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Chemistry of azopyrimidine chelates of $Re^{V}O$, $Re^{III}OPPh_3$ and $Re^{V}NAr$

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Abstract

The concerned azo ligands are L^1, L^2 and L^3 (general abbreviation L) in which the aryl groups are phenyl, *p*-chlorophenyl and *o*,*p*-dichlorophenyl, respectively. The reaction of L^1 with $KReO_4$ in hot concentrated HCl affording $[Re^{V}OCl_3(L^2)]$ (**2a**), is attended with aryl chlorination. A similar reaction with L^2 furnished $[Re^{V}OCl_3(L^3)]$ (**2b**). The oxo complexes spontaneously reacted with PPh_3 and $ArNH_2$ furnishing $[Re^{III}(OPPh_3)Cl_3(L)]$ (**3**) and $[Re^{V}(NAr)Cl_3(L)]$ (**4**), respectively. Unlike **2** and **4**, **3** displays large paramagnetic ^1H NMR shifts. The type **2** species exhibit an irreversible electrochemical $Re^{V} \rightarrow Re^{VI}$ oxidation near 2.2 V versus SCE. In type **4** species the Re^{VI}/Re^{V} couple occurs near 1.5 V and in type **3** species the Re^{IV}/Re^{III} couple lies near 1.2 V. Structure determination of **2b**, $[Re^{III}(OPPh_3)Cl_3(L^1)]$ (**3a**) and $[Re^{V}(NC_6H_4Cl\text{-}p)Cl_3(L^2)]$ (**4b**) have revealed uniform meridional geometry. In **2b** the Re–O and in **4b** the Re–N (imide) distances are 1.666(10) and 1.719(6) Å, respectively, consistent with triple bonding. The Re–N bonds lying *trans* to the oxo oxygen **2b** and to the imide nitrogen in **4b** are substantially lengthened. The Re–N(azo) lengths are 2.072(13), 1.957(9) and 2.003(6) Å in **2b**, **3a** and **4b**, the corresponding N–N distances being 1.25(2), 1.318(11) and 1.305(9) Å, respectively. In **3a** dπ(Re)-π* (azo) back-bonding is clearly present and in **4b** electron flow to the azo (π*) orbital occurs via the route $ArN \rightarrow Re^{V} \rightarrow$ azo(π*). The corresponding route in **2b** is less effective because the oxo group is a poorer donor compared with the imido group. In the lattice of **4b** noncovalent Cl···Cl and aromatic π-stacking are present.

Keywords: Azopyrimidine chelates; Rhenium azo chelates; Rhenium pyrimidine chelates; Rhenium azopyrimidine chelates

1. Introduction

This work stems from our interest in the synthesis, structure and reactions of new oxorhenium(V) reagents incorporating chelation by heterocyclic donor sites [1,2]. Recently we initiated a programme on the rhenium chemistry of azoheterocyclic ligands [3,4] which have pronounced π-acidic [5–10] properties. In the present work we report the first instances of the binding of rhenium by 2-(arylazo)pyrimidines. Oxorhenium(V) chelates have been isolated. The synthesis is attended with spontaneous and regiospecific chlorination of the aryl group. The oxo chelates undergo facile transformation to $Re^{III}OPPh_3$ and $Re^{V}NAr$ species upon treatment with PPh_3 and aromatic amines, respectively. The structure and properties of the azopyrimidine chelate family are described in this work.

2. Experimental

2.1. General considerations

$[ReOCl_3(PPh_3)_2]$ [11], and 2-(arylazo)pyrimidine [12] were prepared by reported methods. Potassium perrhenate and triphenyl phosphine were purchased from Aldrich (USA). For electrochemical work HPLC grade

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acetonitrile was used. All other chemicals and solvents were of reagent grade and were used as received.

UV–Vis spectra (CH_2Cl_2 solution), IR spectra (KBr disk), and ^1H NMR spectra ($CDCl_3$) were recorded on a Shimadzu UVPC 1601 spectrophotometer, a Nicolet Magna IR 750 Series II spectrometer, and a Bruker FT 300 MHz spectrometer, respectively. The numbering scheme used for ^1H NMR assignment is the same as in crystallography. Spin–spin structures are abbreviated as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Cyclic voltammetry (in MeCN, 0.1 M TEAP) was done at a platinum working electrode under nitrogen atmosphere on a PAR model 370-4 electrochemistry system [13]. Microanalyses (C, H, N) were performed using a Perkin–Elmer 2400 Series II elemental analyser.

2.2. Synthesis of [$ReOCl_3(L)$] (**2**)

The complexes were prepared by the same general methods. Details are given for [$ReOCl_3(L^2)$] (**2a**).

