Pergamon

Polyhedron Vol. 16, No. 12, pp. 2093–2104, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0277-5387/97 $17.00+0.00

PII: S0277-5387(96)00505-0

Redox interconversion of $[Re^{V}O]^{3+} \rightleftharpoons [Re^{III}]^{3+}$ centers in octahedral 4,6-dimethyl-pyrimidine-2-thiolate/triphenylphosphine rhenium(V) and rhenium(III) mixed complexes

Gianantonio Battistuzzi, Marco Borsari and Raffaele Battistuzzi*

Department of Chemistry, University of Modena, 41110 Modena, Italy

(Received 30 July 1996; accepted 16 October 1996)

Abstract—Reaction of *trans*-$[ReOX_2(EtO)(PPh_3)_2]$ (X = Cl, Br, I) with 4,6-dimethylpyrimidine-2-(1H)-thione (pymSH) in 1 : 1 molar ratio in refluxing acetone, rapidly formed $[ReOX_2(pymS)(PPh_3)]$ (X = Cl, Br, I) compounds and PPh_3 in good yields. Upon increasing the refluxing time (5–6 h), the above products react in a 1 : 2 molar ratio producing the paramagnetic *trans*-$[ReX_2(pymS)(PPh_3)_2]$ (X = Cl, Br) species and triphenylphosphine oxide as a result of oxygen transfer from the $[ReO]^{3+}$ core to the PPh_3. The *trans*-$[ReX_2(pymS)(PPh_3)_2]$ (X = Cl, Br) species, in organic solvents at room temperature and in the presence of atmospheric oxygen, are easily oxidized back to $[ReOX_2(pymS)(PPh_3)]$ with the concomitant formation of $O = PPh_3$. These oxidation reactions most likely proceed through the loss of a PPh_3 ligand on the reducing rhenium(III) center, which makes a coordination site available for the oxidative addition of dioxygen which produces a highly reactive rhenium-dioxygen intermediate ($[ReX_2(pymS)(PPh_3)(O_2)]$). The time course of the aerial oxygenation reactions at room temperature was inferred from the rate [$K_m = (1.30 \pm 0.05) \times 10^{-2}\ h^{-1}$] of disappearance of the paramagnetic *trans*-$[ReX_2(pymS)(PPh_3)_2]$ (X = Cl, Br) species, monitored by VIS-NIR and ^1H NMR spectroscopy. Spectroscopic (UV-VIS-NIR, ^1H and ^{31}P NMR), magnetic and electrochemical properties of the complexes are discussed. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: thiopyrimidine; rhenium(V;III) complexes; cyclic-voltammetry; NMR spectra; electronic spectra; kinetics.

The synthesis and X-ray structural characterization of some rhenium(III) and rhenium(V) 4,6-dimethyl-pyrimidine-2-thiolate/triphenylphosphine mixed complexes has been described by us recently [1]. We noticed that whereas solid $[ReX_2(pymS)(PPh_3)_2] \cdot C_3H_6O$ (X = Cl, Br) complexes can be handled in air for some time without significant degradation, a relatively slow oxygenation occurs, in organic solvents ($CHCl_3$, CH_3COCH_3, C_6H_6) at room temperature, in the presence of atmospheric oxygen. In fact, the starting orange solutions once exposed to air at room temperature, turned to yellow–green yielding, after a few days, proton NMR patterns perfectly coincident with those of the corresponding rhenium(V) $[ReOX_2(pymS)(PPh_3)]$ (X = Cl, Br) complexes. This behavior is very interesting in the light of the following considerations. The transfer of an oxygen atom from a metal center to a substrate is one of the fundamental reactions of transition metal-oxo complexes [2,3] of great relevance in biological systems, organic synthesis and industrial processes. The same can be said for the system in which the same reduced metal-center possesses such an electron donor ability as to react with molecular oxygen [4–7] and promote the homolytic scission of the O—O bond in the transient M—(O_2)—L species followed by reoxidation to the starting metal-oxo species and oxygenation of the organic substrate (L). In this paper, besides describing a more convenient synthesis of the rhenium(V) and rhenium(III) pyrimidine-2-thiolate/triphenylphosphine mixed complexes, we have compared their struc-

---

*Author to whom correspondence should be addressed.

ture and chemistry with related complexes [1] and studied their electrochemical and spectroscopic (UV-VIS-NIR, and ^{1}H NMR) properties in $CHCl_3$ and $CDCl_3$ solution. Moreover, the kinetics of oxygenation of the rhenium(III) *trans*-$[ReX_2(pymS)(PPh_3)_2]$ (X = Cl, Br) to $[ReOX_2(pymS)(PPh_3)]$ rhenium(V) complexes in the presence of atmospheric oxygen at room temperature have been investigated.

EXPERIMENTAL

Materials

Trans-$[ReOX_2(EtO)(PPh_3)_2]$ (X = Cl, Br, I) precursors were prepared by literature methods [8–10]; 4,6-dimethylpyrimidine-2(1H)-thione (pymSH) was obtained with the method previously reported [11]. Chloroform, acetone (RPE, C. Erba) and deuterochloroform (100% D, Jansen Chimica) were used as received.

Preparation of the complexes $[ReOCl_2(pymS)(PPh_3)]$ *and* $[ReCl_2(pymS)(PPh_3)_2] \cdot C_3H_6O$

Trans-$[ReOCl_2(EtO)(PPh_3)_2]$ (0.6 mmol) and pymSH (0.6 mmol) were suspended in acetone (15 cm^3) and refluxed upon stirring for 10 min. On heating, the solution became clear and green in colour. Upon cooling to 0°C for about 6–8 h, the green microcrystalline product was filtered off, washed with acetone and dried *in vacuo*. Found: C, 42.6, H, 3.2; N, 4.1; S, 4.7. Calc. for $[ReOCl_2(pymS)(PPh_3)]$: C, 42.7; H, 3.3; N, 4.1; S, 4.7%. Yield: 0.284 g (70%). On standing at room temperature in a stoppered flask, the green mother liquor (8–10 cm^3) became darker and after 3–4 days a mixture of red–orange and (fewer) green-emerald crystals separated. Slow evaporation of the residual mother liquor afforded a slimy brown residue and large white crystals which on analysis resulted to be triphenylphosphine oxide. (Found: C, 77.6, H, 5.4. Calc. for $O{=}PPh_3$: C, 77.6; H, 5.4%). From the mixture of crystals a further amount of pure green $[ReOCl_2(pymS)(PPh_3)]$ compound was obtained by removing the very soluble red-orange crystals of $[ReCl_2(pymS)(PPh_3)_2]$ with 4–5 cm^3 of benzene on a sintered-glass Gooch. On standing at room temperature in the presence of atmospheric oxygen, the orange-colored benzene solution slowly turned to yellow–green, giving green crystals of $[ReOCl_2(pymS)(PPh_3)]$. If the refluxing time of the starting reaction was increased to 6 h, the dark-brown solution gave rise to a homogeneous red–orange product whose amount increased on cooling on ice. The product washed with acetone, dried *in vacuo* and analyzed resulted to be $[ReCl_2(pymS)(PPh_3)_2] \cdot C_3H_6O$. Yield 0.206 g (35%). Found: C, 55.0; H, 4.4; N, 2.8; S, 3.2. Calc. for $[ReCl_2(pymS)(PPh_3)_2] \cdot C_3H_6O$: C, 55.2; H, 4.4; N, 2.9; S, 3.3%.

