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Synthesis, structural, and spectroscopic study of rhenium(III) and rhenium(V) 4,6-dimethylpyrimidine-2-thiolate/triphenylphosphine mixed complexes: Crystal and molecular structure of $|ReCl_2(pymS)(PPh_3)_2| \cdot C_3H_6O$ and $|ReOCl_2(pymS)(PPh_3)|$

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Abstract

4,6-dimethylpyrimidine-2(1H)-thione reacts with rhenium(V) precursors *trans*-$|ReOX_3(PPh_3)_2|$ (X = Cl, Br) in acetone, to afford two classes of crystalline pyrimidinethiolate/triphenylphosphine mixed complexes: *trans*-$|Re^{III}X_2(C_6H_7N_2S)(PPh_3)_2| \cdot C_3H_6O$ and $|Re^{V}OX_2(C_6H_7N_2S)(PPh_3)|$ (X = Cl, Br). The crystal structures of *trans*-$|ReCl_2(C_6H_7N_2S)(PPh_3)_2| \cdot C_3H_6O$ **(I)** and $|ReOCl_2(C_6H_7N_2S)(PPh_3)|$ **(II)** have been determined from single-crystal dif-

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fractometer data and refined to R factors of 0.0496 and 0.0365, respectively. **(I)** crystallizes in the triclinic space group $P\bar{1}$ with a = 16.875(4), b = 13.969(7), c = 9.510(2) Å; α = 81.78(2)°, β = 85.15(12)°, γ = 107.97(8)° and Z = 2. The coordination geometry around the rhenium center exhibit mutually *trans* phosphine groups and chloride ligands disposed *trans* to the nitrogen and sulfur donors of the pyrimidinethiolate ligand which form a four-membered chelate ring with the metal. **(II)** crystallizes in the monoclinic space group $P2_1/c$ with a = 12.554(3), b = 10.501(1), c = 19.200(5) Å; β = 106.54(2)° and Z = 4. The rhenium atom presents a very distorted octahedral configuration with a chlorine atom *trans* to phosphine ligand in the axial position and the N,S-chelate ligand in the equatorial plane with the sulfur donor atom *trans* the $Re{=}O_{oxo}$ group. The compounds were characterized also by means of ir and nmr spectroscopic measurements; reaction pathways are discussed on the basis of structural data.

Introduction

The heterocyclic molecules containing the tautomeric system:

$$-NH-C(X)- \rightleftarrows -N{=}C(XH)- \quad (X{=}O,\ S)$$

include a number of important biological compounds, notably sulfur- and oxygen-containing purine and pyrimidine bases. The coordination chemistry displayed by the sulfur derivatives of pyrimidines is of noticeable current interest since they can coordinate both in the ''thione'' and in the tautomeric ''thiolate'' form (Raper, 1985) binding to a single metal ion either through nitrogen (Skapski and Woode, 1979) or sulfur (Bret *et al.*, 1983; Bravo *et al.*, 1986), or through both donor atoms (Abbot *et al.*, 1978; Goodgame *et al.*, 1978; Cartwright *et al.*, 1979; Cotton and Jlsley, 1981; Latham *et al.*, 1986; Rosenfield *et al.*, 1987; Romero-Molina *et al.*, 1987) or bridging two metal centers (Goodgame *et al.*, 1984, 1986, 1988).

Being particularly interested in the coordinating ability of this type of ligand, in this report, we have examined the reactions of the 4,6-dimethylpyrimidine-2(1H)-thione (pymSH) with *trans*-$|ReOX_3(PPh_3)_2|$ (X = Cl, Br) rhenium(V) precursors and we have isolated the new pyrimidine-2-thiolate/triphenylphosphine mixed complexes: $|Re^{III}X_2(C_6H_7N_2S)(PPh_3)_2|\cdot C_3H_6O$ and $|Re^{V}OX_2(C_6H_7N_2S)(PPh_3)|$ (X = Cl, Br). The complexes have been characterized by means of ir and nmr spectroscopy and the chloro-compounds also by single-crystal X-ray structural analysis.

Experimental

Materials

Rhenium(VII) oxide (Strem Chemicals, Inc.) and triphenylphosphine (BDH Chemicals) were used as received. All other chemicals were reagent grade. *trans*-|$ReOCl_3(PPh_3)_2$| was obtained as described by Parsall (1977); *trans*-|$ReOBr_3(PPh_3)_2$| was prepared by the method of Chatt and Rowe (1962); 4,6-dimethylpyrimidine-2(1H)-thione was prepared by the method previously reported (Battistuzzi and Peyronel, 1978).

Preparation of the complexes: |$Re^{III}Cl_2(C_6H_7N_2S)(PPh_3)_2$|·$C_3H_6O$ **(I)**, |$Re^{V}OCl_2(C_6H_7N_2S)(PPh_3)$| **(II)**

trans-|$ReOCl_3(PPh_3)_2$| (0.5 mmol) was suspended in acetone (10 ml). After addition of solid $C_6H_8N_2S$ (1 mml) the suspension was refluxed with stirring for 30 min. On heating, the solution became clear and green in color and a yellow crystalline solid precipitated immediately. Upon cooling to room temperature, the solution was filtered to remove the yellow insoluble $C_6H_8N_2S \cdot HCl$. Anal. Found: C, 40.70; H, 5.10; N, 15.80; S, 18.12. Calcd. for $C_6H_9ClN_2S$: C, 40.76; H, 5.13; N, 15.85; S, 18.15%. On standing, at room temperature, the green mother liquor became dark in color and after 3 or 4 days afforded a mixture of red-orange |$ReCl_2(C_6H_7N_2S)(PPh_3)_2$|·$C_3H_6O$ **(I)** and emerald-green |$ReOCl_2(C_6H_7N_2S)(PPh_3)$| **(II)** as crystals suitable for x-ray diffraction measurements. The precipitate was separated by filtration, washed with acetone, and dried under vacuum. The red-orange crystals were easily removed manually leaving the emerald-green plates. Anal. of **(I)**, Found: C, 55.00; H, 4.32; N, 2.83; S, 3.20. Calcd. for $C_{45}H_{43}Cl_2N_2OP_2ReS$: C, 55.16; H, 4.42; N, 2.86; S, 3.27%. Anal. of **(II)**, Found: C, 42.64; H, 3.25; N, 4.10; S, 4.73. Calcd. for $C_{24}H_{22}Cl_2N_2OPReS$:C, 42.68; H, 3.30; N, 4.15; S, 4.75%.

Alternatively pure |$ReOCl_2(C_6H_7N_2S)(PPh_2)$| compound was obtained by adding solid $C_6H_8N_2S$ to a suspension of the *trans*-|$ReOCl_3(PPh_3)_2$| (molar ratio 2 : 1) in tetrahydrofuran and refluxing for 1 h, or in $CHCl_3$ under stirring for 2 h at room temperature. After removal of precipitated $C_6H_8N_2S \cdot HCl$, to the deep-green solutions was added an equal volume of ligroine (b.p. 100–130°). A slow concentration of the solutions at room temperature gave a better yield of the pure green product recrystallizable as emerald-green plates from acetone. The products have elemental analyses, ir and nmr spectra identical with those of the corresponding complex **(II)**.

|$Re^{III}Br_2(C_6H_7N_2S)(PPh_3)_2$|·$C_3H_6O$, |$Re^{V}OBr_2(C_6H_7N_2S)(PPh_3)$|

Solid $C_6H_8N_2S$ (1 mml) was added under stirring to a suspension of *trans*-|$ReOBr_3(PPh_3)_2$| (0.5 mml) in acetone (15 ml) and the resulting mixture was heated under reflux for 2 h, giving an orange solution and a mixture of yellow ($C_6H_8N_2S \cdot HBr$) and green |$ReOBr_2(C_6H_7N_2S)(PPh_3)$| microcrystals. After standing overnight, the product was collected by filtration. Pure green |$ReOBr_2(C_6H_7N_2S)(PPh_3)$| was obtained removing the very soluble $C_6H_8N_2S \cdot HBr$ (confirmed by elemental analysis), with several washings with MeOH, in which the green microcrystals of the complex are almost insoluble. Anal. Found: C, 37.70; H, 2.90; N, 3.60; S, 4.12. Calcd. for $C_{24}H_{22}Br_2N_2OPReS$: C, 37.72; H, 2.90; N, 3.66; S, 4.20%. By slow concentration, at room temperature, the clear and orange mother liquor separated a red-orange crystalline compound. The product was collected, washed with acetone, ether, and dried *in vacuo*. Anal. Found: C, 50.40; H, 4.00; N, 2.57; S, 2.95. Calcd. for $C_{45}H_{43}Br_2N_2OP_2ReS$: C, 50.56; H, 4.05; N, 2.62; S, 3.00%.