To a hot solution of $KReO_4$ (250 mg, 0.86 mmol) in 10 ml of concentrated hydrochloric acid was added 962 mg (5.2 mmol) of L^1. The resulting mass was stirred magnetically and heated to reflux for 1.5 h. A dark solid started depositing from the solution which was then cooled to room temperature (r.t.). The solid collected by filtration was made acid-free by washing several times with water. It was finally washed with *n*-hexane and then dried in vacuo over fused calcium chloride. Yield: (362 mg, 80%). *Anal*. Calc. for $C_{10}H_7Cl_4N_4ORe$: C, 22.78; H, 1.34; N, 10.63. Found: C, 22.88; H, 1.39; N, 10.67%. UV–Vis (λ_{max} (nm) (ε, M^{-1} cm^{-1})): 531 (2900); 375 (5760). IR (cm^{-1}, KBr pellet): 1000 (Re–O), 1341 (N=N). ^1H NMR ($CDCl_3$) δ: H1 9.26 (d, *J* 4.5 Hz); H2 6.71 (t, *J* 5.2Hz); H3 8.88 (d, *J*, 5.4 Hz); H6, H10 7.93 (d, *J* 8.8 Hz); H7 H9 7.57 (d, *J* 7.8 Hz).

2.2.1. [$ReOCl_3(L^3)$] (**2b**)

Anal. Calc. For $C_{10}H_6Cl_5N_4ORe$: C, 21.38; H, 1.08; N, 9.98. Found: C, 21.49; H, 1.12; N, 9.90%. UV–Vis (λ_{max} (nm) (ε, M^{-1} cm^{-1})): 529 (2750), 372 (5980). IR (cm^{-1}, KBr pellet): 1000 (Re–O), 1340 (N=N). ^1H NMR ($CDCl_3$) δ: H1 9.24 (d, *J* 4.5 Hz); H2 6.65 (t, *J*, 4.8 Hz); H3 8.86 (d, *J* 6.0 Hz); H6 7.77 (d, *J* 8.7 Hz); H7 7.40 (d, *J* 8.7 Hz); H9 7.51 (s).

2.3. Synthesis of [$Re(OPPh_3)Cl_3(L)$] (**3**)

The same general methods were used for all the complexes. The case for [$Re(OPPh_3)Cl_3(L^2)$] (**3b**) is detailed below.

To a solution of (**2a**) (100 mg, 0.19 mmol) in 15 ml of dichloromethane was added 252 mg (0.96 mmol) of PPh_3. The pink solution turned yellowish brown instantly, and it was stirred for 5 min at r.t. The solvent was then removed under reduced pressure, and the solid thus obtained was subjected to column chromatography on a silica-gel column (60–120 mesh). The yellowish brown band was eluted using benzene–acetonitrile (25:1.5) mixture, and from the eluate **3b** was obtained in pure form. Yield: (108 mg, 70%). *Anal.* Calc. for $C_{28}H_{22}Cl_4N_4OPRe$: C, 42.60; H, 2.81; N, 7.10. Found: C, 42.65; H, 2.96; N, 7.19%. UV–Vis (λ_{max} (nm) (ε, M^{-1} cm^{-1})): 443 (4800); 334 (9260). IR (cm^{-1}, KBr pellet): 1120 (O=P), 1397 (N=N).^1H NMR ($CDCl_3$) δ: H1, −39.5 (ill resolved); H2, 50.6 (ill-resolved); H3, −25.5 (ill-resolved); H6, H10, 35.5 (d, *J* 7.8 Hz); H7, H9, 9.45 (d, *J* 7.5Hz); aromatic multiplets, 7.69–6.29.

2.3.1. [$Re(OPPh_3)Cl_3(L^3)$] (**3c**)

Anal. Calc. for $C_{28}H_{21}Cl_5N_4OPRe$: C, 40.80; H, 2.57; N, 6.80. Found: C, 40.76; H, 2.64; N, 6.89%. UV–Vis (λ_{max} (nm) (ε, M^{-1} cm^{-1})): 445 (4550); 339 (8760). IR (cm^{-1}, KBr pellet): 1121 (O=P), 1396 (N=N). ^1H NMR ($CDCl_3$) δ: H1, −39.7 (ill-resolved); H2, 50.8 (ill-resolved); H3, −25.6 (ill-resolved); H6, 35.9 (d, *J* 8.0 Hz); H7, 11.9 (d, *J*, 8.0 Hz); H9, 9.41 (s); aromatic multiplets; 7.62–6.23.