$[ReOBr_2(pymS)(PPh_3)]$ *and* $[ReBr_2(pymS)(PPh_3)_2] \cdot C_3H_6O$

Solid pymSH (0.6 mmol) was added with stirring to a suspension of *trans*-$[ReOBr_2(EtO)(PPh_3)_2]$ (0.6 mmol) in 15 cm^3 of acetone. The resulting mixture, heated under reflux for 15 min, yielded a green-olive clear solution and a bright-green product. After cooling on ice the compound was filtered off, washed with acetone and dried. Yield: 0.367 g (80%). Found: C, 37.7; H, 2.9; N, 3.6; S, 4.2. Calc. for $[ReOBr_2(pymS)(PPh_3)]$: C, 37.7; H, 2.9, N, 3.7; S, 4.2%. The mother liquor was taken to dryness by rotary evaporation and the oily residue treated with acetone (3 cm^3). Upon cooling on ice an orange-red product precipitated. The solid was washed twice with 1 cm^3 of acetone followed by diethyl ether and finally dried *in vacuo*. Yield 0.135 g (12%). Found: C, 50.5; H, 4.0; N, 2.5; S, 3.0. Calc. for $[ReBr_2(pymS)(PPh_3)_2] \cdot C_3H_6O$: C, 50.5; H, 4.0; N, 2.6; S, 3.0%. Also in this case, if the starting reaction was carried out with the same $[ReOBr_2(EtO)(PPh_3)_2]$:pymSH molar ratio (1 : 1) in acetone with a refluxing time of 6 h, the green-olive solution became brown-orange and the initial amount of the bright-green product decreased. After cooling, the remaining green $[ReOBr_2(pymS)(PPh_3)]$ solid was filtered off, washed with acetone, dried and analyzed. Yield 0.267 g (56%). The microcrystalline red-orange $[ReBr_2(pymS)(PPh_3)_2] \cdot C_3H_6O$ compound separated from the mother liquor after 2 days. The solid was collected, washed with a 1 cm^3 of acetone and dried. Yield 0.231 g (36%). Found: C, 50.5; H, 4.0; N, 2.6; S, 3.0%.

Red–orange *trans*-$[ReX_2(pymS)(PPh_3)_2] \cdot C_3H_6O$ (X = Cl, Br) complexes were also obtained with a good yield (92%) starting from $[ReOX_2(pymS)(PPh_3)]$ (X = Cl, Br) and PPh_3 in 1 : 2 molar ratio and refluxing the acetone mixture for about 6 h.

$[ReOI_2(pymS)(PPh_3)]$

The complex was prepared from *trans*-$[ReOI_2(EtO)(PPh_3)_2]$ with the same procedure outlined above for the chloro- and bromo-derivatives, but using a refluxing time of 2 h. After standing overnight the brick-red microcrystalline solid was filtered off, washed twice with 1 cm^3 of acetone followed by diethyl ether and dried *in vacuo*. Yield: 0.438 g (85%). Found: C, 33.5; H, 2.6; N, 3.2 S, 3.7. Calc. for $[ReOI_2(pymS)(PPh_3)]$: C, 33.6; H, 2.6; N, 3.3; S, 3.7%.

Analyses and physical measurements

Elemental analyses (C, H, N, S) were performed on a Carlo Erba Model 1106 Elemental Analyzer. Room temperature magnetic susceptibilities were measured by the Gouy method and corrected for diamagnetism by Pascal's constants. IR spectra were recorded in KBr pellets (4000–400 cm^{-1}) and in powdered polyethylene pellets (400–50 cm^{-1}) on a Bruker-IFS 113 V F.T.I.R. spectrophotometer. Diffuse reflectance (240–2400 nm) and solution spectra ($C \approx 10^{-3}$ mol dm^{-3} in $CHCl_3$, between 500–2400 nm) were recorded on a Perkin-Elmer UV-VIS-NIR Spectrometer Lamda 19. Electronic absorption spectra between 240–500 nm, of 4,6-dimethylthiopyrimidine-2(1H)-thione, triphenylphosphine and their rhenium(V) and rhenium(III) complexes ($C \approx 10^{-5}$ mol dm^{-3} in $CHCl_3$), were recorded with a Cecil CE 66005 double beam spectrophotometer. Proton and ^{31}P NMR spectra were obtained using a Bruker-AMX 400 instrument at $27 \pm 0.1\,^{\circ}$C in $CDCl_3$. Chemical shifts in δ/ppm have been quoted downfield and upfield from $SiMe_4$ and from 85% H_3PO_4 in D_2O, respectively. Conductivity measurements of the complexes were performed on fresh 10^{-3} mol dm^{-3} solutions in $CHCl_3$ at 25°C with a Jenway 4020 Conductivity Meter. For kinetic measurements (VIS-NIR, ^{1}H NMR) some graduated flasks (5 cm^3) were filled with a solution 10^{-3} mol dm^{-3} in $CHCl_3$ or $CDCl_3$ of *trans*-[ReX_2(pymS)$(PPh_3)_2$]·C_3H_6O (X = Cl, Br) and allowed to stand open in the presence of air at room temperature. Prior to each measurement the volume of the graduated flask was made up to 5 cm^3 with $CHCl_3$ or $CDCl_3$. Cyclic voltammetry measurements were performed on 10^{-4}–10^{-5} mol dm^{-3} CH_2Cl_2 solutions of the complexes with a PAR Model 273A Potentiostat/Galvanostat under argon as well as in air and in O_2 atmosphere at $25 \pm 0.1\,^{\circ}$C. CH_2Cl_2 (Fluka) was dried over molecular sieves. Tetrabutyl-ammonium perchlorate was used as base electrolyte and the ionic strength of the solutions was kept constant (0.1 mol dm^{-3}). A three-electrode arrangement was employed with a glassy-carbon working electrode (GC; PAR), a platinum ring (1 cm^2) as a secondary electrode, and a silver wire as pseudo-reference electrode. All reduction potentials were determined with respect to an internal reference cobaltocene/cobaltocenium couple and are referred to the NHE. The redox potential of the cobaltocene/cobaltocenium couple with respect to the silver wire pseudo-reference electrode was 0.710 V *vs* NHE. The use of a ferrocene/ferrocenium couple as an internal standard gives E_p values referred to the NHE, very similar to those obtained using the cobaltocene/cobaltocenium couple. Potential scan rate between 0.01 and 0.5 V s^{-1} were used.

RESULTS AND DISCUSSION

General

Trans-dihalo(ethoxo)oxobis(triphenylphosphine)-rhenium(V), [ReO(EtO)$(PPh_3)_2$] (X = Cl, Br, I), complexes are readily available and versatile intermediates which, compared with *trans*-[$ReOX_3(PPh_3)_2$] (X = Cl, Br), provide a more direct route for obtaining mononuclear octahedral 4,6-dimethylpyrimidine-2-thiolate/triphenylphosphine [$ReOX_2$(pymS)(PPh_3)] rhenium(V) (X = Cl, Br, I) and *trans*-[ReX_2(pym-S)$(PPh_3)_2$]·C_3H_6O (X = Cl, Br) rhenium(III) mixed complexes.

Reactions between *trans*-[$ReOX_2$(EtO)$(PPh_3)_2$], (X = Cl, Br, I) precursors and 4,6-dimethyl-pyrimidine-2(1H)-thione (pymSH), (molar ratio 1 : 1) in refluxing acetone (10–15 min) resulted in the rapid formation of solid [$ReOX_2$(pymS)(PPh_3)] (X = Cl, Br, I) complexes in good yield (70–85%). By subsequent slow evaporation, the mother liquors afforded small amounts of red–orange *trans*-[ReX_2(pymS)$(PPh_3)_2$]·C_3H_6O (X = Cl, Br) compounds and white crystals of triphenylphosphine oxide. Upon increasing the refluxing time to 5–6 h, the yield of [$ReOX_2$(pymS)(PPh_3)] complexes decreased to *ca* 60% and the amount of red–orange *trans*-[ReX_2(pymS)$(PPh_3)_2$]·C_3H_6O (X = Cl, Br) increased to *ca* 40%.