Analyses

Carbon, hydrogen, nitrogen, and sulfur were analyzed with a C. Erba elemental analyzer Model 1106.

Physical measurements

IR spectra were obtained on the solids in KBr pellets (4000–400 cm^{-1}) and in Nujol mulls on polythene (500–50 cm^{-1}) with Perkin-Elmer 521 and 180 spectrophotometers, respectively. ^1H nmr spectra of precursors, free ligand and its rhenium complexes were recorded on a Varian XL-200 spectrometer and on a JEOL Fourier Transform nmr spectrometer, Model FX 90Q, at 23°C in $CDCl_3$. Chemical shifts in δ/ppm have been quoted downfield (and upfield) from tetramethylsilane.

X-ray data collection

Crystal data and details of data collection are reported in Table 1. For **(I)** the space group was determined by the refinements, for **(II)** determination was from systematic absences; the measured density was determined by flotation. Cell dimensions were obtained in both cases from least-squares refinements of the θ angular parameters of 15 and 14 reflections for **(I)** and **(II)**. The data were corrected for Lorenz and polarization effects; absorption correction was not applied.

Structure determination and refinements

Both structures were solved by Patterson and Fourier techniques, and refined by full-matrix least-squares with isotropic and then anisotropic thermal

Table 1. Experimental data for crystallographic analyses

Compound	(I) $|ReCl_2(C_2H_7N_2S)(PPh_3)_2| \cdot C_3H_6O$	(II) $|ReOCl_2(C_6H_7N_2S)(PPh_3)|$
Formula	$C_{45}H_{43}Cl_2N_2OP_2ReS$	$C_{24}H_{22}Cl_2N_2OPReS$
M.W.	978.97	674.59
Space group	$P\bar{1}$	$P2_1/c$
a(Å)	16.875(14)	12.554(3)
b(Å)	13.969(7)	10.501(1)
c(Å)	9.510(2)	19.200(5)
α(deg)	81.78(2)	90.0
β(deg)	85.15(12)	106.54(2)
γ(deg)	107.97(8)	90.0
V(Å^3)	2091(2)	2426(1)
Z	2	4
D_c(Mg m^{-3})	1.557	1.847
D_{obs}(mg m^{-3})	1.58	1.87
Reflection for lattice parameters number	15	14
θ range (deg)	20.5–24.0	21.6–23.9
F(000)	982	1312
Temperature (K)	294	294
Crystals size (mm^3)	0.26 × 0.29 × 0.42	0.42 × 0.46 × 0.55
Diffractometer	Siemens AED	Siemens AED
μ (cm^{-1})	32.33	54.66
Number of reflections omitted in the final refinement	10	—
Scan speed (deg min.$^{-1}$)	3–6	3–6
Scan width (deg)	$1.20 + 0.35 \tan\theta$	$1.20 + 0.35 \tan\theta$
Radiation	Mo-$K\alpha$	Mo-$K\alpha$
θ range (deg)	3–23	3–24
h range	±19	−22.21
k range	−14, 16	0,12
l range	0,10	0,13
Standard reflection	−4 8 1	8 0 0
Max. intensity variation	4.5%	4.7%
Scan mode	ω-2θ	ω-2θ
Number of measured reflections	6485	4252
Conditions for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Number of reflections used in the refinement	5415	2782
$R_{int} = \Sigma(I - \langle I \rangle)/\Sigma I$	0.0177	0.0154
Min. max. height in final $\Delta\rho$(e Å^{-3})	−1.23, 1.70	−0.74, 0.85
Number of refined parameters	466	296
$R = \Sigma|\Delta F|/\Sigma|F_0|$	0.0496	0.0365
$R_w = [\Sigma w(\Delta F)^2/\Sigma w F_0^2]^{1/2}$	0.0502	0.0378
$k, g[w = k/(\sigma^2(F_0) + g F_0^2)]$	$1.0, 4.91 \times 10^{-3}$	$0.72, 3.05 \times 10^{-3}$

parameters. Hydrogens were placed at the calculated position. The *R* indices of the final structure factor calculations were 0.0496 and 0.0365 for **(I)** and **(II)**, respectively.

The scattering factors for neutral atoms were taken from the International Tables for X-ray Crystallography (1974). The calculations were carried out on the CRAY X/MP Computer of the Consorzio per la gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (CINECA, Casalecchio, Bologna), with the financial support of the University of Parma by using SHELX-76 system of programs (Sheldrick, 1976) and ORTEP for drawings (Johnson, 1965). The final fractional coordinates and thermal parameters for non-hydrogen atoms are given in Tables 2 and 3 for **(I)** and **(II)**, respectively; lists of observed and calculated structural factors and hydrogen atom parameters with complete bond distances and angles are available as supplementary material.

Description of the structures and discussion

In **(I)** the surrounding of rhenium can be depicted as very distorted octahedral; the two phosphines occupy two *trans* positions, Cl(1), Cl(2), S and N(1) atoms lie roughly in the plane normal to this direction (Fig. 1). The distortion is particularly evident from the angle on the metal in the chelate N, S ring of 67.1(3)°, the other *cis* angles range from 86.8(2)° to 100.5(2)° related to the Cl(1)—Re—P(1) and Cl(1)—Re—Cl(2) angles, respectively (Table 4).

The two Re—P bond distances 2.456(4), 2.446(4) Å are not significantly different and are well comparable with the literature values, e.g., 2.431(4)–2.475(2) Å in $|Re(OH)Cl_3(PEt_2Ph)_2|$ and in the compounds cited therein (Sacerdoti *et al.*, 1982); 2.457(4), 2.461(4) Å in $|ReCl_3(NPhCOMe)(PEt_2Ph)_2|$ and 2.470(1) Å in $|ReCl_3(NPhOMe)(PEt_2Ph)_2|$ (Bright and Ibers, 1968). The two triphenylphosphine molecules are mutually *trans*, probably for steric reasons, the interbond angle of 173.9(2)° shows only a moderate displacement from the linearity; the structural parameters involving P and phenyl rings are normal; the rings result planar within experimental errors.

The two chlorines, *cis* one to another, show bond distances which are slightly but significantly different: 2.343(4), 2.370(3) Å ($\Delta/\sigma = 5.4$); the longer one involves Cl(2) and is *trans* to the N(1) chelate atom. These distances are in the range of the values found for other Re–Cl terminal bonds: 2.359(4) Å in $Cs_3Re_3Cl_{12}$ (Robinson *et al.*, 1963); 2.357(4), 2.362(4) Å in $|Re_2OCl_3(C_2H_5COO)_2(PPh_3)_2|$ (Cotton *et al.*, 1969); 2.325(2)–2.363(2) Å in $|(t\text{-but})_4N|_2Re_2Cl_8$ (Cotton *et al.*, 1976).

