Å)	23.3819(2)	18.4798(3)	19.1709(3)	14.9149(2)	14.2133(2)
<i>c</i> (Å)	23.3819(2)	30.0706(4)	22.0801(4)	21.7857(4)	17.1411(2)
α (°)	90	90	90	90	84.453(1)
β (°)	90	106.034(1)	102.443(1)	98.604(1)	77.566(1)
γ (°)	90	90	90	90	89.917(1)
$U(Å^3)$	12783.2(2)	11571.1(3)	4120.3(1)	3805.5(1)	2659.3(1)
Z	8	8	4	4	2
$D_{\rm c} ({\rm g} {\rm cm}^{-3})$	1.474	1.530	1.591	1.655	1.382
μ (cm ⁻¹)	27.48	30.33	33.83	35.61	5.43
$\theta_{\min} - \theta_{\max}$ (°)	3.1-27.5	2.8-27.5	3.1-28.0	3.2-28.0	2.9-28.0
Unique reflections	4883	11872	9777	8949	12791
R _{int}	0.043	0.057	0.045	0.058	0.045
Observed reflections	3019	8722	7214	6403	10595
$[I > 2\sigma(I)]$					
R (observed reflections)	0.0481	0.0454	0.0343	0.0455	0.0537
wR (all reflections)	0.1582	0.1155	0.0751	0.1166	0.1307
S	1.13	1.03	1.03	1.09	1.13
$\Delta \rho_{\rm max}; \Delta \rho_{\rm min} \ ({\rm e} \ {\rm \AA}^{-3})$	1.30; -0.70	0.81; -1.41	0.83; -1.60	1.37; -1.76	1.83; -0.55

of 1 was very poor (ca. 10%) and a green-yellow product 7 (yield ca. 30%) was collected (Scheme 2b).

The complexes of both metals are air stable but they decompose slowly in solution over a period of days. Finally, repeated attempts to obtain chelate complexes with H_2L^{1-3} by addition of a base or a proton sponge to reaction mixture have been unsuccessful. All IR spectra of complexes 1-6 exhibit a broad intense band in the range $3000-2500 \text{ cm}^{-1}$ due to the stretching vibrations of the N-H groups involved in hydrogen bonds. The medium intensity bands observed in the range 1600- 1400 cm^{-1} may be assigned to (N–C–N) ring. A medium absorption peak at ca. 1090 cm^{-1} is characteristic of PPh₃ moiety. Proton NMR spectra, recorded in CDCl₃ solution and at room temperature, of the metal complexes 1-6 show a pattern typical of diamagnetic compounds. A downfield shift of the N-H resonances with respect to those of the uncoordinated ligands (δ 13.9– 14.45 in 1–6, δ 11.8–12.6 in H₂L¹⁻³) is in agreement with the presence of N-H···Cl hydrogen bonds. Aromatic protons do not undergo significant chemical shifts. Finally, a singlet observed at δ 2.2 and at δ 2.9 in the spectrum of **2** and **5** is attributed to methyl protons. The ${}^{31}P$ NMR spectra of rhenium complexes 1-3 display a singlet in negative region at δ -0.72, 3.0 and -1.2 for the coordinated PPh_3 moiety of 1, 2 and 3, respectively. Phosphorus NMR spectra of the corresponding technetium complexes 4-6 show very broad profiles; such behavior was previously attributed to the coupling of ³¹P nuclei with the quadrupolar ⁹⁹Tc center [17].

The chemistry of five coordinate complexes of rhenium(III) and technetium(III) with mono- and polydentate thiolate ligands is well documented [18-22]. The first example of a structurally characterized trigonal bipyramidal (tbp) rhenium(III) complex [Re(SAr)₃(NC-Me)(PPh₃)] with monodentate arylthiolate ligands was reported by Dilworth and co-workers [18a]. This complex was obtained by reduction of the oxo-Re(V) compound $[ReO(SAr)_4]^-$ with PPh₃ or by substitution reaction of [ReCl₃(PPh₃)₂(NCMe)] with the arylthiolate anion. The same author reported an interesting tbp Tc(III) complex [Tc(PPh₃)(Smetetraz)₃(NCMe)] (Smetetraz = 2-mercapto-methyltetrazolate anion) together with oxo-[TcO(Smetetraz)₄]⁻ and nitrido-[TcN(Smetet raz_{4} ²⁻ complexes [18f]. In any case, no chelate comwere isolated. Similarly, pounds analogous technetium(III) complexes were obtained by reduction of the corresponding oxo-technetium(V) complex $[TcO(tmbt)_4]^-$ (Htmbt = 2,3,5,6-tetramethylbenzenethiol) with phosphines or alkyl isocyanides or, alternatively by $[TcCl_6]^{2-}$ [18b,c]. The thiolates are in equatorial plane and the axial positions are occupied by π -accepting ligands such as CO, MeCN, PR₃ and py. A series of tbp complexes of M(III) (M = Re, Tc) containing tripodal tetra- or tridentate thiolate ligands, XS_3 (X = N, P) and XS_2 (X = S, O) have been described and structurally characterized [19-22]. In all these complexes, the etheroatom X is always in axial site and sulfur atoms in equatorial positions of the trigonal bipyramid. From these studies, it appears that the tbp