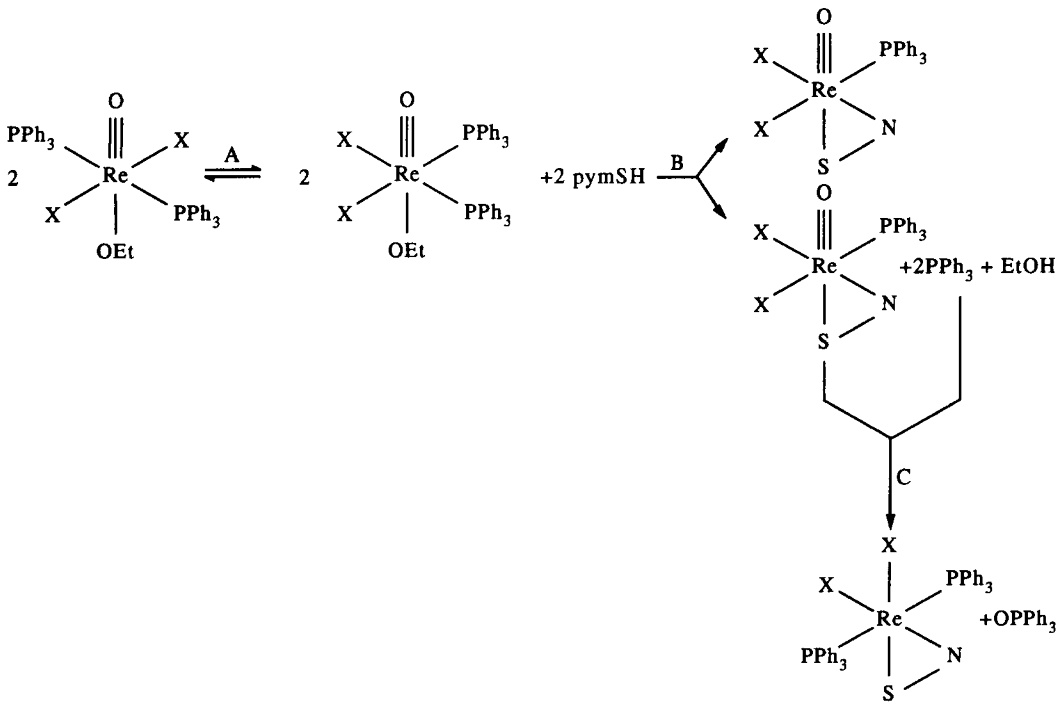
From these results, the formation of the rhenium(V) mixed complexes, in refluxing acetone, can be interpreted in terms of a *trans* → *cis* isomerization [12] of the *trans*-[$ReOX_2$(EtO)$(PPh_3)_2$] (X = Cl, Br, I) precursors (Scheme 1, step A) (*trans* and *cis* notation refers to the arrangement of phosphine ligands), followed by substitution of pymSH in thiol form for EtO$^-$ and an equatorial PPh_3 with formation of [$ReOX_2$(pymS)(PPh_3)] (X = Cl, Br, I) complexes, PPh_3 and ethanol (step B).

Reduction of the rhenium(V) oxo-complexes leading to the formation of *trans*-[ReX_2(pymS)$(PPh_3)_2$] (X = Cl, Br) rhenium(III) species, is no doubt consecutive to the formation of the [$ReOX_2$(pymS)(PPh_3)] (X = Cl, Br) complexes. In fact, after formation of the thiolate oxo-complexes, if the reaction mixtures are further refluxed for 5–6 h, the displaced phosphine reacts with [$ReOX_2$(pymS)(PPh_3)] (two equiv. of PPh_3 per rhenium are required) affording mixed pyrimidinethiolate/triphenylphosphine rhenium(III) (theoretical yield 50%) and O = PPh_3 species (Step C), according to the overall reaction Scheme.

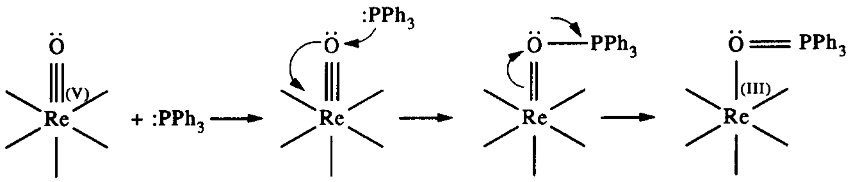
Regarding the well-known capacity of PPh_3 to interact with the Re≡O bond in rhenium(V) oxo-complexes to form rhenium(III) compounds [13], it seems reasonable to suppose that the initial events, i.e. the nucleophilic attack of PPh_3 on the oxygen atom, possibly involving a vacant π^* orbital of the $[ReO]^{3+}$ fragment, and a concerted two-electron transfer to Re, are followed by the cleavage of the ReO triple bond and formation of the Re—O═PPh_3 moiety, (Scheme 2).

The facile substitution [14] of PPh_3 for phosphine oxide in the coordination sphere and the subsequent rearrangement of the intermediate to *trans*-[ReX_2(pymS)$(PPh_3)_2$] (X = Cl, Br) complete the reaction.

The close similarity of the chemical and spectroscopic properties (IR, ^{1}H NMR) of the present complexes with related compounds described previously [1], provides strong evidence in favour of identical stoichiometries and structures. Analogously to the chloro- and bromo-rhenium(V) oxo-complexes



Scheme 1.



Scheme 2.

[1], the $[ReOI_2(pymS)(PPh_3)]$ compound shows an IR band at 970 cm^{-1} and a doublet at 190 and 175 cm^{-1} which can be assigned to ν(Re—O) and ν(Re—I), respectively.

Magnetic moments, electronic and ^{1}H NMR spectra

The diamagnetism of all the $[ReOX_2(pymS)(PPh_3)]$ (X = Cl, Br, I) complexes, suggests, in accordance with structural studies [1], that the rhenium(V) $[5d^2]$ ion is in a highly distorted octahedral field with the oxo-ligand (the Re≡O 1.670 Å is formally a triple bond) playing a major role. This gives a non-degenerate low-lying energy level $b_2(d_{xy})$ in which the two *d*-electrons are paired.

The complexes possess strikingly similar solid-state electronic spectra (Fig. 1) and, when dissolved in $CHCl_3$ form yellow–green (chloride and bromide) or wine red (iodide) stable non-conducting solutions, which have electronic spectra very similar to those of the solid complexes. From this it follows that these species retain their identity in solution. The solution spectra (Table 1) exhibit intense (ε, 29000–5000 dm^3 mol^{-1} cm^{-1}) composite absorptions in the 240–400 nm range and much weaker (ε, 370–50 dm^3 mol^{-1} cm^{-1}) bands in the 450–950 nm region. The high-intensity peaks in the UV region are the result of interligand electronic transitions of the $pymS^-$ [15] and PPh_3 [16] ligands, probably associated with ligand-to-metal charge-transfer transitions. The bands at lower energy, which show rather similar fea-

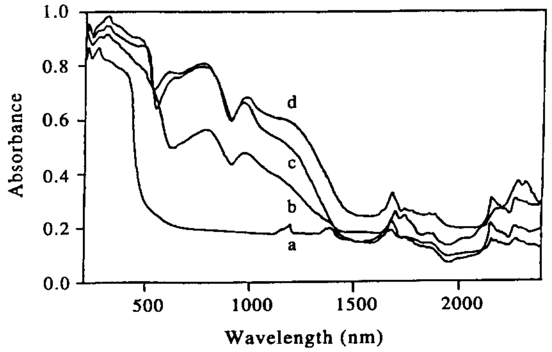


Fig. 1. Diffuse reflectance spectra of: (a) pymSH; (b) $[ReOI_2(pymS)(PPh_3)]$; (c) $[ReOBr_2(pymS)(PPh_3)]$; (d) $[ReOCl_2(pymS)(PPh_3)]$.

tures to those reported for other mononuclear octahedral compounds having a $[ReO]^{3+}$ core [17–20] presumably arise from *d–d* transitions. Although the ligand field symmetry in the present complexes is C_1 ($[ReOX_2NSP]$), we use the MO scheme devised for $[MeOX_5]^{2-}$ species (C_{4v} symmetry) [2,21] to tentatively assign the bands between 610–960 nm to components of a $^3E_g[b_{2g}(xy)^1e_g(xz,yz)^1 \leftarrow b_{2g}(xy)^2]$ excited state that is split [22] by strong spin-orbit coupling (ξ $[Re^V] = 3700$ cm^{-1}, [23]) interactions, and the band between 460–500 nm to $^1E_g[(b_{2g})^1(e_g)^1] \leftarrow {}^1A_{1g}[(b_{2g})^2]$ singlet → singlet transitions, respectively.