The Re-S bond 2.409(4) Å fall in the expected range: 2.354(4)–2.483(4) Å in $|Re(C_7H_{14}S_4)(PPh_3)(NNCOPh)|$ (Nicholson *et al.*, 1985); $(HNEt_3)|Re_2(NNC_6H_5)_2(SPh)_7|$ 2.438(8)–2.459(8) Å for terminal bonds only

Table 2. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($\times 10^3$ Å^2 for Re, $\times 10^2$ Å^2 for the other atoms) for $|ReCl_2(C_6H_7N_2S)(PPh_3)_2| \cdot C_3H_6O_2$

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re	2390(0)	2156(0)	2825(0)	28.6(3)	23.2(3)	19.7(3)	−2.9(2)	−2.4(2)	2.5(2)
Cl(1)	1523(2)	563(2)	4103(3)	4.4(2)	2.6(1)	3.4(2)	0.2(1)	−0.2(1)	−0.1(1)
Cl(2)	2223(2)	1909(3)	439(3)	5.1(2)	6.2(2)	2.2(1)	−1.2(1)	−0.9(1)	1.7(2)
P(1)	1142(2)	2696(2)	2967(3)	3.4(1)	2.6(2)	3.2(2)	−0.5(1)	−0.6(1)	0.5(1)
P(2)	3540(2)	1427(2)	2716(3)	3.1(2)	3.0(2)	2.4(1)	−0.5(1)	−0.5(1)	0.6(1)
S	3331(2)	3886(2)	2110(3)	4.1(2)	2.5(1)	4.0(2)	0.5(1)	0.0(1)	−0.4(1)
N(1)	2807(6)	2846(7)	4587(10)	3.5(5)	2.8(5)	3.0(5)	−0.5(4)	0.3(4)	0.3(4)
N(2)	3728(7)	4506(8)	4576(13)	4.8(7)	4.0(6)	5.5(7)	−0.8(5)	−1.0(6)	0.7(5)
C(1)	768(8)	2681(9)	4823(14)	4.1(7)	3.9(7)	4.4(7)	−0.6(6)	−0.1(6)	1.5(6)
C(2)	1184(8)	3476(11)	5503(15)	4.9(8)	5.0(9)	4.8(8)	−2.4(7)	−0.8(6)	1.7(7)
C(3)	981(12)	3435(14)	6893(7)	8.1(1.2)	7.3(1.2)	6.4(9)	−2.8(8)	−1.5(8)	2.9(1.0)
C(4)	298(12)	2565(15)	7695(18)	9.2(1.2)	11.0(1.3)	5.3(9)	−1.0(9)	0.0(9)	6.3(1.1)
C(5)	−81(9)	1796(13)	7087(16)	5.0(8)	7.5(1.1)	5.1(9)	−1.3(8)	−0.7(7)	2.2(8)
C(6)	140(8)	1858(10)	5607(15)	4.1(7)	4.2(8)	5.4(8)	−0.8(6)	0.3(6)	1.5(6)
C(7)	201(7)	1936(9)	2337(13)	3.3(6)	3.7(7)	4.4(7)	0.0(6)	−0.8(5)	0.6(5)
C(8)	−501(9)	2254(11)	2381(17)	4.5(8)	4.3(8)	8.2(1.0)	0.3(7)	−2.7(8)	0.6(6)
C(9)	−1214(9)	1613(14)	1815(18)	3.6(7)	8.9(1.3)	8.8(1.0)	0.8(9)	−2.3(7)	1.1(8)
C(10)	−1255(9)	719(10)	1335(16)	5.5(9)	3.7(7)	7.8(9)	1.2(7)	−2.8(7)	0.5(6)
C(11)	−555(9)	448(11)	1309(15)	4.9(8)	5.5(8)	6.6(9)	−2.1(7)	−1.4(7)	−0.2(7)
C(12)	174(8)	1009(9)	1823(14)	4.2(7)	3.8(7)	5.3(8)	−0.4(6)	−0.6(6)	0.3(6)
C(13)	1217(8)	3945(9)	1971(15)	4.1(7)	2.6(6)	5.5(9)	0.1(6)	−1.2(6)	0.8(5)
C(14)	1660(10)	4261(11)	610(16)	7.0(1.0)	4.8(9)	6.1(9)	−0.9(7)	−3.5(8)	0.4(7)
C(15)	1690(11)	5113(10)	−277(16)	8.8(1.1)	4.0(8)	6.5(9)	0.7(7)	−3.3(8)	0.1(7)
C(16)	1252(14)	5744(13)	292(28)	11.7(1.4)	3.8(1.0)	18.1(2.0)	0.8(1.1)	−8.6(1.4)	0.3(1.0)
C(17)	843(13)	5459(12)	1615(27)	9.6(1.4)	3.9(8)	13.0(1.8)	−1.7(1.0)	−3.7(1.3)	2.6(9)
C(18)	842(10)	4589(12)	2503(20)	6.3(9)	4.3(9)	9.5(1.3)	−1.2(8)	−1.0(9)	2.3(7)
C(19)	3373(7)	238(8)	1969(12)	2.8(6)	3.2(6)	3.5(6)	−0.8(5)	−0.1(5)	0.7(5)
C(20)	4049(9)	−90(10)	1616(15)	6.0(8)	4.6(8)	5.1(8)	−0.8(6)	−1.6(7)	2.0(7)
C(21)	3929(9)	−980(10)	1126(16)	6.0(9)	4.1(7)	6.4(9)	−1.7(7)	−0.8(7)	2.2(7)
C(22)	3141(10)	−1518(10)	931(14)	8.6(1.1)	3.6(7)	4.4(8)	−1.4(6)	−0.4(7)	2.5(7)
C(23)	2460(10)	−1200(10)	1228(16)	6.5(1.0)	3.9(8)	6.8(9)	−2.7(7)	−2.4(7)	1.8(7)
C(24)	2578(8)	−317(10)	1728(13)	5.0(8)	4.7(7)	4.9(7)	−2.7(6)	−1.9(6)	1.6(6)
C(25)	3790(8)	1093(10)	4495(13)	4.2(7)	5.6(8)	2.9(6)	0.1(6)	−0.5(5)	1.4(6)
C(26)	4223(8)	1857(11)	5206(12)	4.1(7)	6.9(9)	3.0(6)	−2.1(6)	−1.4(5)	1.1(7)
C(27)	4323(9)	1619(13)	6620(15)	5.6(9)	8.5(1.2)	3.9(7)	−1.5(8)	−2.3(7)	1.4(8)
C(28)	4004(10)	645(15)	7339(16)	6.0(1.0)	11.8(1.4)	3.9(9)	−0.1(9)	−1.8(8)	3.4(1.0)
C(29)	3586(11)	−136(14)	6634(17)	6.9(1.1)	10.3(1.3)	5.5(9)	2.5(9)	−0.8(8)	3.4(1.0)
C(30)	3493(9)	77(11)	5193(15)	6.1(9)	5.3(8)	4.4(8)	1.3(6)	−1.2(7)	1.7(7)
C(31)	4538(7)	2250(9)	1676(13)	3.0(6)	3.4(6)	4.3(7)	−0.7(5)	0.3(5)	0.7(5)
C(32)	5323(7)	2331(10)	2147(13)	2.3(5)	5.6(8)	3.7(6)	−1.5(6)	0.8(5)	0.3(5)
C(33)	6050(8)	2963(10)	1224(13)	2.6(6)	4.3(7)	7.3(8)	−2.6(7)	0.0(6)	0.1(6)
C(34)	6013(8)	3493(10)	−62(14)	4.2(7)	4.4(7)	4.7(7)	1.6(6)	1.4(6)	1.0(6)
C(35)	5251(9)	3391(10)	−508(15)	6.3(9)	4.1(7)	5.6(8)	2.0(6)	2.4(7)	0.7(6)
C(36)	4499(9)	2781(11)	351(14)	4.4(8)	5.8(8)	4.4(8)	−0.4(6)	0.5(6)	1.6(7)
C(37)	3330(7)	3786(7)	3909(12)	3.8(6)	1.6(4)	4.6(6)	−0.3(4)	−1.1(5)	0.3(4)
C(38)	2180(9)	1612(10)	6800(13)	6.9(9)	4.5(8)	2.4(6)	−0.5(5)	−0.8(6)	0.4(6)
C(39)	2723(8)	2618(10)	6033(12)	3.7(7)	4.4(7)	2.8(6)	−0.9(5)	−0.6(5)	0.9(6)
C(40)	3148(9)	3367(11)	6757(14)	5.0(8)	5.9(9)	4.3(7)	−2.7(7)	−1.3(6)	1.3(7)
C(41)	3651(9)	4313(11)	5998(14)	5.2(8)	4.9(9)	5.5(8)	−3.2(7)	−1.8(6)	1.3(7)
C(42)	4169(12)	5185(13)	6780(21)	8.3(1.2)	6.1(1.1)	9.4(1.3)	−3.4(9)	−3.6(1.0)	0.3(9)
O(A)	2401(6)	6903(7)	6511(11)	15.7(3)					
C(1A)	3183(9)	6917(12)	4336(17)	14.5(4)					
C(2A)	2409(10)	6793(12)	5242(17)	11.3(4)					
C(3A)	1670(9)	6827(11)	4601(16)	15.0(4)					