2.4. Synthesis of [$Re(OPPh_3)Cl_3(L^1)$] (**3a**) from [$ReOCl_3(PPh_3)_2$]

To a suspension of [$ReOCl_3(PPh_3)_2$] (100 mg, 0.12 mmol) in 20 ml of benzene was added 30 mg (0.16 mmol) of L^1, and the mixture was stirred for 30 min. The solvent was then removed under reduced pressure. The solid thus obtained was dissolved in 5 ml of dichloromethane and subjected to column chromatography in the same manner as described earlier. An yellowish brown band was eluted out with benzene–acetonitrile (25:1.5) mixture. The required complex **3a** was then obtained from the eluate as yellowish microcrystals. Yield: (46 mg, 50%). *Anal.* Calc. for $C_{28}H_{23}Cl_3N_4OPRe$: C, 44.54; H, 3.07; N, 7.42. Found: C, 44.63; H, 3.18; N, 7.54%. UV–Vis (λ_{max} (nm) (ε, M^{-1} cm^{-1})): 448 (4500); 337 (9730). IR (cm^{-1}, KBr pellet): 1122 (O=P), 1395 (N=N). ^1H NMR ($CDCl_3$) δ: H1, −39.4 (ill-resolved); H2, 50.2 (ill resolved); H3, −25.7 (ill-resolved); H6, H10, 35.7(d, *J* 8.0 Hz); H7, H9, 9.51 (t, *J* 7.3 Hz); H8, 7.23 (t, *J* 7.5 Hz).

2.5. Synthesis of [$Re(NC_6H_4Cl\text{-}p)Cl_3(L^2)$] (**4b**) from [$ReOCl_3(L^2)$] (**2a**)

To a warm solution of **2a** (100 mg, 0.19 mmol) in 10 ml of toluene was added an excess of *p*-chloro aniline (121 mg, 0.95 mmol), and the mixture was heated to reflux for 1 h. During this time the colour changed from pinkish red to red–violet. The solvent was then removed under reduced pressure, and the solid thus obtained was subjected to column chromatography. The violet band was eluted using toluene–acetonitrile (25:1) mixture,

and from the eluate **4b** was obtained in pure form. Yield: (85 mg, 70%). *Anal.* Calc. for $C_{16}H_{11}Cl_5N_5Re$: C, 30.18; H, 1.74; N, 11.00. Found: C, 30.29; H, 1.67; N, 11.10%. UV–Vis (λ_{max} (nm) (ε, M^{-1} cm^{-1})): 510 (2700); 326 (6450). IR (cm^{-1}, KBr pellet): 1396 (N=N). ^1H NMR ($CDCl_3$) δ: H1, 9.34 (d, *J* 6.0 Hz); H2, 6.68 (t, *J* 5.1 Hz); H3, 9.16 (d, *J* 4.1 Hz); H6, H10, 7.48 (d, *J* 9.0 Hz); H7, H9, 7.32 (d, *J* 9.0 Hz); H12, H16, 7.23 (ill resolved); H13, H15, 7.17 (d, *J* 8.7 Hz).

2.6. Synthesis of $[Re(NC_6H_5)Cl_3(L^1)]$ (**4a**) from $[ReOCl_3(PPh_3)_2]$

To a suspension of $[ReOCl_3(PPh_3)_2]$ (100 mg, 0.12 mmol), in 20 ml of toluene was added 56 mg (0.30 mmol) of L^1, and the mixture was allowed to reflux for 2 h. The resulting red–violet solution was evaporated under reduced pressure. The solid mass thus obtained was dissolved in 5 ml of dichloromethane and was subjected to column chromatography on a silica-gel column as mentioned above. A red–violet band was eluted using toluene–acetonitrile (25:1) mixture. Solvent removal from the eluate afforded **4a** in pure crystalline form. Yield (47 mg, 65%). *Anal*. Calc. for $C_{16}H_{13}Cl_3N_5Re$: C, 33.84, H, 2.31; N, 12.33. Found: C, 33.77; H, 2.35; N, 12.38%. UV–Vis (λ_{max} (nm) (ε, M^{-1} cm^{-1})): 512 (2550); 323 (6800). IR (cm^{-1}, KBr pellet): 1397 (N=N). ^1H NMR ($CDCl_3$) δ: H1, 9.36 (d, *J* 6.0 Hz); H2, 6.69 (t, *J* 4.7 Hz); H3, 9.14 (d, *J* 4.5 Hz); H6, H10, 7.54 (d, *J* 6.0 Hz); H7, H9, 7.28 (multiplet); H8, 7.28 (multiplet); H12, H16, 7.20 (multiplet); H13, H15, 7.20 (multiplet).