The chloro- and bromo-derivatives of the rhenium(III) complexes, $[ReX_2(pymS)(PPh_3)_2]\cdot C_3H_6O$, show room temperature magnetic moments of 1.96 and 1.93 B.M., respectively. These values are typical of low-spin d^4 rhenium(III) ion in mononuclear octahedral systems.[24] Deviation from the spin-only value 2.83 B.M., is to be ascribed to the large spin-orbit coupling ($\xi = 2500$ cm^{-1} for Re^{III} [25]) which gives a diamagnetic ground state.

The electronic absorption spectra (Table 1) of both rhenium(III) complexes, in freshly prepared $CHCl_3$ solution, are similar to those of the corresponding solids. The spectra are dominated by two intense bands at 243 and 260 nm due to interligand electronic transitions of PPh_3 and chelate $pymS^-$ ligands. In addition, a number of less intense (ε 7750–2425 dm^3 mol^{-1} cm^{-1}) absorptions appear between 350 and 510 nm, which fall at higher wavelengths in the bromo- as compared to the chloro-compound and that can be assigned to a combination of ligands-to-metal charge transfer and *d–d* bands. In the 950–2400 nm region, the solid state reflectance spectra (Fig. 2), exhibit four broad bands which are more readily seen in the solution spectra, at 960 ($\varepsilon = 5.0$ dm^3 mol^{-1} cm^{-1}), 1360–1420 ($\varepsilon = 27.0$ dm^3 mol^{-1} cm^{-1}), 1770–1780 (ε, 200–300 dm^3 mol^{-1} cm^{-1}) and 2150 nm (ε, 60–80 dm^3 mol^{-1} cm^{-1}) (Figs 3 and 4, spectra (a)). These low-energy spectra are rather similar to those exhibited

Table 1. Diffuse reflectance (DR) and $CHCl_3$ solution (S) ($C = 10^{-5}, 10^{-3}$ mol dm^{-3}) electronic spectral data (nm) of pymSH and its Re^{III} and Re^V complexes at room temperature (ε, dm^3 mol^{-1} cm^{-1} in parentheses)

pymSH	DR	260s	312s	355sh	1190mw	1380w	1698m	1738m	1850m	2018msh	2170m	2154br
	S		291 (16172)	363 (2948)						2280ms	2320ms	
$[ReCl_2(pymS)(PPh_3)_2]\cdot Ac$	DR		264s	351sh			430sh	563sh	962ms	1290mbr	1780mbr	2154br
	S	243 (33600)	260 (24635)	340 (5384)	360 (5279)	400sh	443 (3340)	496 (2015)	960 (5.4)	1360 (26.8)	1770 (198)	2150 (64)
$[ReBr_2(pymS)(PPh_3)_2]\cdot Ac$	DR		269s	352s	380sh		440sh	575sh	973ms	1342mbr	1785mbr	2154br
	S	243 (34540)	264 (25890)	334sh	366 (7747)	410 (4426)	446 (3478)	508 (2425)	959 (4.6)	1421 (26.3)	1778 (316)	2155 (78)
$[ReOCl_2(pymS)PPh_3]$	DR		266s	311s	382sh		452sh	611m	758m	972m		
	S	243 (22880)	263 (18980)	350sh			462 (371)	614 (59.4)	746 (54)	905sh		
$[ReOBr_2(pymS)PPh_3]$	DR		263s	302s	383sh		490sh	630sh	762m	960m		
	S	243 (22937)	264 (17570)	345sh		400sh	478 (376)	627 (63)	758 (77)	910sh		
$[ReOI_2(pymS)PPh_3]$	DR		267s	306s	385sh		509sh	652sh	781m	966m		
	S	243 (28880)	265 (20462)	345 (5261)		400sh	490sh		782 (156.4)	918sh		

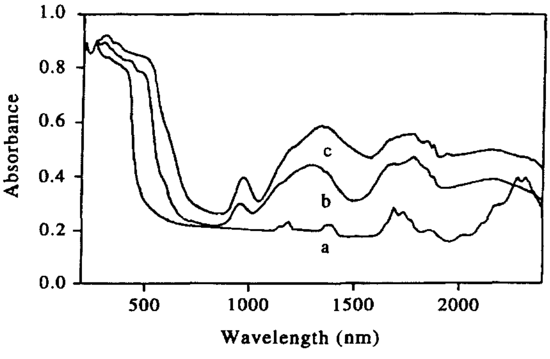


Fig. 2. Diffuse reflectance spectra of: (a) pymSH; (b) $[ReCl_2(pymS)(PPh_3)_2]\cdot C_3H_6O$; (c) $[ReBr_2(pymS)(PPh_3)_2]\cdot C_3H_6O$.

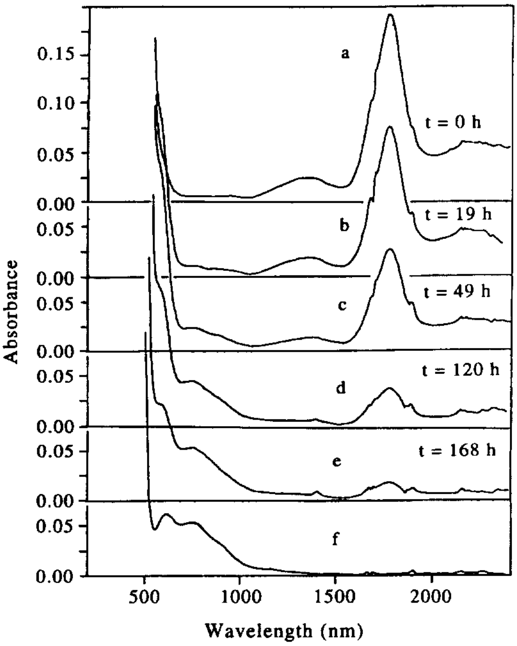


Fig. 3. Time dependence of absorption spectra of the $[ReCl_2(pymS)(PPh_3)_2] \cdot C_3H_6O$ complex in $CHCl_3$ ($C = 10^{-3}$ mol dm^{-3}) in the presence of atmospheric oxygen compared with that of (f) $[ReOCl_2(pymS)(PPh_3)]$.

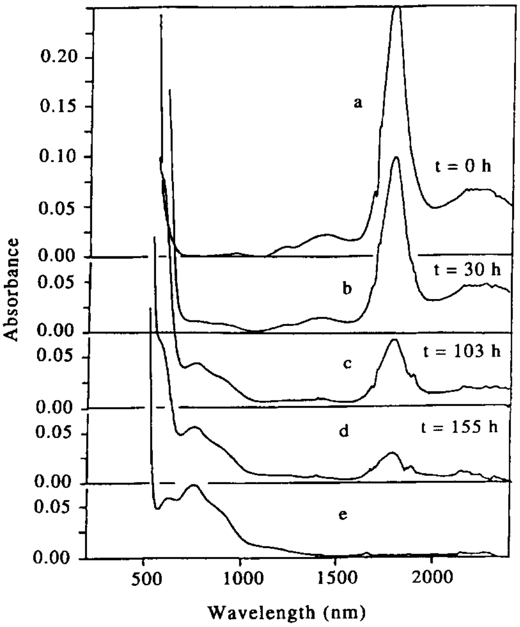


Fig. 4. Time dependence of absorption spectra of the $[ReBr_2(pymS)(PPh_3)_2] \cdot C_3H_6O$ complex in $CHCl_3$ ($C = 10^{-3}$ mol dm^{-3}) in the presence of atmospheric oxygen compared with that of (e) $[ReBr_2O(pymS)(PPh_3)]$.

by $[ReX_3(1{,}2\text{-bis(diphenylphosphino)-ethane})_2]$ (X = Cl, Br) [26], $[ReX_2(\text{diphenylphosphine etane})_2]X$ (X = Cl, Br) [27] complexes and octahedral $[OsX_6]^{2-}$ (X = F, Cl, Br, I) anions [28] [Os^{IV} ($t_{2g}{}^4e^0$) is isoelectronic with Re^{III}]. Although the spectral bands for the present rhenium(III) complexes (C_s symmetry) are expected to differ from those required for an O_h symmetry in agreement with Walton [26], we tentatively assign the well-resolved peak at *ca.* 1780 nm to spin-allowed ${}^3T_{1g}(\Gamma_1) \rightarrow {}^3T_{1g}(\Gamma_3,\Gamma_5)$ excitation between levels of the ground state ${}^3T_{1g}(t_{2g}{}^4)$ split by large spin-orbit coupling. Moreover, the two weaker bands at higher energy might be due to the formally spin-forbidden triplet → singlet ${}^3T_{1g}(\Gamma_1) \rightarrow {}^1T_{2g}$; ${}^1E_g$ transitions.