Table 3. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($\times 10^3$ Å^2 for Re, $\times 10^2$ Å^2 for the other atoms) for $|ReOCl_2(C_6H_7N_2S)(PPh_3)|$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re	2763(0)	1580(0)	1359(0)	36.9(2)	32.8(2)	27.6(2)	1.8(2)	11.0(1)	−3.1(2)
Cl(1)	3763(2)	3296(3)	1058(2)	7.1(2)	6.0(2)	5.9(2)	1.4(1)	2.3(2)	−1.9(2)
Cl(2)	1290(2)	2195(3)	406(1)	5.8(1)	7.4(2)	3.4(1)	1.5(1)	0.2(1)	−0.4(1)
S	2130(2)	2990(2)	2217(1)	3.7(1)	2.9(1)	3.7(1)	0.0(1)	0.4(1)	0.5(1)
P	1556(2)	108(2)	1777(1)	3.1(1)	2.3(1)	2.4(1)	0.1(1)	0.8(1)	0.2(1)
O	3394(5)	315(6)	1127(3)	5.2(4)	4.2(4)	5.0(4)	−0.9(3)	1.9(3)	−0.0(3)
N(1)	3908(6)	1748(6)	2404(4)	3.0(4)	2.5(4)	4.0(4)	0.2(3)	1.1(3)	−0.5(3)
N(2)	3821(6)	2905(7)	3445(4)	3.9(4)	3.4(4)	2.6(4)	0.1(3)	0.2(3)	−0.2(3)
C(1)	1640(7)	−1503(8)	1458(4)	2.8(4)	3.2(4)	2.8(4)	−0.5(4)	0.7(3)	0.3(4)
C(2)	1569(7)	−1699(9)	730(5)	4.4(5)	3.9(6)	3.8(5)	−0.9(5)	1.1(4)	−0.3(4)
C(3)	1484(8)	−2922(10)	470(6)	5.1(6)	4.8(6)	4.4(6)	−2.0(5)	0.2(5)	0.4(5)
C(4)	1478(8)	−3950(10)	909(6)	4.8(6)	4.0(6)	7.3(8)	−2.5(6)	0.7(6)	0.1(5)
C(5)	1569(8)	−3731(8)	1621(6)	5.0(6)	1.7(5)	7.3(8)	0.1(5)	1.2(5)	0.3(4)
C(6)	1635(8)	−2530(9)	1899(5)	5.0(6)	3.8(5)	3.8(6)	1.0(4)	1.5(5)	0.1(4)
C(7)	1975(7)	2(8)	2757(4)	3.8(5)	2.8(5)	1.7(4)	0.1(3)	0.7(4)	0.1(4)
C(8)	3014(7)	−472(8)	3108(4)	4.0(5)	4.1(5)	2.3(4)	0.5(4)	0.7(4)	0.1(4)
C(9)	3407(8)	−429(10)	3842(5)	5.0(6)	4.3(6)	4.4(6)	1.6(5)	0.2(5)	−0.4(5)
C(10)	2794(9)	84(10)	4250(5)	7.8(7)	5.3(6)	2.2(5)	0.0(5)	0.3(5)	−1.6(6)
C(11)	1745(10)	539(10)	3913(5)	7.7(8)	5.7(6)	3.3(6)	−0.8(5)	2.1(6)	0.1(6)
C(12)	1328(8)	489(9)	3165(5)	5.6(6)	3.9(5)	3.4(5)	0.8(4)	1.8(5)	1.6(5)
C(13)	58(7)	407(8)	1499(4)	3.0(5)	4.2(5)	2.5(4)	0.4(4)	0.8(4)	0.1(4)
C(14)	−374(7)	1609(9)	1474(5)	3.9(5)	3.9(6)	4.4(5)	0.3(5)	1.1(4)	1.5(5)
C(15)	−1512(9)	1778(10)	1293(5)	5.8(7)	6.3(8)	3.7(5)	0.1(5)	1.5(5)	2.1(6)
C(16)	−2218(8)	754(13)	1122(6)	3.5(6)	8.8(9)	4.4(6)	1.3(6)	1.2(5)	0.4(6)
C(17)	−1797(8)	−452(12)	1158(6)	3.5(6)	8.4(9)	8.0(8)	0.6(7)	1.8(6)	−1.5(6)
C(18)	−643(8)	−625(9)	1336(6)	4.4(6)	3.9(6)	6.4(6)	0.3(5)	1.7(5)	−0.5(5)
C(19)	3387(7)	2524(8)	2767(5)	3.9(5)	2.2(4)	3.6(5)	−0.2(4)	1.6(4)	−0.2(4)
C(20)	5526(8)	575(12)	2310(6)	3.6(6)	7.9(9)	7.0(7)	−1.9(6)	0.2(5)	2.3(6)
C(21)	4943(8)	1363(9)	2717(5)	3.3(5)	4.4(6)	4.9(6)	0.3(4)	1.1(5)	−0.7(4)
C(22)	5419(8)	1772(9)	3433(5)	3.2(5)	5.5(6)	4.5(6)	0.5(5)	0.0(5)	0.1(5)
C(23)	4852(8)	2498(9)	3783(5)	4.3(6)	3.4(5)	4.1(6)	−0.1(4)	0.9(5)	−0.8(4)
C(24)	5319(10)	2891(12)	4553(5)	6.3(7)	7.8(8)	3.2(5)	−0.8(6)	0.3(5)	−1.4(7)

(Nicholson and Zubieta, 1985); 2.399(4) Å in $|ReCl_5tu|^-$ (Lis and Starynowicz, 1985); in $|Re_2(SC_6H_4Me\text{-}4)_7(NO)_2|^-$ 2.439(6)-2.455(6) Å only for terminal bonds (Blower *et al.*, 1985).

The rhenium-nitrogen bond distance 2.115(10) Å does correspond to a single bond in agreement with that found in $|ReCl_2(NPhMe)(PhNCHPhO)(PPh_3)|$ 2.15(1) Å, in $|ReCl_2(NPhMe)(MeNCHPhO)(PPh_3)|$ 2.13(1) Å (Rossi *et al.*, 1984), 2.191(8)-2.150(9) Å in $|ReO_2en_2|Cl$ and 2.139(9)-2.143(12) Å in $|ReO_2py_4|Cl \cdot 2H_2O$ (Lock and Turner, 1978). In the chelate ring the rhenium is out of the plane determined form the N(1), C(37) and S atoms only 0.060(6) Å; the 4,6-dimethylpyrimidine-2-thiolate ligand is planar and the rhenium lies

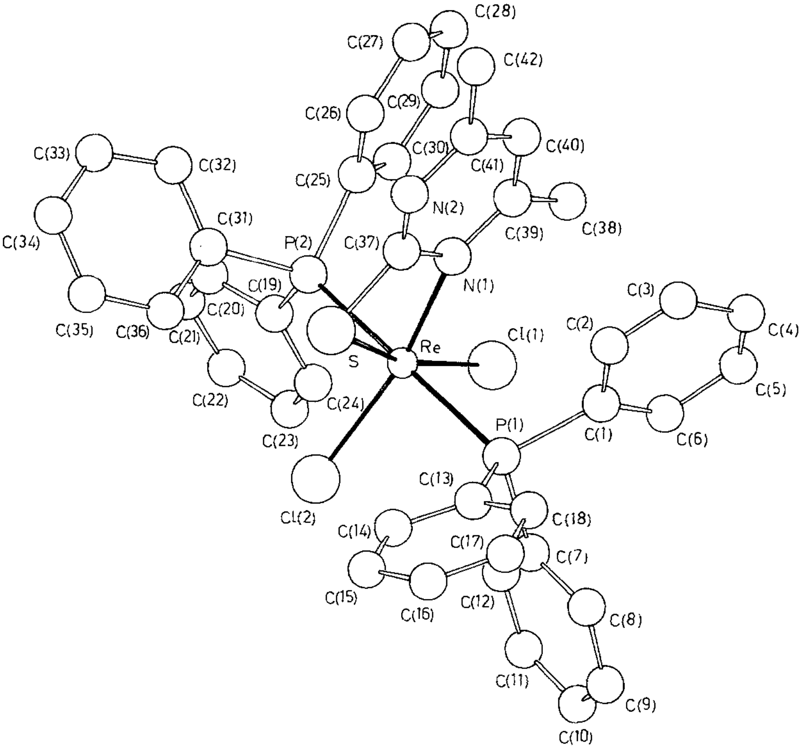


Fig. 1. Perspective view of the $|ReCl_2(C_6H_7N_2S)(PPh_3)_2|$ complex molecule.

in this plane. Bond distances and angles in this anion are in the range expected, only the S—C(37)—N(1) 109.9(8)° and S—C(37)—N(2) 126.1(9)° angles show relevant differences from 120° ideal value and this deformation can be attributed to the constrains exerted by N,S-chelation of the ligand. Packing is mainly determined by Van der Waals contacts in which the oxygen atom of acetone molecule is also involved (Table 6(a)).