2.7. X-ray crystallography

Single crystals of **2b**, **3a** and **4b** were grown by slow diffusion of hexane into dichloromethane solution. Cell parameters were determined by a least-squares fit of 30 machine-centred reflections ($14^\circ \le 2\theta \le 28^\circ$). Data were collected by the ω scan technique in the range $3^\circ \le 2\theta \le 50^\circ$ for **2b** and $3^\circ \le 2\theta \le 47^\circ$ for **3a** and **4b** on a Nicolet R3*m*/*V* four-circle diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation at 25 °C. Two check reflections after each 198 reflections showed no significant intensity reduction. All data were corrected for L_p effects and absorption [14].

In all the cases metal atoms were located from Patterson maps, and the rest of the nonhydrogen atoms emerged from successive Fourier synthesis. The structures were refined by full-matrix least-squares procedures on F^2. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions [$U = 0.08$ Å^2]. Calculations were performed using the SHELXTL V5.03 [15] program package. Significant crystal data are listed in Table 1.

Table 1
Crystallographic data for $[ReOCl_3(L^3)]$ (**2b**), $[Re(OPPh_3)Cl_3(L^1)]\cdot H_2O$ (**3a**)$\cdot H_2O$ and $[Re(NC_6H_4Cl\text{-}p)Cl_3(L^2)]$ (**4b**)

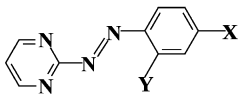
	2b	**3a**	**4b**
Empirical formula	$C_{10}H_6Cl_5N_4ORe$	$C_{28}H_{25}Cl_3N_4O_2PRe$	$C_{16}H_{11}Cl_5N_5Re$
Formula weight	561.64	773.04	636.75
Crystal system	orthorhombic	monoclinic	triclinic
Space group	*Pbca*	$P2_1/n$	$P\bar{1}$
a (Å)	10.450(4)	9.390(5)	9.604(3)
b (Å)	11.596(5)	21.014(9)	10.834(3)
c (Å)	25.549(9)	15.023(5)	11.383(3)
α (°)			63.40(2)
β (°)		96.25(4)	71.32(2)
γ (°)			84.59(2)
V (Å^3)	3096(2)	2947(2)	1001.6(5)
Z	8	4	2
D_{calc} (Mg m^{-3})	2.410	1.742	2.111
μ (mm^{-1})	8.713	4.483	6.745
θ Range (°)	1.59–25.00	1.67–23.50	2.11–23.50
R [a], wR_2 [b] [$I > 2\sigma(I)$]	0.0549, 0.0924	0.0434, 0.1147	0.0300, 0.0843
Goodness-of-fit on F^2	1.071	0.905	0.762

[a] $R = ||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

3. Results and discussion

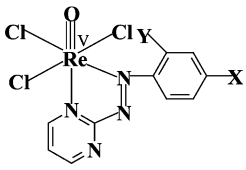
3.1. Synthesis

The three azopyrimidine ligands [12], (**1**), concerning this work are L^1, L^2 and L^3. Ligand L^1 reacted virtually quantitatively with $KReO_4$ in hot concentrated hydrochloric acid furnishing the pink coloured complex **2a** of ligand L^2. In this reaction the metal oxidation state changes from $+7 \rightarrow +5$ and the aryl group is chlorinated at *para*-position. Upon using the L^2 ligand in the above synthesis, chlorination occurs at the *ortho*-position and the complex **2b** is isolated. Aryl chlorination is an integral part of this synthesis. In the strongly acidic reaction medium metal reduction in presence of L appears to be attended with incipient generation of electrophilic Cl^+ which chlorinates. The net observed reaction in the case of L^2 is stated in Eq. (1) where L^3 is a chlorinated derivative of L^2. One instance of this type of chlorination was observed earlier in the case of 2-(phenylazo)pyridine [4].



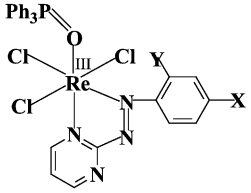
L^1 (X = Y = H)
L^2 (X = Cl, Y = H)
L^3 (X = Y = Cl)

1



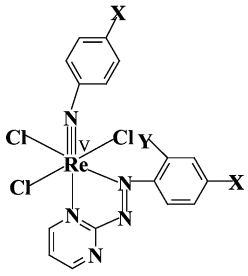
(2a) [$ReOCl_3(L^2)$]
(2b) [$ReOCl_3(L^3)$]

2



(3a) [$Re(OPPh_3)Cl_3(L^1)$]
(3b) [$Re(OPPh_3)Cl_3(L^2)$]
(3c) [$Re(OPPh_3)Cl_3(L^3)$]