The ^{1}H NMR spectra of the $[ReOX_2(pymS)(PPh_3)]$ (X = Cl, Br, I) oxo-complexes in $CDCl_3$ solution show similar features, suggesting that the stereochemistry of the compounds is the same. Each resonance appears as a doublet (Table 2), which is indicative of the presence of two isomers. The relative intensities of the individual components of the doublets indicate that the molar ratio between the isomers, (which at room temperature remain constant with time) is 1 : 4 for the chloro- and bromo-derivatives and about 2 : 3 for the iodo-derivative. The signals observed in the regions 2.41–3.13, 6.69–6.91, and 7.36–7.83 ppm are closely similar to those previously found for the $[ReOCl_2(pymS)(PPh_3)]$ compound in the same solvent [1], and correspond to $—CH_3$, $—CH$ of pymS ligand and triphenylphosphine protons, respectively.

The presence of two isomers for $[ReOBr_2(pymS)(PPh_3)]$ and an isomeric ratio for $[ReOCl_2(pymS)(PPh_3)]$ different to that observed previously [1] may be ascribed to the phenomena reflecting the reaction of the tautomeric thione and thiol forms of the thiopyrimidine ligand with different $[ReOX_3(PPh_3)_2]$ and $[ReOX_2(EtO)(PPh_3)_2]$ (X = Cl, Br) precursors. However, given that the oxygenation reaction at room temperature in $CDCl_3$ solution of $[ReX_2(pymS)(PPh_3)_2] \cdot C_3H_6O$ (X = Cl, Br) species in the presence of atmospheric oxygen gives rise to the same pair of isomers for both $[ReOX_2(pymS)(PPh_3)]$ (X = Cl, Br), but with different ratios (1 : 2 for chloride and about 1 : 6 for bromide), it also turns out that the polarity of solvent, together with the temperature and reaction time, plays a role in the control of the isomer ratio.

The present $[ReX_2(pymS)(PPh_3)_2] \cdot C_3H_6O$ (X = Cl, Br) complexes possess the same structure of the complexes previously prepared [1] since, in $CDCl_3$ solution they show the same distinctive Knight-shifted ^{1}H NMR signals typical of mononuclear octahedral paramagnetic rhenium(III) species [29,30] whose sharpness is due to fast electronic relaxation of the metal center.[31] The spectrum of $[ReCl_2(pymS)(PPh_3)_2] \cdot C_3H_6O$ is shown in Fig. 5(a) and resonances assignments for both chloro- and bromo-compounds are listed in Table 2.

Kinetics studies

The remarkable spectroscopic (VIS-NIR, ^{1}H NMR) differences between rhenium(V) and rhe-

Table 2. ^1H NMR chemical shifts (δ/ppm) of pymSH and its Re^{III} and Re^{V} complexes in $CDCl_3$, at 27 ± 0.1 C

	—CH_3	—CH	Ph	—CH_3 (acetone)	—NH
pymSH	2.44 (s, 6 H)	6.48 (s, 1 H)			12.90 (b)
[$ReCl_2(pymS)(PPh_3)_2$] · Ac	−6.38 (s, 3 H) −1.10 (s, 3 H)	1.00 (s, 1 H)	14.27 (b, 12 H) 8.79 (b, 18 H)	2.18 (s, 6 H)	
[$ReBr_2(pymS)(PPh_3)_2$] · Ac	−5.77 (s, 3 H) −0.45 (s, 3 H)	1.15 (s, 1 H)	14.27 (b, 12 H) 8.75 (b, 18 H)	2.18 (s, 6 H)	
[$ReOCl_2(pymS)PPh_3$]	3.13 (s) 2.66 (s) 2.54 (s) 2.41 (s) (6 H)	6.91 (s) 6.69 (s) (1 H)	7.83 (m) 7.67 (m) 7.49 (m) 7.36 (m) (15 H)		
[$ReOBr_2(pymS)PPh_3$]	2.74 (s) 2.71 (s) 2.47 (s) 2.43 (s) (6 H)	6.73 (s) 6.69 (s) (1 H)	7.83 (m) 7.65 (m) 7.45 (m) 7.38 (m) (15 H)		
[$ReOI_2(pymS)PPh_3$]	2.79 (s) 2.74 (s) 2.54 (s) 2.51 (s) (6 H)	6.84 (s) 6.76 (s) (1 H)	7.83 (m) 7.65 (m) 7.52 (m) 7.38 (m) (15 H)		

nium(III) complexes and the spectral changes which occur with time at room temperature for $CHCl_3$ or $CDCl_3$ solutions of [$ReX_2(pymS)(PPh_3)_2$] (X = Cl, Br) species in aerobic conditions, allow the kinetic of conversion of [$ReX_2(pymS)(PPh_3)_2$] complexes to [$ReOX_2(pymS)(PPh_3)$] (X = Cl, Br) to be monitored with both VIS-NIR and ^1H NMR spectroscopic techniques. Analysis of the time-dependent absorption spectra reported in Fig. 3 (spectra: a, b, c, d, e) and Fig. 4 (spectra: a, b, c, d), shows that in $CHCl_3$ solution the [$ReX_2(pymS)(PPh_3)_2$] (X = Cl, Br) species originate in a few days time solution spectra which approximate to those showed by the corresponding [$ReOX_2(pymS)(PPh_3)$] chloro- (Fig. 3, spectrum f) and bromo- (Fig. 4, spectrum e) complexes in the same solvent. This indicates that the rhenium(III) species are indeed oxidized by atmospheric oxygen.

For the kinetic study of the disappearance of the rhenium(III) species we have selected the wavelength at about 1780 nm. The molar absorbance of this strong band remarkably decreases with time while a new band envelope centered between 600–900 nm appears (Figs 3, 4). The plots of $\log A_0/A_x$ *vs* time (A_0 = absorbance at $t = 0$, A_x = absorbance at $t = t_x$) are linear, showing that the disappearance of [$ReX_2(pymS)(PPh_3)_2$] (X = Cl, Br) species is a first-order process with a rate constant of 1.32×10^{-2} and 1.35×10^{-2} h^{-1} for chloro- and bromo-derivative, respectively. Additional support for the gradual oxygenation of the paramagnetic Re^{III} species is provided by proton NMR spectra. Figure 5 shows the ^1H NMR spectra of the [$ReCl_2(pymS)(PPh_3)_2$] · C_3H_6O complex in a freshly prepared solution (Fig. 5(a)) and after 118 h exposure to atmospheric oxygen (Fig. 5(b)).

Figure 6 shows that the sharp resonances at −6.38, −1.10, 1.00, 8.79 and 14.27 ppm, corresponding to —CH_3, —CH and meta-para and orto-protons of heterocyclic and phosphine ligands, respectively decrease with time. This is paralleled by the appearance and increase in intensity of new signals due to the formation of the two isomers of the [$ReOX_2(pymS)(PPh_3)$] species. The rate of disappearance of the [$ReX_2(pymS)(PPh_3)_2$] (X = Cl, Br) complexes was monitored by following the decrease of the integrated intensities of each resonance over a 118 h period.

From the average slope of the linear $\log A_0/A_x$ *vs* time plots (A_0 = integrated area of the peak at $t = 0$, A_x = integrated area of some peak for $t = t_x$) for each signal, rate constants of 1.24×10^{-2} and 1.27×10^{-2} h^{-1} for chloro- and bromo-derivatives were obtained, respectively. These values are close to those obtained from spectrophotometric measurements.