Scheme 2.

geometry is stabilized by thiolate anions and π -accepting coligands. In particular, tripodal tetradentate ligands XS₃ enforce a tbp coordination geometry. The compounds 1–6 were recrystallized from dichloromethane and benzene and single-crystal X-ray structure analyses of 1 and 3 showed that they possess a trigonal bipyramidal structure.

ORTEP [23] views of complexes 1 and 3 are shown in Figs. 1 and 2. Selected interatomic distances and angles are given in Table 2 and hydrogen bond parameters in Table 3.

In compound 1, the overall geometry about the Re atom of the cationic complex can be described as trigonal bipyramidal with the equatorial plane comprising the three thiolate ligands and the apical positions occupied by a Cl anion and a triphenylphosphine. The complex is situated on a crystallographic threefolded axis. The neutral 1*H*-benzimidazole-2-thiol ligands H_2L^1 are linked to Re(III) atoms 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 three ligands are linked to each other by means of a cyclic N–H···Cl···H–N hydrogen bond

system and are arranged to form a sort of "calyx" around the coordinated Cl1 anion.

In both compounds, the Re–S(thiolate) distances in the range 2.23–2.26 Å are significantly shorter than Re–S ones in octahedral or bipyramidal trigonal complexes of Re(V) and Re(III) with aryl-monothiolates, where the Re–S distances are in the range 2.28–2.32 Å [3e,24–28]. The lengthening of Re–Cl1 distances of 2.473(1) and 2.465(1) Å with respect to the standard Re–Cl distance of 2.36 Å [29] can be accounted in terms of *trans* influence exerted by the triphenylphosphine group.

The cationic complex 3 displays an analogous coordination geometry to that observed in 1. In this case, the basal ligands are three 1*H*-imidazole-2-thiol molecules linked in cycle by bifurcated hydrogen bonds involving all the N–H moieties, three Cl^- anions and a water molecule. The second water molecule bridges two Cl ions, Cl2 and Cl3, belonging to two different cyclic arrangements.

Compound 7 was identified by X-ray analysis as the paramagnetic Re(IV) complex [Ph₃PC(Me)₂CH₂CO-Me][ReCl₅(PPh₃)]. Details of analytical and spectro-



Fig. 1. An ORTEP view of complex **1** showing thermal ellipsoids at 30% probability.



Fig. 2. An ORTEP view of complex $\mathbf{3}$ showing thermal ellipsoids at 30% probabilit.

scopic data are reported in Section 2. This complex is isostructural to the technetium analog reported by Bandoli and co-workers [30] in a study concerning the reactions of pertechnetate with triphenylphosphine. A picture of ionic couple of compound 7 is given in Fig.

Table 2
Selected bond distances (Å) and angles (degrees) for compounds 1 and
3

	1	3
Bond distances (Å)		
Re1-Cl1	2.473(1)	2.465(2)
Re1–P1	2.332(2)	2.326(2)
Re1-S1	2.245(2)	2.235(2)
Re1-S2		2.250(1)
Re1-S3		2.258(1)
S1-C1	1.735(8)	1.767(6)
S2-C4		1.764(7)
S3-C7		1.760(6)
N1-C1	1.333(10)	1.325(7)
N2C1	1.327(10)	1.330(8)
N3-C4		1.331(8)
N4-C4		1.329(8)
N5-C7		1.318(8)
N6-C7		1.336(8)
Bond angles (°)		
Cl1-Re1-P1	180	178.83(5)
Cl1-Re1-S1	91.96(6)	93.32(5)
Cl1-Re1-S2		92.52(5)
Cl1-Re1-S3		91.27(5)
P1-Re1-S1	88.04(6)	87.71(5)
P1-Re1-S2		87.49(5)
P1-Re1-S3		87.74(5)
S1-Re1-S1	120	
S1-Re1-S2		117.56(6)
S1-Re1-S3		118.99(6)
S2-Re1-S3		122.95(6)
Re1-S1-C1	107.2(3)	111.7(2)
Re1-S2-C4		110.3(2)
Re1-S3-C7		109.2(2)