In $|ReOCl_2(C_6H_7N_2S)(PPh_3)|$ **(II)** coordination around the rhenium is very distorted octahedral, the triphenylphosphine molecule is *trans* to the Cl(1) atom (Fig. 2): the P—Re—Cl(1) angle is 169.1(1)°, the plane approximately normal to this direction is occupied by the sulfur and N(1) atom of the organic chelate ligand, the oxygen, and the Cl(2) atom. The *cis* angles, excluding the S—Re—N(1) angle 65.4(2)° which is related by the N,S-chelation, fall in the range 79.4(1)-102.5(2)°, those *trans* are 155.(2)-169.1(1)° showing a relevant distortion.

The Re—P bond distance 2.455(3) Å (Table 5) is strictly similar to the

Table 4. Selected bond distances (Å) and angles (deg) in (I)

Re—Cl(1)	2.343(4)	P(1)—C(7)	1.82(7)	N(1)—C(39)	1.35(1)
Re—Cl(2)	2.370(3)	P(1)—C(13)	1.82(1)	N(2)—C(37)	1.30(2)
Re—P(1)	2.446(4)	P(2)—C(19)	1.85(1)	N(2)—C(41)	1.33(2)
Re—P(2)	2.456(4)	P(2)—C(25)	1.81(1)	C(38)—C(39)	1.46(2)
Re—S	2.409(4)	P(2)—C(31)	1.83(1)	C(39)—C(40)	1.38(2)
Re—N(1)	2.115(10)	S—C(37)	1.70(1)	C(40)—C(41)	1.39(2)
P(1)—C(1)	1.82(1)	N(1)—C(37)	1.36(1)	C(41)—C(42)	1.59(2)
Cl(1)—Re—Cl(2)	100.5(2)	P(2)—Re—S	93.1(2)		
Cl(1)—Re—P(1)	86.8(2)	P(2)—Re—N(1)	91.5(4)		
Cl(1)—Re—P(2)	87.6(2)	S—Re—N(1)	67.1(3)		
Cl(1)—Re—S	165.5(1)	Re—P(1)—C(1)	110.4(5)		
Cl(1)—Re—N(1)	98.4(3)	Re—P(1)—C(7)	118.8(5)		
Cl(2)—Re—P(1)	89.8(2)	Re—P(1)—C(13)	118.5(5)		
Cl(2)—Re—P(2)	88.8(2)	Re—P(2)—C(19)	118.1(5)		
Cl(2)—Re—S	94.0(1)	Re—P(2)—C(25)	110.6(5)		
Cl(2)—Re—N(1)	161.1(3)	Re—P(2)—C(31)	116.4(4)		
P(1)—Re—P(2)	173.9(2)	Re—S—C(37)	81.6(4)		
P(1)—Re—S	92.9(2)	Re—N(1)—C(37)	101.4(7)		
P(1)—Re—N(1)	91.8(3)	Re—N(1)—C(39)	139.8(9)		
C(1)—P(1)—C(7)	102.6(6)	C(37)—N(1)—C(39)	119(1)		
C(1)—P(1)—C(13)	106.4(6)	C(37)—N(2)—C(41)	119(1)		
C(7)—P(1)—C(13)	98.2(6)	N(1)—C(39)—C(38)	121(1)		
C(19)—P(2)—C(25)	103.7(6)	N(1)—C(39)—C(40)	118(1)		
C(19)—P(2)—C(31)	101.6(6)	N(2)—C(41)—C(42)	118(1)		
C(25)—P(2)—C(31)	105.0(7)	N(2)—C(41)—C(40)	120(1)		
S—C(37)—N(1)	109.9(8)	C(39)—C(40)—C(41)	120(1)		
S—C(37)—N(2)	126.1(9)	C(38)—C(39)—C(40)	121(1)		
N(1)—C(37)—N(2)	124(1)	C(40)—C(41)—C(42)	122(1)		

values found in the structure of **(I)** so that similar considerations can be applied, but in this compound the phosphorus atom is *trans* to the Cl(1) atom and this difference seems to be unimportant.

The two Re—Cl bond distances show values significantly different ($\Delta/\sigma = 18.6$), the one (Re—Cl(1) = 2.360(3) Å) is in the range found in **(I)** and also in several chloro-oxo complexes of rhenium(V): e.g., $|Re(OH)Cl_3(PEt_2Ph)_2|$ 2.364(2)-2.428(2) Å (Sacerdoti *et al.*, 1982); 2.347(7)-2.425(7) Å in $|ReO(H_2O)Cl_3(tu)|$ (Lis, 1977); 2.365(3)-2.426(4) Å in $|Re_2O_2Cl_4(PPh_3)_2(salem)|$ (Bombieri *et al.*, 1978); 2.344(4), 2.388(3) Å in $|ReOCl_2(PPh_3)(PhOCNNCMe)|$ (Hursthouse *et al.*, 1979). The Re-Cl(2) distance 2.293(2) Å, out of the range of the previously quoted values and slightly longer than the value of 2.236(10) Å found in $ReCl_2(NO)_2(SbPh_3)_2$ (Fenske *et al.*, 1983), cannot be justified by *trans* effect being opposite in **(I)** and **(II)** to the coordinate nitrogen atom which show not significantly different bond val-

Table 5. Selected bond distances (Å) and angles (deg) for (II)

Re—Cl(1)	2.360(3)	P—C(1)	1.813(9)	N(1)—C(21)	1.33(1)
Re—Cl(2)	2.293(2)	P—C(7)	1.807(8)	N(2)—C(23)	1.34(1)
Re—S	2.507(2)	P—C(13)	1.830(9)	C(20)—C(21)	1.47(2)
Re—P	2.455(3)	S—C(19)	1.702(8)	C(21)—C(22)	1.40(1)
Re—O	1.670(7)	C(19)—N(1)	1.36(1)	C(22)—C(23)	1.35(2)
Re—N(1)	2.117(7)	C(19)—N(2)	1.32(1)	C(23)—C(24)	1.49(1)
Cl(1)—Re—Cl(2)	87.4(1)	S—Re—N(1)	65.4(2)		
Cl(1)—Re—S	90.0(1)	P—Re—O	88.3(2)		
Cl(1)—Re—P	169.1(1)	P—Re—N(1)	93.3(2)		
Cl(1)—Re—O	102.5(2)	O—Re—N(1)	94.2(3)		
Cl(1)—Re—N(1)	84.5(2)	Re—P—C(1)	112.1(3)		
Cl(2)—Re—S	91.3(1)	Re—P—C(7)	110.8(3)		
Cl(2)—Re—P	90.3(1)	Re—P—C(13)	118.4(3)		
Cl(2)—Re—O	110.3(2)	Re—S—C(19)	80.0(3)		
Cl(2)—Re—N(1)	155.3(2)	Re—N(1)—C(19)	103.9(6)		
S—Re—P	79.4(1)	Re—N(1)—C(21)	135.7(6)		
S—Re—O	155.2(2)				
C(1)—P—C(7)	105.5(4)	N(1)—C(21)—C(20)	120.1(9)		
C(1)—P—C(13)	102.4(4)	N(1)—C(21)—C(22)	116.1(9)		
C(7)—P—C(13)	106.5(4)	N(2)—C(23)—C(22)	120.9(9)		
S—C(19)—N(1)	110.6(7)	N(2)—C(23)—C(24)	116.5(9)		
S—C(19)—N(2)	125.0(7)	C(20)—C(21)—C(22)	123.8(9)		
N(1)—C(19)—N(2)	124.4(8)	C(21)—C(22)—C(23)	121.7(9)		
C(19)—N(1)—C(21)	120.2(8)	C(22)—C(23)—C(24)	122.6(9)		
C(19)—N(2)—C(23)	116.8(8)				