Unfortunately, owing to the overlapping signals of the triphenylphosphine protons which generate a complicated pattern in the aromatic region (7.85–7.35 ppm) (Fig. 5(b)), the time dependence of the ^1H NMR spectra of both [$ReX_2(pymS)(PPh_3)_2$] (X = Cl, Br) complexes do not provide any information whether, in addition to the coordinated phosphine of the [$ReOX_2(pymS)(PPh_3)$] product, the displaced mol-

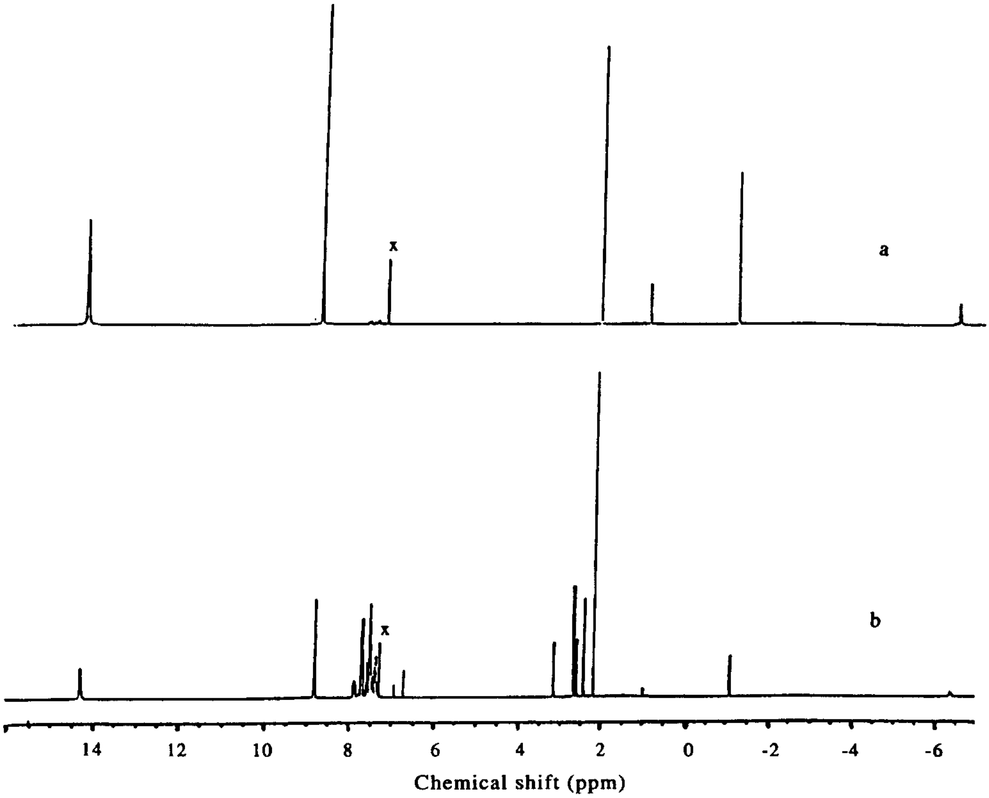


Fig. 5. 1H NMR spectra of $[ReCl_2(pymS)(PPh_3)_2] \cdot C_3H_6O$ recorded in $CDCl_3$: (a) fresh solution, (b) after standing in the presence of air for 118 h. The asterisks mark solvent peaks.

ecule of PPh_3 is present as it is or as triphenylphosphine oxide. This uncertainty has been removed by comparing the time course of the ^{31}P NMR spectra in $CDCl_3$ of the $[ReBr_2(pymS)(PPh_3)] \cdot C_3H_6O$ complex with those of PPh_3, $O{=}PPh_3$ and $[ReOBr_2(pymS)(PPh_3)]$ species. The spectrum of $[ReOBr_2(pymS)(PPh_3)]$ shows a single resonance at -33.20 ppm shifted upfield from the free PPh_3 (-7.85 ppm), while in a freshly prepared solution of paramagnetic $[ReBr_2(pymS)(PPh_3)_2]$ compound no ^{31}P signal was detected due to the line broadening caused by the paramagnetic center. When air is freely admitted into the sample, for example for a period of 55 h, a pair of signals, with about the same intensity, appear at -33.15 and 28.00 ppm. The former corresponds to that of the sample of $[ReOBr_2(pymS)(PPh_3)]$ and the latter is the "finger-print" of free triphenylphosphine oxide [32]. This result together with VIS-NIR and ^1H NMR data, confirms that the $[ReX_2(pymS)(PPh_3)_2]$ ($X = Cl$, Br) species upon exposure to atmospheric oxygen in organic solvents, undergo a concerted oxygenation of the metal center and of the released phosphine according to the overall reaction:

$$[ReX_2(pymS)(PPh_3)_2] + O_2 \rightarrow [ReOX_2(pymS)(PPh_3)] + O{=}PPh_3$$

Although interaction of dioxygen, as four-electron acceptor, with reduced transition metal ions is expected to be rather complex [33], we tentatively propose the following pathway for the reported reaction. In the first step the reducing rhenium(III) center, also due to its electronic unsaturation (16 valence electrons), allows the complex to undergo oxidative dioxygen addition reaction promoted by the dissociation [13,34] of a PPh_3 ligand. In the following step, the released PPh_3 base, interacting with a transient rhenium–dioxygen intermediate, causes scission of the polarized oxygen–oxygen bond [35], thus leading to a concerted stoichiometric formation of $[ReOX_2(pymS)(PPh_3)]$ ($X = Cl$, Br) and $O = PPh_3$ species. Since no intermediate adducts are observed, at least in the time scale of our experiments, the reaction must be fast.

Electrochemical measurements

Cyclic voltammetry measurements, performed on the *trans*-$[ReX_2(pymS)(PPh_3)_2] \cdot C_3H_6O$ complexes ($X = Cl$, Br) in methylene chloride, show two signals (Fig. 7). The electrochemical data are reported in Table 3. The peak current of the two waves is the same