3



(4a) [$Re(NC_6H_5)Cl_3(L^1)$]
(4b) [$Re(NC_6H_4Cl)Cl_3(L^2)$]

4

$$Re^{VII}O_4^- + L^2 + 5HCl \rightarrow \underset{\mathbf{2b}}{[ReOCl_3(L^3)]} + 3H_2O + Cl^- \quad (1)$$

The type **2** species are potent oxygen atom transfer reagents which react, Eq. (2), smoothly with PPh_3 in benzene affording the yellowish brown phosphine oxide complex **3**. The complex **3a** incorporating L^1 was afforded by the reaction of $[ReOCl_3(PPh_3)_2]$

$$\mathbf{2} + PPh_3 \rightarrow \underset{\mathbf{3}}{[Re^{III}(OPPh_3)Cl_3(L)]} \quad (2)$$

with the ligand, thus avoiding aryl chlorination.

The Re^VO oxygen atom in **2** can be eliminated in the oxide form by reacting with excess arylamines, in toluene, Eq. (3) affording violet coloured imido species of type **4**. The complex $[Re(NC_6H_5)Cl_3(L^1)]$ has been prepared from $[ReOCl_3(PPh_3)_2]$ and L^1, the imido group arising via azo splitting [4].

$$\mathbf{2} + ArNH_2 \rightarrow \underset{\mathbf{4}}{[Re^V(NAr)Cl_3(L)]} + H_2O \quad (3)$$

3.2. Spectra

Spectral data are given in Section 2. The type **2** and type **3** complexes, respectively, display Re≡O and P=O stretches near 1000 and 1120 cm^{-1}, respectively. The N=N stretch in the complexes generally occur near 1390 cm^{-1}. The type **2**, **3** and **4** species display a charge transfer band in the visible region near 530, 445 and 510 nm, respectively. The rhenium(V) species **2** and **4** are diamagnetic and display well-resolved ^1H NMR spectra in the region 5–10 ppm. On the other hand the rhenium(III) complexes **3** are paramagnetic and show large shift [3,4,16] in their ^1H NMR spectra. The protons of the L ligand span the chemical shift range from +51 to −40 ppm.

3.3. Electrochemistry

All the complexes reported in this work are electroactive in acetonitrile solution. Reduction potential data are listed in Table 2 and representative voltammograms are shown in Fig. 1. The oxo complexes display an irreversible one-electron $Re^V \rightarrow Re^{VI}$ oxidation near 2.2 V versus SCE. The imido ligand is a superior electron donor than the oxo ligand and the metal is more easily oxidised in the imido species of type **4**, the reduction potential of the quasireversible Re^{VI}/Re^V couple being ~1.5 V. In the phosphine oxide species the Re^{IV}/Re^{III}

Table 2
Cyclic voltametric data in acetonitrile solution (0.1 M TEAP) [a]

Compound	$E_{1/2}$ (V) (ΔE_p (mV))	
	az/az$^-$	Re^{n+1}/Re^n
2a	0.18(80)	2.16 [b]
2b	0.17(70)	2.18 [b]
3a	−0.46 [c]	1.20(100)
3b	−0.42 [c]	1.19(60)
3c	−0.40 [c]	1.18(80)
4a	−0.31(60)	1.52(80)
4b	−0.22(80)	1.56(80)

[a] Conditions: working electrode, platinum; reference electrode, SCE; scan rate 50 mV s^{-1}. $E_{1/2} = 1/2(E_{pa} + E_{pc})$ where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively, $\Delta E_p = E_{pc} - E_{pa}$; $n = 5$ for compound **2** and **4** and $n = 3$ for compound **3**.
[b] E_{pa}.
[c] E_{pc}.

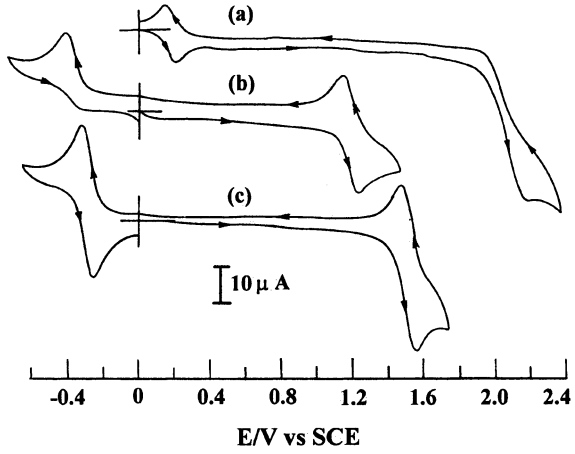


Fig. 1. Cyclic voltammograms of ≈ 10^{-3} mol dm^{-3} solutions of (a) $[ReOCl_3(L^2)]$ (**2a**), (b) $[Re(OPPh_3)Cl_3(L^2)]$ (**3b**) and (c) $[Re(NC_6H_5)Cl_3(L^1)]$ (**4a**) in acetonitrile solution at a platinum working electrode.