Table 6. Intermolecular contacts less than 3.60 Å

(a) In (I)		(b) In (II)	
Cl(2) · · · C(38$^{\mathrm{i}}$)	3.55(1)	Cl(2) · · · C(3$^{\mathrm{iii}}$)	3.49(1)
N(2) · · · C(42$^{\mathrm{ii}}$)	3.54(2)		
C(10) · · · C(23$^{\mathrm{iii}}$)	3.43(2)		
C(10) · · · C(38$^{\mathrm{iv}}$)	3.31(2)		
C(11) · · · C(11$^{\mathrm{iii}}$)	3.58(2)		
C(11) · · · C(38$^{\mathrm{iv}}$)	3.44(2)		
C(15) · · · O$^{\mathrm{i}}$	3.52(2)		
C(22) · · · C(33$^{\mathrm{v}}$)	3.54(2)		
C(33) · · · C(42$^{\mathrm{vi}}$)	3.51(3)		
C(33) · · · O$^{\mathrm{vi}}$)	3.50(2)		

i = $x, y, z - 1$
ii = $1 - x, 1 - y, 1 - z$
iii = $\bar{x}, \bar{y}, \bar{z}$
iv = $\bar{x}, \bar{y}, 1 - z$
v = $1 - x, \bar{y}, \bar{z}$
vi = $1 - x, 1 - y, 1 - z$

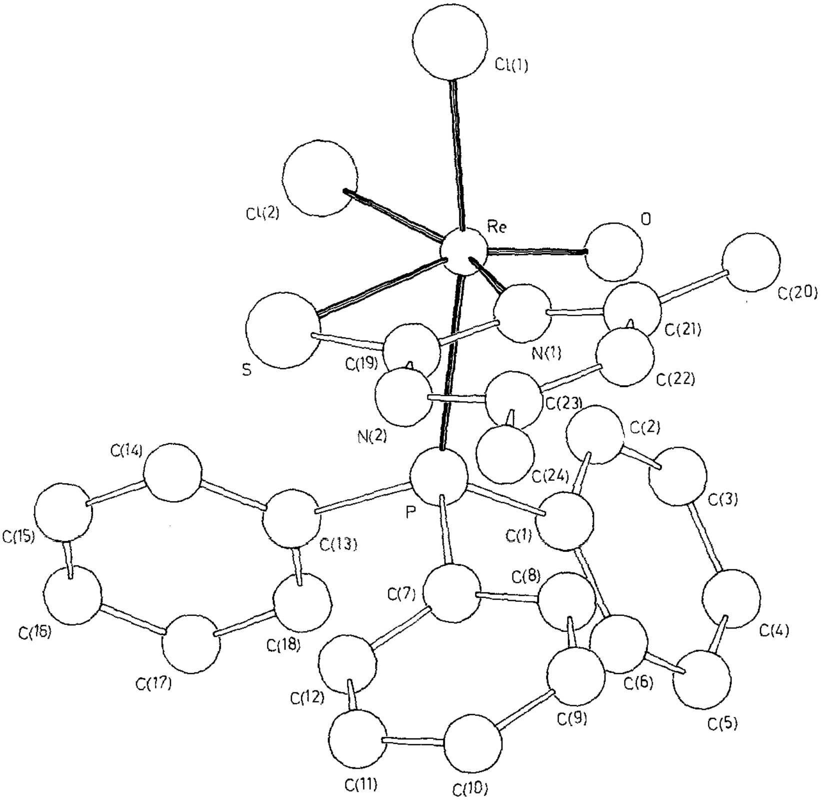


Fig. 2. Perspective view of the $|ReOCl_2(C_6H_7N_2S)(PPh_3)|$ complex molecule.

ues, but should be accounted by the different repulsive interactions exerted on this atom by its neighboring in the octahedron. In fact, in **(I)** and **(II)** the non-bonding distances involving Cl(2) atom have the same trend and comparable values, while in **(I)** the Cl(1) · · · Cl(2) distance 3.624(5) Å is longer than Cl(2) · · · O 3.273(6) Å interaction in **(II)** so that in this last case a less repulsive interaction and steric hyndrance can be hypothesized.

The Re—O bond 1.670(7) Å compares well with the values found in some Re(V)—oxo complexes: $|ReO(OEt)Cl_2py_2|$ 1.684(7) Å (Lock and Turner, 1977), $|Pt(NH_3)_4|_2|Re_2O_3(CN)_8|$ 1.698(7) Å (Shandles *et al.*, 1971), $|ReO(H_2O)Cl_2tu_2|Cl$ 1.654(10) Å (Lis, 1976), $|ReOCl_2(PPh_3)(acac)|$ 1.69(1) Å (Lock and Che'ng Wan, 1975), $|Re_2O_2Cl_4(PPh_3)_2(salen)|$ (Bombieri *et al.*, 1978), and these values correspond to that of triple bond (Sacerdoti *et al.*, 1982, 1984; Shustorovich *et al.*, 1975; Gilli *et al.*, 1982).

The Re—S distance 2.507(2) Å is different from the value 2.409(4) Å found in **(I)** ($\Delta/\sigma = 21.9$) and this weakening of the bond may be attributed to the *trans* effect due to the presence of the oxo group; on the contrary the Re—N bond 2.117(7) Å shows no significant difference from that in **(I)**.

The organic molecule shows small but significant displacements from the planarity, Re is out from this mean plane only 0.050(1) Å. Bond distances and angles in this ligand are similar to those in **(I)** and in the 4,6-dimethylpirimidine-2(1H)-thione hydrochloride (Battaglia *et al.*, 1986), but also in this case in the chelate ring the S—C(19)—N(1) angle is significantly smaller than the expected value. N, S-chelation in these ligand type is less usual and was found in complexes as |$Co(C_6H_7N_2S)_3$| (Cartwright *et al.*, 1979), |$Co(C_4H_4N_2S)_2Cl_2$| (Abbot *et al.*, 1978), |$Ru(C_5H_4NS)_2(PPh_3)_2$| (Fletcher and Skapski, 1972), |$Sn(C_5H_4NS)_2Cl_2$| (Masaki *et al.*, 1978). In Table 7 are quoted some structural parameters involving the chelate rings: a comparison of these data shows that, except the |$Co(C_4H_4N_2S)_2Cl_2$| compound, the deformation of these four-membered chelate rings are very similar and mainly due to geometrical constraints.

Reaction mechanisms

Reactions between *trans*-|$ReOX_3(PPh_3)_2$| (X = Cl, Br) precursors and 4,6-dimethylpyrimidine-2(1H)-thione (pymSH) in boiling acetone results in the formation of red-orange |$Re^{III}X_2$(pymS)(PPh_3)$_2$|$\cdot C_3H_6O$ and emerald-green |$Re^{V}OX_2$(pymS)(PPh_3)| (X = Cl, Br) monomeric octahedral complexes. The solid compounds are stable if stored under inert atmosphere; conductivity measurements in dichloromethane solution show their nonionic character. The presence of solvate acetone in paramagnetic |ReX_2(pymS)(PPh_3)$_2$|$\cdot C_3H_6O$ (X = Cl, Br) complexes was confirmed by elemental analyses, ir and nmr spectroscopy, and in the chloride compound also by X-ray results.

On the basis of the experimental results, it seems probable that the formation of the rhenium(V) pyrimidinethiolate/triphenylphosphine mixed complexes in acetone, can be interpreted in terms of partial *trans* → *cis* isomerization (Johnson *et al.*, 1964; Chatt *et al.*, 1969) of the *trans*-|$ReOX_3(PPh_3)_3$| (X = Cl, Br) precursors (*trans* and *cis* notation refers to the arrangement of phosphine ligands), followed by pymSH in thiol form, for X (X = Cl, Br *trans* to Re=O) and equatorial PPh_3 substitution with formation of |$ReOX_2$(pymS)(PPh_3)| complex and pymSH$\cdot$HX (X = Cl, Br) and PPh_3 species.