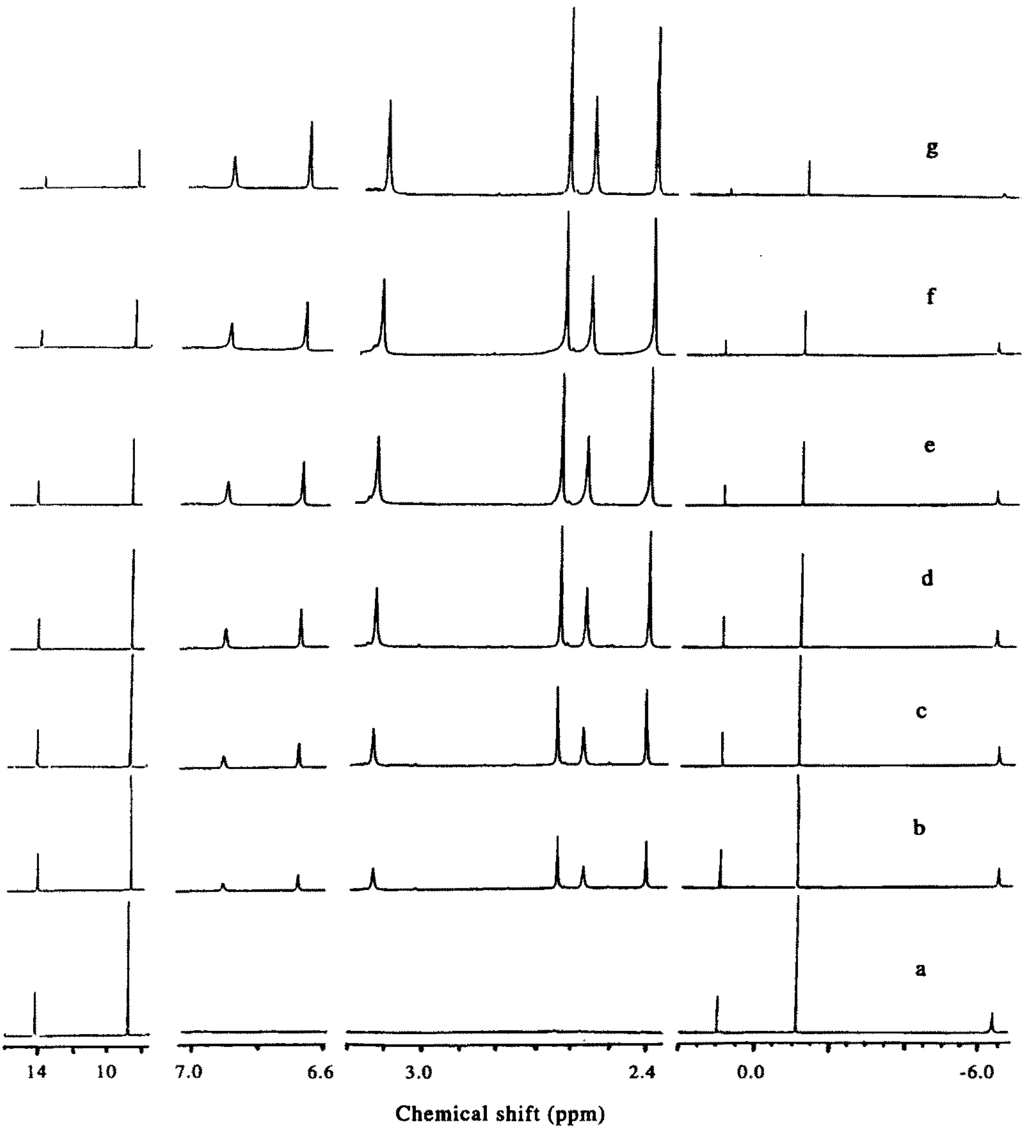


Fig. 6. Time dependence ^{1}H NMR spectra of [$ReCl_2(pymS)(PPh_3)_2$] · C_3H_6O complex in $CDCl_3$ in the presence of atmospheric oxygen. The spectrum (a) was taken on freshly prepared solution and the subsequent spectra were recorded after (b) 16.5; (c) 24.75; (d) 40.5; (e) 66.25; (f) 90.25 and (g) 118.0 h.

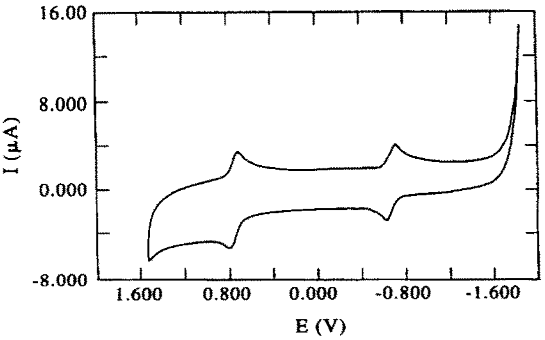


Fig. 7. Typical cyclic voltammogram under Argon, for [$ReX_2(pymS)(PPh_3)_2$] · C_3H_6O (X = Cl, Br) complexes as demonstrated by the voltammogram of [$ReBr_2(pymS)(PPh_3)_2$] · C_3H_6O taken in CH_2Cl_2 ($C = 10^{-4}$ mol dm^{-3}) scan rate of 0.5 V s^{-1}.

and is linearly proportional to both concentration of the complex and $v^{1/2}$ (v = scan rate). The peak-to-peak separation varies from 70 to 90 mV. Analysis of the electrochemical results indicates that the processes are quasi-reversible, single-electronic and diffusion controlled. The anodic signal at more positive potential can be attributed to the reversible oxidation of the complex, while the cathodic signal at more negative potential to the reversible reduction:

Couple I $[ReX_2(pymS)(PPh_3)_2] \rightleftharpoons [ReX_2(pymS)(PPh_3)_2]^+ + e^-$

Couple II $[ReX_2(pymS)(PPh_3)_2] + e^- \rightleftharpoons [ReX_2(pymS)(PPh_3)_2]^-$ (X = Cl, Br)

When X = Cl, the complex is more difficult to

Table 3. Electrochemical data (under Argon) of the complexes *trans*-$[ReX_2(pymS)(PPh_3)_2] \cdot C_3H_6O$ (X = Cl, Br) in CH_2Cl_2 ($C = 10^{-4}$ mol dm^{-3}), $T = 25$°C, base electrolyte TBAP 0.1 mol dm^{-3}, scan rate 0.5 V s^{-1}

	Couple I					Couple II				
	E_{pc} (V)	I_{pc} (μA)	E_{pa} (V)	I_{pa} (μA)	ΔE (V)	E_{pc} (V)	I_{pc} (μA)	E_{pa} (V)	I_{pa} (μA)	ΔE (V)
X = Cl	0.607	2.15	0.684	2.21	0.080	−0.856	1.98	−0.781	2.05	0.075
X = Br	0.722	2.06	0.802	2.15	0.080	−0.699	1.88	−0.631	1.93	0.068

reduce and is oxidized more easily due to the different coordinating ability of the chloride with respect to bromide ion. No kinetics process has been observed for the range of scan rate investigated. The CV curves of the chloro- and bromo-complexes of the rhenium(III) show that both the redox processes are reversible. In the presence of air or in O_2 atmosphere, the CV curves change with time and with O_2 pressure, until they correspond to those of the authentic rhenium(V) oxo-complexes. Time course of the decrease of the current values (I_{pc}) of the CV curves, shows that the disappearance of the $[ReX_2(pymS)(PPh_3)_2]$ (X = Cl, Br) species follows a pseudo-first order process with rate constants at 25°C of 1.2×10^{-2} (chloride), 1.3×10^{-2} h^{-1} (bromide) and 12.9×10^{-2} (chloride), 13.2×10^{-2} h^{-1} (bromide) in air and in O_2 atmosphere (1.1 bar), respectively.

Cyclic voltammetry measurements have been performed also on the rhenium(V) oxo-complexes $[ReOX_2(pymS)(PPh_3)]$ (X = Cl, Br, I). CV curves (Fig. 8) on the freshly prepared solutions show a quasi-reversible peak couple (I, II) at anodic potential values and an irreversible wave (III) in the cathodic range (Table 4). All the peak currents increase linearly with increasing complex concentration and $v^{1/2}$, but the current of the peak III is twice that of peaks I and II. Analysis of the CV curves indicates that the electrochemical process corresponding to the peaks couple I and II is reversible, single-electronic and diffusion controlled, while that of peak III is irreversible, two-electronic and diffusion controlled. The ratio between the peak currents of I and II is unity at $v = 0.6$ V s^{-1}, while it decreases with decreasing v. This fact indicates the presence of a relatively slow kinetic process following the oxidation step. These results allow us to propose a mechanism for the redox processes of peaks I and II:

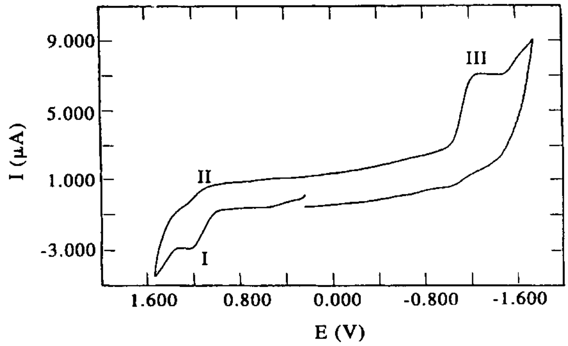


Fig. 8. Typical cyclic voltammogram under Argon, for $[ReOX_2(pymS)(PPh_3)]$ (X = Cl, Br, I) complexes as demonstrated by the voltammogram of $[ReOBr_2(pymS)(PPh_3)]$ taken in CH_2Cl_2 ($C = 10^{-4}$ mol dm^{-3}) at scan rate of 0.5 V s^{-1}.

$$[ReOX_2(pymS)(PPh_3)] \rightleftharpoons$$

$$[ReOX_2(pymS)(PPh_3)]^+ + e^- \quad (X = Cl, Br, I)$$

$$\downarrow \text{ slow}$$

degradation products

The electrochemical process corresponding to peak III indicates that the two-electronic reduction of the complex causes a remarkable modification or even destruction of the complex. In fact, reduction of rhenium(V) to rhenium(III) is accompanied by the breaking of the Re=O bond, which would justify the irreversibility of the reduction process. After a few hours all the signals decrease in intensity and definition. However, the observed reduction data for the rhenium(V) oxo-complexes, also in the presence of