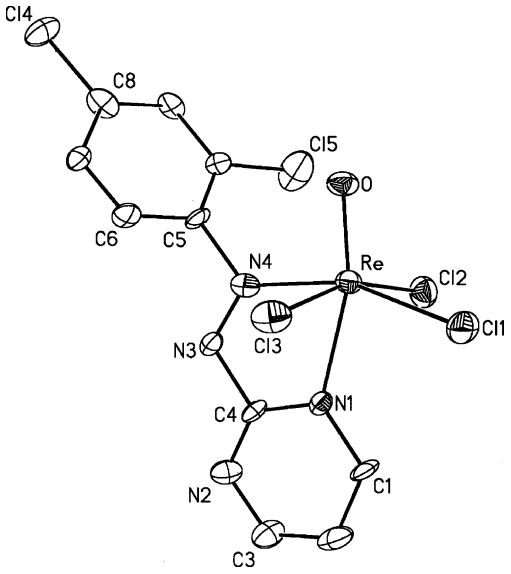


Fig. 2. Molecular view and atom labelling scheme for $[ReOCl_3(L^3)]$ (**2b**). All nonhydrogen atoms are represented by 30% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity.

couple occur near 1.2 V. The metal reduction potentials of the present complexes are significantly higher (by ~ 0.2 V) than those of corresponding complexes incorporating chelation by 2-(arylazo)pyridine [4] and 2-(arylazo)imidazole [3] reflecting the milder inferior overall donor ability of the 2-(arylazo)pyrimidine ligand.

All the complexes also display a response at negative potentials assignable to azo reduction [5,6] consistent with the relatively low-lying nature of the azo π* orbital which can thus participate in back-bonding (see structure of (**3a**)).

3.4. Structure

The structure of $[ReOCl_3(L^3)]$ (**2b**) shown in Fig. 2 authenticates the chlorination reaction of Eq. (1). In the distorted octahedral coordination sphere the $ReCl_3$ fragment is meridionally disposed. The Cl1, Cl2, Cl3 and N4 atoms constitute an excellent plane with mean deviation 0.01 Å. The metal atom is displaced from the plane towards the oxo oxygen atom by 0.36 Å. The chelate ring is planar (mean deviation 0.03 Å) and the pyrimidine ring is coplanar with it. The pendant dichlorophenyl ring makes a dihedral angle of 65° with this plane. Selected bond parameters are collected in Table 3. The Re–O distance in **2b**, 1.666(10) Å lies well within the range 1.68 ± 0.03 Å which is usually spanned by $Re^{V}O$ species [1–3]. Idealised $Re^{V}{\equiv}O$ and $Re^{V}{=}O$ lengths are estimated to be 1.60 and 1.75 Å, respectively, [17,18]. Thus the Re–O bond order in **2b** is close to three ($\sigma^2\pi^4$). The Re–N1 distance, 2.218(13) Å is significantly longer than Re–N4 distance, 2.072 (13) Å reflecting the *trans* influence of the oxo oxygen.

Table 3
Selected bond distances (Å) and angles (°) for **2b**, **3a** and **4b**

	2b	**3a**	**4b**
Bond distances			
Re–O	1.666(10)	2.021(6)	
Re–N5			1.719(6)
Re–N4	2.072(13)	1.957(9)	2.003(6)
Re–N1	2.218(13)	2.022(8)	2.173(6)
Re–Cl1	2.317(4)	2.341(3)	2.350(2)
Re–Cl2	2.337(5)	2.326(3)	2.393(2)
Re–Cl3	2.336(5)	2.336(3)	2.331(2)
N3–N4	1.25(2)	1.318(11)	1.305(9)
P–O		1.501(7)	
Bond angles			
O–Re–N4	90.4(5)	100.6(3)	
N5–Re–N4			93.5(3)
O–Re–N1	160.7(5)	174.6(3)	
N5–Re–N1			162.4(3)
N4–Re–N1	70.4(5)	74.0(4)	72.5(2)
O–Re–Cl1	109.3(4)	91.5(2)	
N5–Re–Cl1			103.7(2)
N4–Re–Cl1	159.5(4)	167.0(3)	162.8(2)
N1–Re–Cl1	90.0(3)	93.9(3)	90.8(2)
O–Re–Cl2	99.3(4)	88.1(2)	
N5–Re–Cl2			90.0(2)
N4–Re–Cl2	97.0(4)	95.6(2)	93.8(2)
N1–Re–Cl2	81.6(3)	92.7(3)	80.6(2)
Cl1–Re–Cl2	85.6(2)	89.56(13)	87.41(8)
O–Re–Cl3	98.8(4)	88.5(2)	
N5–Re–Cl3			102.9(2)
N4–Re–Cl3	85.3(4)	87.0(2)	98.4(2)
N1–Re–Cl3	82.1(3)	90.9(3)	88.0(2)
Cl1–Re–Cl3	86.2(2)	88.57(13)	85.65(8)
Cl2–Re–Cl3	161.7(2)	176.04(10)	166.50(8)
C11–N5–Re			164.3(5)