Table 3	
Hydrogen bond parameters (Å and °) for compounds 1 and 3	

D–H···A	D–H	$H{\cdot}{\cdot}{\cdot}A$	$D{\cdots}A$	$D – H \cdot \cdot \cdot A$
1				
N1–H···Cl2 (y,z,x)	0.86 ^a	2.30	3.133(8)	162
N2-H··· $Cl2$	0.86 ^a	2.21	3.042(8)	163
3				
$N1-H \cdot \cdot \cdot C12$	0.86 ^a	2.38	3.198(5)	159
$N2-H \cdot \cdot \cdot C13$	0.86 ^a	2.30	3.102(5)	155
N3–H···Cl4	0.86 ^a	2.15	3.013(6)	177
$O1-H \cdot \cdot \cdot C14$	b		3.104(5)	
N4–H···Cl3	0.86 ^a	2.28	3.118(6)	164
N5–H···O1	0.86 ^a	1.87	2.725(7)	172
N6–H···Cl2	0.86 ^a	2.28	3.136(6)	176
$O2-H \cdot \cdot \cdot C12$	b		3.109(7)	
$O2-H \cdot \cdot \cdot C13$	b		3.176(7)	
(1/2 - x, 1/2 - y, -z)				

^a H calculated.

^b H not determined.

3 and selected bond distances and angles for the anion are shown in Table 4. The crystal is isomorphous with that containing technetium instead of rhenium. The anion displays an approximate octahedral symmetry with the values of bond distances and angles very similar to those observed in technetium complex.



Fig. 3. An ORTEP view of the ionic couple of compound 7 showing thermal ellipsoids at 30% probability.

 Table 4

 Selected bond distances (Å) and angles (°) for compound 7

Bond distances ()	å)		
Re1–Cl1	2.371(1)	Re1–Cl4	2.319(1)
Re1-Cl2	2.335(1)	Re1–Cl5	2.334(1)
Re1–Cl3	2.361(1)	Re1–P1	2.550(1)
Bond angles (°)			
Cl1-Re1-Cl2	89.06(3)	Cl2-Re1-P1	92.18(3)
Cl1-Re1-Cl3	92.65(3)	Cl3-Re1-Cl4	92.20(4)
Cl1-Re1-Cl4	90.12(4)	Cl3-Re1-Cl5	175.53(3)
Cl1-Re1-Cl5	90.36(3)	Cl3–Re1–P1	85.77(3)
Cl1-Re1-P1	177.95(3)	Cl4–Re1–Cl5	91.09(4)
Cl2-Re1-Cl3	87.83(3)	Cl4–Re1–P1	88.63(3)
Cl2-Re1-Cl4	179.19(3)	Cl5–Re1–P1	91.29(3)
Cl2-Re1-Cl5	88.92(3)		

3.2. Synthesis and characterization of $[M(PPh_3)_2-Cl_2(L^{4,5})]$ (M = Re, 8, 9; M = Tc, 10, 11)

Ligand exchange reactions carried out with $HL^{4,5}$ in similar experimental conditions of 1–6 afforded orange-red [Re(PPh₃)₂Cl₂(L^{4,5})] (8, 9), bright red [Tc(PPh₃)₂Cl₂(L⁴)] (10), and magenta [Tc(PPh₃)₂Cl₂(L⁵)] (11) derivatives, respectively (Scheme 3). Formation of these products did not depend on ligand concentration. If the reaction of [ReCl₃(PPh₃)₂(NCMe)] with HL⁵ was performed in air, a mixture of three species was obtained. The first has been authenticated as 9 based on IR and NMR spectroscopy. The others, one yellow and one green, respectively, will be discussed elsewhere. It is interesting to note that the corresponding technetium(III) precursor led in any case to the chelate com-



pound 11. Apart from that, notable differences in reactivity between the Re(III) and Tc(III) precursors were not observed. Rhenium(III) chelate complexes 8 and 9 were also isolated in satisfactory yield (8, 70%; 9, 50%) from KReO₄ in the same reaction conditions of 1 (Scheme 3).