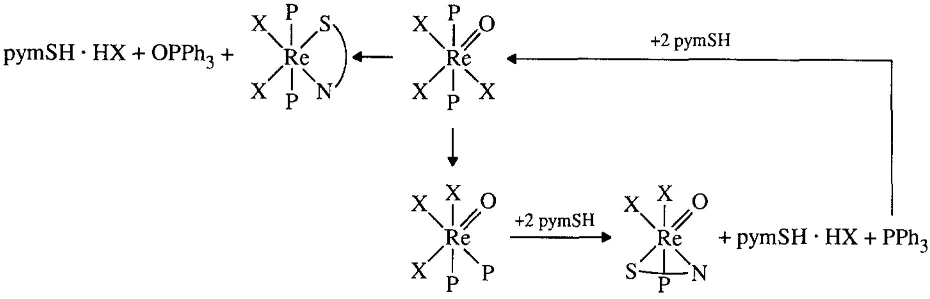
Reduction of the rhenium(V) to rhenium(III) leading to the formation of *trans*-|ReX_2(pymS)(PPh_3)$_2$|$\cdot C_3H_6O$ (X = Cl, Br) involves, besides one halide

Table 7. Structural parameters in some N,S-chelate rings (Å and degree)

	Me—S	Me—N	S—C	C—N	S—Me—N	Me—S—C	S—C—N	Me—N—C
$\lvert ReCl_2(C_6H_7N_2S)(PPh_3)_2\rvert \cdot C_3H_6O$[a]	2.409(4)	2.115(10)	1.70(1)	1.36(1)	67.1(3)	81.6(4)	109.9(8)	101.4(7)
$\lvert ReOCl_2(C_6H_7N_2S)(PPh_3)\rvert$[b]	2.507(2)	2.117(7)	1.702(8)	1.36(1)	65.4(2)	80.0(3)	110.6(7)	103.9(6)
$\lvert Co(C_6H_7N_2S)_3\rvert$[c]	2.252(2)	1.986(5)	1.724(6)	1.351(7)	72.58(14)	79.2(2)	109.3(4)	98.8(3)
	2.255(2)	1.976(5)	1.723(6)	1.356(7)	72.47(14)	79.4(2)	108.7(4)	99.4(4)
	2.269(2)	1.975(5)	1.738(6)	1.365(7)	72.35(13)	79.5(2)	107.8(4)	100.3(3)
$\lvert Ru(C_5H_4NS)_2(PPh_3)_2\rvert$[d]	2.437(2)	2.115(6)	1.732(9)	1.34 av.	66.6(2)	80.1(3)	110.1(6)	103.1(6)
	2.434(2)	2.132(7)	1.747(9)	—	67.7(2)	80.6(3)	109.8(6)	101.8(5)
$\lvert CoCl_2(C_4H_4N_2S)_2\rvert$[e]	2.960(2)	2.098(4)	—	1.388(8)	59.12(13)	71.9(2)	116.2(3)	111.8(3)
$\lvert SnCl_2(C_5H_4NS)_2\rvert$[f]	2.467(3)	2.271(9)	1.729(12)	1.352(15)	66.2(3)	81.8(4)	113.9(8)	98.1(7)
	2.462(3)	2.256(9)	1.751(12)	1.340(15)	66.0(3)	81.9(14)	112.2(8)	100.0(7)

[a] (I), present paper.
[b] (II), present paper.
[c] Cartwright *et al.* (1979).
[d] Fletcher and Skapski (1972).
[e] Abbot *et al.* (1978).
[f] Masaki *et al.* (1978).

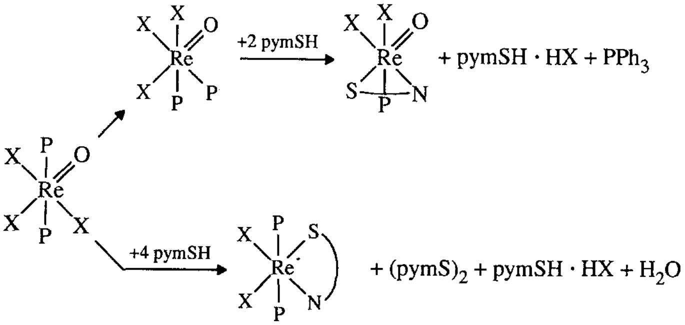
displacement, mainly oxygen transfer from the remaining *trans*-|ReOX$_3$(PPh$_3$)$_2$| precursor, probably to the free PPh$_3$, giving OPPh$_3$, pymSH·HX (*X* = Cl, Br) and the mixed thiolate/PPh$_3$ rhenium(III)-complex according to the scheme:



Scheme 1.

The capacity of PPh$_3$ to interact with Re=O bond in rhenium(V) complexes and yield rhenium(III) compounds and OPPh$_3$ has already been demonstrated (Rouschias and Wilkinson, 1967; Rossi *et al.*, 1982).

Alternatively, the reduction of the rhenium(V) in the *trans*-|ReOX$_3$(PPh$_3$)$_2$| with subsequent formation of *trans*-|Re^{III}X$_2$(pymS)(PPh$_3$)$_2$|·C$_3$H$_6$O compound, can be interpreted as a competitive reaction to the *trans* → *cis* isomerization of the precursor, in terms of partial oxidation of the ligand in thiol form, to yield the corresponding disulphide (highly soluble in acetone), according to the overall reaction scheme:



Scheme 2.

This view, which emphasized the knowability of pyrimidinethione ligands to stabilize a preferred electronic configuration of the central metal ion through reduction, viz. copper(II) → copper(I) (Battistuzzi and Peyronel, 1978; Goodgame *et al.*, 1978; Castan, 1981), is supported by several examples of oxidation of potential tautomeric thione ⇄ thiol heterocyclic ligands to disulfides, promoted *via* reduction of free (Ottensen *et al.*, 1974; Lunden *et al.*, 1978; Simmons *et al.*, 1979; Constable and Raithby, 1987) or complexed (Po *et al.*, 1980) transition metal ions.

Infrared studies

Table 8 contains some significative ir absorption bands of the free pymSH ligand, its disulfide and those of the rhenium thiolate complexes together with their correlation and probable assignments.

The ir spectra (4000–400 cm^{-1}) of the complexes, very similar one to another, exhibit bands due to ring vibrations in the range 1580–1330 cm^{-1}, characteristic for $\nu(C \overset{...}{-} C)$ and $\nu(C \overset{...}{-} N)$ skeletal stretching motions of "aromatic six-membered heterocyclic rings" (Katritzki, 1959; Spinner, 1960; Simmons *et al.*, 1979) and bands due to mixed ν(NCN), ν(NCS), and ν(CS) modes in the range 1270–1150 cm^{-1}. This absorption pattern, therefore, is closer to that of bis-|2-(4,6-dimethylpyrimidyl)|-disulfide (Battistuzzi, 1979) and to those of the S-methylpyrimidines (Spinner, 1960; Gauthier and Lebas, 1979; 1980; Mille *et al.*, 1979), rather than to that of the "nonaromatic" neutral ligand (Battistuzzi and Peyronel, 1978; Gupta *et al.*, 1986). This fact, together with the absence of absorption bands assignable to N-H modes, clearly indicates that the ligands in the reported complexes exist in the deprotonated thiolate form. Moreover, in line with x-ray structural results, the frequency shifts observed in the spectra of the complexes in comparison with related bands of the free ligands and of the disulfide agree well with a N, S-chelation of the pymS- anion (Latham *et al.*, 1986).

The oxo-complexes $|ReOX_2(pymS)(PPh_3)|$ (X = Cl, Br) show in the medium energy ir range, a strong band around 970–960 cm^{-1} assigned to $\nu(Re{=}O)$ mode. The small shift in comparison with the $\nu(Re{=}O)$ in the starting complexes (chloride $\nu(Re{=}O)$ at 967 cm^{-1}, bromide $\nu(Re{=}O)$ at 978 cm^{-1}) makes this absorption band not to be significantly influenced by the other ligand surrounding rhenium.