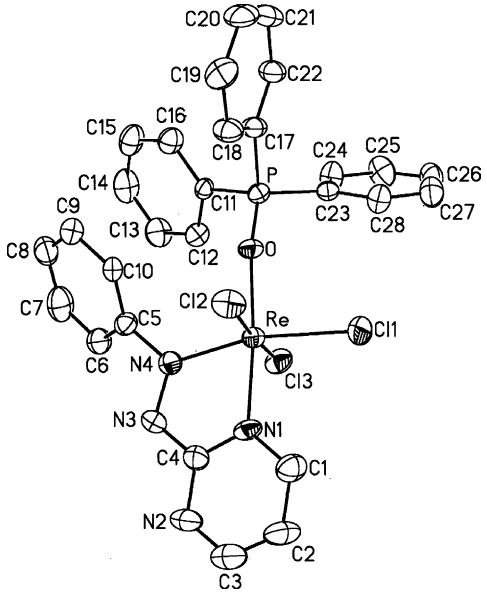


Fig. 3. Molecular view and atom labelling scheme for $[Re(OPPh_3)Cl_3(L^1)]$ (**3a**). All nonhydrogen atoms are represented by 30% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity.

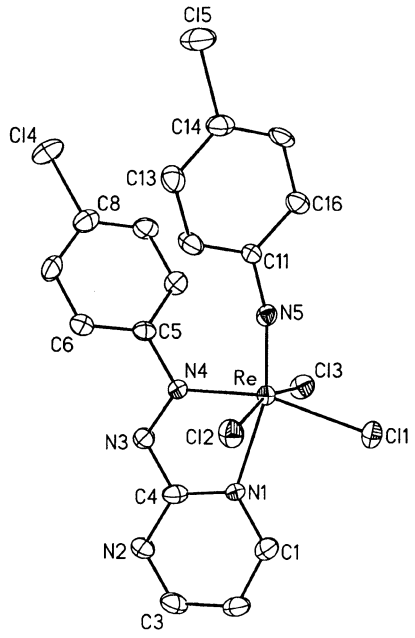


Fig. 4. Molecular view and atom labelling scheme for [Re(NC_6H_4Cl-*p*)Cl_3(L^2)] (**4b**). All nonhydrogen atoms are represented by 30% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity.

The structure of [Re($OPPh_3$)Cl_3(L^1)] (**3a**) is shown in Fig. 3. It has the same gross meridional geometry as observed in **2b**. The Re–O, 2.021(6) Å, length has increased by 0.36 Å compared with that in **2b** due to the decrease of bond order from 3 to 1. In effect the metal atom has descended away from the oxygen atom into a pseudo-plane defined by C11, Cl2, Cl3 and N4 (mean deviation 0.15 Å). The chelate ring is only approximately planar (mean deviation 0.06 Å) and the planar pyrimidine ring makes a dihedral angle of 6.9° with the chelate ring. The pendant phenyl ring is inclined to the chelate ring by 46°. The Re–N1 length, 2.022(8) Å (Table 3) in **3a** is ~0.2 Å shorter than that in **2b** due to elimination of *trans* influence. The Re–N4 length, 1.957(9) Å is also shorter (by ~0.1 Å) in **3a** reflecting the π-basicity of trivalent rhenium [2,3,19] which engages in substantial back-bonding with the π*(azo) orbital. It is significant that N–N length in **3a** is 0.06 Å longer than that in **2b**. Lastly, among the centroids of the four triangular faces with O as the common vertex, that of the face defined by O1, Cl1 and Cl3 lie closest to the P atom: 2.88 Å (the other distances are in the range 3.09–3.19 Å). The initial nucleophilic attack of PPh_3 on $Re^{V}O$ may have occurred from the side of the face above noted which is also the least hindered.