On the contrary, we were unable to obtain the corresponding technetium compounds; dark green uncharacterized materials were formed. The chelate compounds 8-11 are indefinitely stable as solids as well as in solu-The infrared spectra of the complexes tion. $[M(PPh_3)_2Cl_2(L^{4,5})]$ (M = Re, Tc) 8–11 do differ from those discussed above due to the absence of hydrogen bonds indicative of deprotonation of HL^{4,5} ligands. Proton NMR spectra of 8-11 show sharp proton signals characteristic of paramagnetic complexes in agreement with d⁴ octahedral configurations. Their paramagnetism can be seen by chemical shifts of the phenyl protons of PPh₃ as well as by those of ligands. In addition, no signal is observed in ³¹P MNR spectra. Comparing rhenium with the corresponding technetium complexes, an analogous pattern may be observed in all spectra, although the signals of the latter compounds spread in a wider range with respect to the former and are not well resolved. In particular, the phosphinic proton resonances occur as two multiplets at δ 8.1–8.7 and δ 13.6–13.9 (ratio 3:2) for 8 and 9 and do not undergo a significant chemical shift in comparison with those of the rhenium(III) precursor (δ 8.8 and δ 13.9). In fact, Re(III) complexes having PPh₃ as ligand in an octahedral arrangement exhibit aromatic proton signals in a very similar range [31,32]. The spectra of 10 and 11 show three multiplets at δ 16.5–16.8, 9.5–9.8 and 7.6–8.1 in the ratio 2:1:2, which are attributed to aromatic protons of PPh₃ in *ortho*, *para* and *meta* positions, respectively [33]. The NMR spectrum of [TcCl₃(PPh₃)₂(NCMe)] shows the same pattern at δ 15.8, 10.0 and 7.8, respectively. The four aromatic protons of ligands HL^{4,5} in 8–11 resonate as a triplet-doublet-doublet-triplet pattern of equal intensity (see Section 2).

From analytical data and spectroscopic measurements, we may conclude that 8-11 are monosubstituted octahedral M(III) complexes. The X-ray structure analyses of 8 and 11 confirmed that the central metal atom is in an octahedral environment. ORTEP view of complex 8 is shown in Fig. 4. Selected bond distances and angles are given in Table 5. The octahedral Re(III) neutral complex displays two triphenylphosphine, in trans position, each other and the basal plane occupied by two Cl atoms and the bidentate (N,S)-benzothiazole-2-thiolate anion. The Re1-S bond distance of 2.442(2) Å is in agreement with those observed in Re (N,S) pyridinethiolato derivatives, which displays values from 2.35 to 2.53 Å [3e,34,35]. The Re1-N1 distance of 2.118(6) Å is shorter than those observed in pyridinethiolate compound, where the Re-N distances range from 2.14 to 2.26 Å. This shortening could be due to the narrow N1–Re1–S1 bite angle of $69.2(1)^\circ$.

In the complex **11** (Fig. 5), which is strictly analogous to complex **8**, the rhenium atom has been replaced by a technetium one and the (N,S) bidentate benzothiazole-2thiolate ligand by a benzoxazole-2-thiolate one. As expected, the geometry is very similar to that of compound **8**, even if the disordered S1, N1, C1, C2, O1 and Cl2 atoms around the Cl1–Tc1···C2 axis affect considerably the accuracy of the relative bond distances and angles (Table 5).

In conclusion, there is a notable difference among ligands used in this work and aryl or alkyl thiolates previously reported. In fact, in the former the –SH fragment is bound to a carbon atom of a heterocylic structure and involved in a thione–thiol equilibrium, which determines their chemical behavior together with the presence of a different heteroatom (N, S, O). Complexes with H_2L^{1-3}



Fig. 4. An ORTEP view of complex **8** showing thermal ellipsoids at 30% probability.