Below 500 cm^{-1}, the far-ir spectra of the complexes show, besides ligand bands and the absorptions due to ν(Re—N), ν(Re—S) and ν(Re—P) modes, whose assignments have not been achieved, two strong bands with a peak-to-peak separation varying from 50 to 10 cm^{-1}, readily assigned to ν(Re—X) stretching modes of mutually *cis*-halides (Mazzi *et al.*, 1980). A comparison of Re—Cl bond distances for $|ReOCl_2(pymS)(PPh_3)|$ shows a significant difference, δ = d|Re—Cl(1)|-d|Re—Cl(2)| = 0.067 Å; the difference for $|ReCl_2(pymS)(PPh_3)_2| \cdot C_3H_6O$ is much less. These effects on the Re—Cl bond (probably present also in the corresponding bromide complexes) are reflected

Table 8. Some medium ir and far-ir bands (cm^{-1}) of ligand, its disulfide and rhenium(V) and rhenium(III) complexes

Assignments	pymSH	(pymS)$_2$	|ReOCl$_2$(pymS)(PPh$_3$)|	|ReCl$_2$(pymS)(PPh$_3$)$_2$|·C$_3$H$_6$O	|ReOBr$_2$(pymS)(PPh$_3$)|	|ReBr$_2$(pymS)(PPh$_3$)$_2$|·C$_3$H$_6$O
ν(NH)	3180s 3140s					
ν(CO)	acetone			1708s		1702s
ring	1623vs	1576vs	1587vs	1575vs	1580vs	1575vs
δ(NH)	1568vs					
Ring	1553vs					
	1533m, sh	1515s	1515m, br	1500w	1505m, br	1495w
	1432s	1420m	1420s, sh	1420s, sh	1420s, sh	1415, s, sh
	1318m	1330s	1350mw	1348m	1344mw	1340m
ν(NCN) + ν(SCN) + ν(CS)	1230vs	1250s, sh	1278s	1260s	1270s	1255s
	1218vs	1239ms				
	1184s	1192ms	1195m, sh	1190m, sh	1190m, sh	1185m, sh
		1172m	1182m	1178m	1180m	1170m
		1168m	1160mw	1160m, sh	1155mw	1150m, sh
ν(Re=O)			968vs		960vs	
ν(Re—X)			358vs	305vs	256vs	204s
			304vs, br	292vs	215vs	198vs, sh
Ligand and other bands			322m, sh	344w, br	326m, sh	335w, br
		302s	296vs, sh		316m	302m
	288 m	286w	282m, sh	284vs, sh	282w, sh	280w
	268m	274mw	245w	255mw		243s
	230m	225vw	222m	222m	226s	227m
		210vw	212w, sh	198w	199vs	
	177m, br	181s, br	185w, br	180w	184m, sh	182m, sh
			151m	153w	143m	142w
	98s, sh	124m	109w, br	105w, sh	103m	105w, br
	84vs		83w, br	85vw	84w	85mw

in the ν(Re—Cl) vibrational frequencies in agreement with Konovalov's (1985) empirical correlation between ν(Re—Cl) frequencies and the interatomic r_{Re-Cl} distances.

Nuclear magnetic resonance studies

^{1}H nmr results are summarized in Table 9 that reports the chemical shifts measured in $CDCl_3$ of the free ligand pymSH, *trans*-$|ReOX_3(PPh_3)_2|$ precursors, $|ReX_2(pymS)(PPh_3)_2| \cdot C_3H_6O$ and $|ReOX_2(pymS)(PPh_3)|$ (X = Cl, Br) complexes. As it is shown, the signals of the two methyl groups and methyno protons of the pymSH ligand and the multiplets due to the triphenylphosphine protons are significantly modified in the rhenium(V) complexes but undergo a very large change in the rhenium(III) complexes. In fact, the latter red-orange complexes display the distinctive Knight-shifted ^{1}H nmr spectra that characterize paramagnetic mononuclear rhenium(III) species (Randall and Show, 1969; Rossi *et al.*, 1982; Corner and Walton, 1987). The presence of unpaired electrons on rhenium(III) affects markedly the resonance signals that are shifted upfield and downfield with respect to the $SiMe_4$ reference peak so that they occur in the +14 ppm to −6 ppm region. The sharp singlet of intensity 3 at 2.45 ppm, due to the two equivalent methyl groups protons in the pymSH free ligand, is now shifted upfield and split in two singlets, each one of intensity 3, occurring at −6.18 ppm and −1.11 ppm respectively; such an assignment is fully confirmed by the proton chemical shifts of the analogous rhenium(III) complex $|ReCl_2(C_4H_3N_2S)(PPh_3)_2| \cdot C_3H_6O$ of the pyrimidine-2(1H)-thione in which the ligand lacks of the methyl groups. The -CH proton of the pymSH is also shifted from 6.50 ppm to 1.06 ppm. A large downfield shift, with respect to $|ReOCl_3(PPh_3)_2|$ protons, is observed for the multiplets with an intensity ratio of 2 : 3, assigned to the ortho- (12 in total), para-, and meta-protons (18 in total) of triphenylphosphine rings, whose peaks occur, respectively, in the complex **(Ia)** at 14.32 ppm and 8.79 ppm.

A similar behavior is exhibited by the complex $|ReBr_2(pymS)(PPh_3)_2| \cdot C_3H_6O$, whose resonance values, although slightly different, are shifted in the same direction.

^{1}H nmr spectra of the green $|ReOBr_2(pymS)(PPh_3)|$ complex display two well-resolved multiplets centered, respectively, at 7.65 ppm and 7.38 ppm, assigned to the ortho-, para-, and meta-protons of the phenylphosphine rings. The relative intensity ratio of 6 to 9 suggests that the former resonance is due to ortho- and the latter to para- and meta-protons. The -CH resonance of the $pymS^-$ ligand is shifted downfield from 6.50 ppm to 6.73 ppm and the singlets due to the methyl protons are split into two singlets, each one of intensity 3, located at 2.61 ppm and 2.41 ppm.

The spectrum of the chloride analogous $|ReOCl_2(pymS)(PPh_3)|$ indicates

Table 9. ^1H nmr chemical shifts (δ/ppm) of $C_6H_8N_2S$ and its rhenium(III) and rhenium(V) complexes in $CDCl_3$ at 23 °C

	Compounds	$-CH_3$	$-CH$	Ph	$-CH_3$ acetone
	$C_6H_8N_2S$	2.45(s, 6H)	6.50(s, 1H)	—	—
	$ReOCl_3(PPh_3)_2$	—	—	7.74(m, 7.43(m, } 15H)	—
	$ReOBr_3(PPh_3)_2$	—	—	7.80(m, 7.44(m, } 15H	—
	$ReCl_2(C_4H_3N_2S)(PPh_3)_2 \cdot C_3H_6O$	—	1.27(s, 2H) 3.61(s, 1H)	14.01(b, 12H) 8.82(b, 18H)	2.18(s, 6H)
(Ia)	$ReCl_2(C_6H_7N_2S)(PPh_3)_2 \cdot C_3H_6O$	−6.18(s, 3H) −1.11(s, 3H)	1.06(s, 1H)	14.32(b, 12H) 8.79(b, 18H)	2.16(s, 6H)
(Ib)	$ReBr_2(C_6H_7N_2S)(PPh_3)_2 \cdot C_3H_6O$	−5.23(s, 3H) −0.44(s, 3H)	1.31(s, 1H)	14.38(b, 12H) 8.76(m, 18H)	2.17(s, 6H)
(IIa)	$ReOCl_2(C_6H_7N_2S)(PPh_3)$	3.12(s, 2.63)s, 2.56(s, 2.39)s, } 6H)	6.90(s, 6.68(s, } 1H)	7.82(m, 7.66(m, 7.49(m, 7.38,(m, } 15H	—
(IIb)	$ReOBr_2(C_6H_7N_2S)(PPh_3)$	2.61(s, 3H) 2.41(s, 3H)	6.73(s, 1H)	7.65(m, 7.38(m, } 15H)	—

that in $CDCl_3$ solution the complex is present in two isomeric forms with a relative abundancy of 40 and 60%. This ratio, at room temperature, remains constant in the time as the patterns are perfectly superimposable also after 7 days.

In the presence of air, the red-orange $|ReX_2(pymS)(PPh_3)_2| \cdot C_3H_6O$ (X = Cl, Br) complexes in $CDCl_3$ solution are slowly oxidized to the corresponding green rhenium(V) oxo-complexes since their proton patterns, after 7 days at room temperature, are perfectly coincident with those of the compounds **IIa** and **IIb** (Table 9).

The behavior of the reported complexes in solution will be the subject of further studies.

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Structure factor intermolecular contacts, thermal parameters, atomic coordinates, and calculation details have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication No. 63095 (89 pages).