A view of [Re(NC_6H_4Cl-*p*)Cl_3(L^2)] (**4b**) is shown in Fig. 4. Like **2b** and **3a** it also has a meridional $ReCl_3$ fragment. The Cl1, Cl2, Cl3 and N4 atoms constitute a good plane (mean deviation 0.03 Å) from which the metal atom is displaced towards imide nitrogen by 0.29 Å (in **2b** the corresponding displacement towards oxo oxygen was 0.36 Å). The chelate ring is planar (mean deviation 0.03 Å) and the pyrimidine ring makes a small dihedral angle (6.6°) with it. The pendant chlorophenyl group is inclined to the chelate ring by 45°. The Re–N5 length, 1.719(6) Å (Re–N5–C11 angle is 164.3°) is consistent with the triple bonding [1,20] (Table 3). The Re–N1 distance is ~0.2 Å longer than the Re–N4 length due to the *trans* influence of the imide nitrogen. The N–N bond in **4b**, 1.305(9) Å, is significantly longer than that in **2b**. This is ascribed to significant electron flow to the azo (π*) via the route ArN→Re^{V}→azo(π*) [3,4,20]. The imido group is a stronger donor than the oxo group and O→Re^{V}→azo(π*) is a less effective route for electron flow.

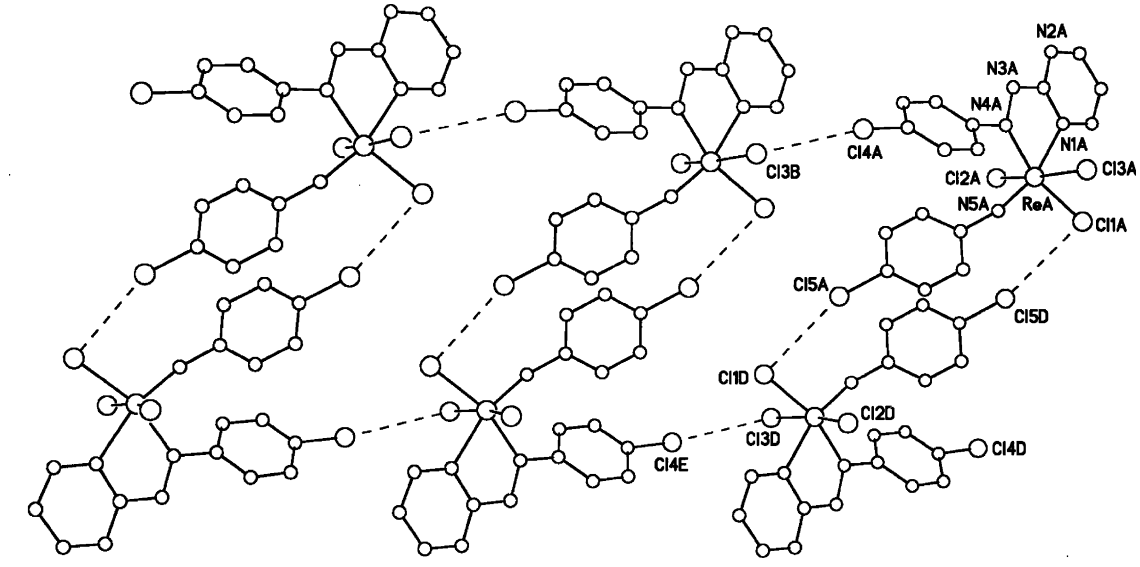


Fig. 5. Nonbonded Cl···Cl contacts and π-stacking in (**4b**).

Neither **2b** nor **3a** displayed any unusual intermolecular contacts. In **4b**, however, noncovalent Cl···Cl and aromatic π stacking are present leading to interlinked dimers as depicted in Fig. 5.

4. Conclusion

The synthesis and characterisation of family of rhenium complexes incorporating chelation by 2-(arylazo)pyrimidine ligands have been achieved. Chelation with $Re^{V}O$ is achieved by reacting with ReO_4^- in concentrated HCl, the process being attended with regiospecific aryl chlorination. The facile reactions of $[Re^{V}OCl_3(L)]$ (**2**) with PPh_3 and $ArNH_2$ have afforded $[Re^{III}(OPPh_3)Cl_3(L)]$ (**3**) and $[Re^{V}(NAr)Cl_3(L)]$ (**4**), respectively. Structure determination has revealed meridional $ReCl_3$ configuration in all the species. The presence of *trans* influence and back-bonding in the structures have been scrutinised. The complexes are electroactive and display Re^{VI}/Re^{V} (**2** and **4**) and Re^{IV}/Re^{III} (**3**) redox in solution. The type **3** species exhibit large paramagnetic shifts in ^1H NMR.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge crystallographic Data Centre, CCDC Nos. 194869, 194870, and 194871 for compounds **2b**, **3a** and **4b**, respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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