Table 5			
Selected bond c	listances (Å) and	angles (°) for	compounds 8 and 11

Compound 8			
Bond distances (A	å)		
Re1-Cl1	2.388(2)	Re1–N1	2.118(6)
Re1-Cl2	2.373(2)	S1-C1	1.760(9)
Re1–P1	2.464(2)	N1-C1	1.378(9)
Re1–P2	2.483(2)	N1-C7	1.377(11)
Re1–S1	2.442(2)	S2-C1	1.714(8)
Bond angles (°)			
Cl1-Re1-Cl2	102.51(6)	P1-Re1-P2	174.27(5)
Cl1-Re1-P1	91.36(6)	P1-Re1-S1	91.87(5)
Cl1-Re1-P2	90.36(6)	P1-Re1-N1	89.9(2)
Cl1-Re1-N1	165.1(2)	P2-Re1-S1	93.38(5)
Cl1-Re1-S1	96.08(6)	P2-Re1-N1	89.9(2)
Cl2-Re1-P1	87.69(5)	S1-Re1-N1	69.2(1)
Cl2-Re1-P2	86.60(5)	C1-S1-Re1	79.2(2)
Cl2-Re1-N1	92.3(2)	C1-N1-Re1	100.5(5)
Cl2-Re1-S1	161.40(6)		
Compound 11			
Bond distances (A	Å)		
Tc1-Cl1	2.368(1)	Tc1-N1	2.101(7)
			2.099(8)
Tc1–Cl2	2.384(17)	SI-CI	1.770(22)
	2.292(15)		1.713(19)
Tc1–P1	2.478(1)	NI-CI	1.330(11)
			1.309(10)
Tc1–P2	2.499(1)	N1-C2	1.387(9)
			1.398(8)
Tc1–S1	2.555(15)	Ol-Cl	1.352(9)
	2.507(18)		1.349(10)
Bond angles (\mathring{A})			
Cl1-Tc1-Cl2	103.4(4)	P1–Tc1–P2	177.14(4)
	99.1(5)		
Cl1-Tc1-P1	90.81(3)	P1-Tc1-S1	88.2(4)
			92.1(4)
Cl1-Tc1-P2	88.16(3)	P1-Tc1-N1	90.7(2)
			90.3(2)
Cl1-Tc1-N1	167.8(2)	P2-Tc1-S1	94.6(4)
	172.6(2)		85.6(4)
Cl1-Tc1-S1	98.6(5)	P2-Tc1-N1	90.8(2)
	105.0(4)		90.4(2)
Cl2-Tc1-P1	87.3(4)	S1-Tc1-N1	69.3(5)
	90.2(5)		87.1(4)
Cl2-Tc1-P2	90.4(4)	C1-S1-Tc1	73.2(6)
	92.6(5)		75.4(7)
Cl2-Tc1-N1	88.8(5)	C1-N1-Tc1	98.9(5)
	88.2(5)		99.8(5)
Cl2-Tc1-S1	157.6(5)		
	155.8(5)		

contain three neutral thiolate ligands on the basal plane and are very similar to the complex reported in the literature [18a–c,f]. The presence of sulfur or oxygen atom in the place of nitrogen in $HL^{4,5}$ induces their spontaneous deprotonation and as a consequence they form classical octahedral paramagnetic chelate species. The same behavior is also observed in the reactions with KReO₄, although they were carried out in acidified solution.



Fig. 5. An ORTEP view of complex **11** showing thermal ellipsoids at 30% probability. The Cl2, S1, C1, N1 and O1 atoms, refined with two independent orientations, are shown only in one position for the sake of clarity.

Finally, it is also worth noting that the corresponding chelate complexes of technetium(III) were not isolated from reduction of pertechnetate.

4. Conclusion

The synthesis and structural characterization of a new family of trigonal bipyramidal technetium(III) and rhenium(III) complexes incorporating three molecules of imidazole-2-thiolate ligands have been successachieved from substitution fully reactions on $[MCl_3(PPh_3)_2(NCMe)]$. These compounds have also been obtained from reduction of $[MO_4]^-$ anions (M = Re, Tc) with PPh₃. Benzothiazole-2-thiol and benzoxazole-2-thiol ligands give rise to paramagnetic octahedral chelate complexes of both metals which have been structurally characterized. These results suggest that the different chemical behavior between the two classes of ligands may be attributed to the substitution of the nitrogen atom in imidazoles by oxygen or sulfur atoms.

5. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 234206–234209 and 243731. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ conts/retrieving.html or on application to CCDC, Union Road, Cambridge CB2 1EZ, UK [fax: +441223-336033, e-mail: deposit@ccdc.cam.ac.uk]

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