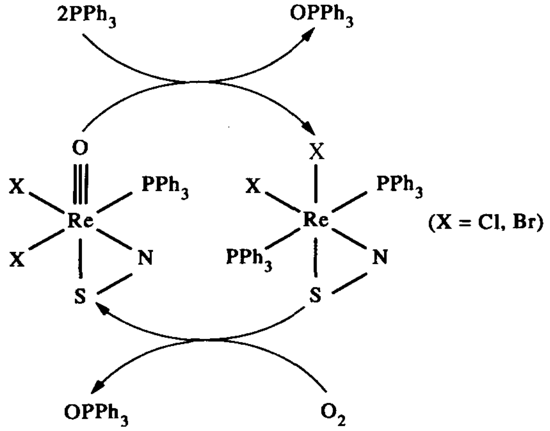
Table 4. Electrochemical data (under Argon) of the complexes $[ReOX_2(pymS)(PPh_3)]$ (X = Cl, Br, I) in CH_2Cl_2 ($C = 10^{-4}$ mol dm^{-3}), $T = 25$°C, base electrolyte TBAP 0.1 mol dm^{-3}, scan rate 0.5 V s^{-1}

	E_p^{I} (V)	I_p^{I} (μA)	E_p^{II} (V)	I_p^{II} (μA)	ΔE (I, II) (V)	E_p^{III} (V)	I_p^{III} (μA)
X = Cl	1.361	1.32	1.205	2.28	0.156	−1.436	4.69
X = Br	1.238	1.45	1.068	2.36	0.170	−1.269	4.56
X = I	1.117	1.48	0.886	2.34	0.231	−1.185	4.66

excess PPh_3, do not correspond to those obtained in the study of the rhenium(III) complexes. In fact, the rate of the electrochemical process is faster than that of the formation of the rhenium(III) complexes starting from rhenium(V) oxo-species and PPh_3, which occurs with time and under reflux. The complexity of the signals given by reductive process already observed for other oxo-complexes of the rhenium(V) [36], can be justified by adsorption processes on the electrode surface and by the reactivity of the reduction products with the solvent.

CONCLUSIONS

In organic solvents, oxo-rhenium(V) and rhenium(III) 4,6-dimethylpyrimidine-2-thiolate/triphenylphosphine mixed complexes, in the presence of a Lewis base as PPh_3 or atmospheric oxygen respectively, undergo redox reactions that intercovert $[ReO]^{3+} \rightleftharpoons [Re]^{3+}$ centers with concerted oxygenation of PPh_3 substrate to $OPPh_3$ according to the catalytic cycle, (Scheme 3).



Scheme 3.

The rhenium(V)-oxo complexes react, under reflux in acetone, with PPh_3 in 1 : 2 molar ratio to form $O{=}PPh_3$ and the *trans*-$[ReX_2(pymS)(PPh_3)_2]$ (X = Cl, Br) complexes. The reduced rhenium(III) species then react readily with atmospheric oxygen and more rapidly under O_2 atmosphere at room temperature in organic solvents ($CHCl_3$, CH_3COCH_3, CH_2Cl_2, C_6H_6), to reconstitute the active oxo-complexes and to oxidize PPh_3 to $O{=}PPh_3$. The present system seems to be an efficient catalytic system for oxygen atom transfer where the catalysis proceeds without the loss of the catalyst.

Acknowledgements—Financial support by the Italian Ministero della Università e della Ricerca Scientifica e Tecnologica (M.U.R.S.T. 40%) is gratefully acknowledged. The NMR and IR spectra were recorded in the Centro Interdipartimentale Grandi Strumenti of University of Modena.

REFERENCES

1. R. Battistuzzi, T. Manfredini, L. P. Battaglia, A. Bonamartini-Corradi and A. Marzotto *J. Cryst. Spectrosc. Res.* 1989, **19,** 513.
2. W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley, New York (1988).
3. R. H. Holm and J. R. Donahue, *Polyhedron* 1993, **12,** 571.
4. R. Barral, C. Bocard, J. Seree de Roch and L. Sajus, *Tetrahedron Lett.* 1972, **17,** 1693.
5. J. S. Valentine, *Chem. Rev.* 1973, **73,** 235.
6. A. V. Savitskii and V. I. Nelyubin, *Russ. Chem. Rev.* (*Engl. Transl.*) 1975, **44,** 110.
7. L. Vaska, *Acc. Chem. Res.* 1976, **9,** 175.
8. J. Chatt and G. A. Rowe, *J. Chem. Soc.* 1962, 4019.
9. N. P. Johnson, C. J. L. Lock and G. Wilkinson, *Inorg. Synth.* 1967, **9,** 147.
10. G. V. Parsall, *Inorg. Synth.* 1977, **17,** 110.
11. R. Battistuzzi and G. Peyronel, *Trans. Met. Chem.* 1978, **3,** 345.
12. D. E. Grove, N. P. Johnson, C. J. L. Lock and G. Wilkinson, *J. Chem. Soc.* 1965, 490.
13. R. R. Conry and J. M. Mayer, *Inorg. Chem.* 1990, **29,** 4862.
14. G. Rouschias and G. Wilkinson, *J. Chem. Soc. A*, 1967, 993.
15. S. P. Gupta, S. Sharma and R. K. Goel, *Spectrochim. Acta, Part A* 1986, **42,** 1171.
16. G. Shaw, *J. Chem. Soc., Chem. Comun.* 1966, 425.
17. F. A. Cotton and S. J. Lippard, *Inorg. Chem.* 1966, **5,** 9.
18. F. A. Cotton, W. R. Robinson and R. A. Walton, *Inorg. Chem.* 1967, **6,** 223.
19. D. Davis and J. E. Fergusson, *Inorg. Chim. Acta* 1976, **4,** 16.
20. K. V. Kotegov, A. A. Amindzhanov and Y. N. Kukushkin, *Russ. J. Inorg. Chem.* (*Engl. Trans.*) 1977, **22,** 1489.
21. H. B. Gray and C. R. Hare, *Inorg. Chem.* 1962, **1,** 363.
22. J. E. Winkler and H. B. Gray, *Inorg. Chem.* 1985, **24,** 346.
23. N. B. Figgis, *Introduction to Ligand Fields*, Wiley, New York (1966).
24. J. E. Fergusson, *Coord. Chem. Rev.* 1966, **1,** 459.
25. A. Earnshaw, B. N. Figgis, J. Lewis and R. D. Peacock, *J. Chem. Soc.* 1961, 3132.
26. J. A. Jaecher, D. P. Murtha and R. A. Walton, *Inorg. Chim. Acta* 1975, **13,** 21.
27. F. Cariati, A. Sgamellotti, F. Morazzoni and V. Valenti, *Inorg. Chim. Acta* 1971, **5,** 531.
28. G. C. Allen, R. Al-Mobarak, G. A. M. El-Sharkawy and K. D. Warren, *Inorg. Chem.* 1972, **4,** 787.
29. E. Randall and D. Shaw, *J. Chem. Soc. A* 1969, 2867.
30. R. Rossi, A. Duatti, L. Magon, U. Casellato, R. Graziani and L. Toniolo, *J. Chem. Soc., Dalton Trans.* 1982, 1949.
31. I. Bertini and C. Luchinat, in *Physical Methods for Chemists* (Edited by R. S. Drago). Saunders College Publishing, New York (1992).

32. N. Burford, *Coord. Chem. Rev.* 1992, **112,** 1.
33. E. I. Ochiai, *Inorg. Nucl. Chem. Lett.* 1974, **10,** 453.
34. R. B. James, S. R. Mikkelsen, T. W. Leung, M. G. Williams and R. Wong, *Inorg. Chim. Acta* 1984, **85,** 209.
35. H. Mimoun, in *Comprehensive Coordination Chemistry* (Edited by G. Wilkinson, R. D. Gillard and J. A. McCleverty) vol. 6, p. 318. Pergamon Press, New York (1987).
36. G. N. Holder and G. A. Montheit, *Trans. Met. Chem.* 1992, **17,** 109.