DALTON
FULL PAPER

Synthesis, structure and properties of $[Re^{V}L(O)Cl_3]$, $[Re^{V}L(NR)Cl_3]$, $[Re^{III}L(OPPh_3)Cl_3]$, and $[Re^{III}L(PPh_3)Cl_3]$ [L = 2-(arylazo)-1-methylimidazole, R = aryl] †

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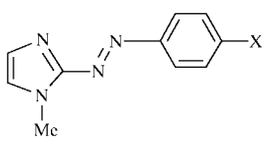
The reaction of $KReO_4$ with L [2-(arylazo)-1-methylimidazole, with aryl = Ph (L^1), C_6H_4Me-*p* (L^2) or C_6H_4Cl-*p* (L^3)] in concentrated HCl afforded $[Re^{V}L(O)Cl_3]$ **1**. Aromatic amines and PPh_3 smoothly converted **1** into $[Re^{V}L(NR)Cl_3]$ **2** and $[Re^{III}L(OPPh_3)Cl_3]$ **3** respectively. Treatment of **3** with PPh_3 yielded $[Re^{III}L(PPh_3)Cl_3]$ **4**. Complexes of type **3** and **4** display large paramagnetic shifts of ^1H NMR lines which spread over ≈60 ppm. Structure determination of $[ReL^1(O)Cl_3]$ **1a**, $[ReL^2(NC_6H_4Me\text{-}p)Cl_3]$ **2a**, $[ReL^3(OPPh_3)Cl_3]$ **3c** and $[ReL^3(PPh_3)Cl_3]$ **4c** has revealed meridional geometry for all except **4c** which is facial. In the latter Re–azo and Re–PPh_3 back bonding is maximized. The metal atom is displaced away from the equatorial plane by ≈0.3 Å towards the oxo ligand in **1a** and the imido ligand in **2a**. The imidazole nitrogen is co-ordinated *trans* to oxo, imido, Ph_3PO and chloride ligands in **1a**, **2a**, **3c** and **4c**, respectively. The azo N=N distance is lengthened by ≥0.05 Å as a result of direct (**3c**, **4c**) or indirect (**1a**, **2a**) Re–azo back bonding. Azo reduction potential values are consistent with the low-lying nature of the azo(π*) orbital. The metal reduction potentials follow the trends: Re^{VI}–Re^{V}, **1** > **2** (imido better donor than oxo); Re^{IV}–Re^{III}, **4** > **3** (stabilization of t_2 by Re^{III}–PPh_3 back bonding).

Oxorhenium(v) chemistry is of current interest.[1–3] As part of our activity [1,4–7] on new $Re^{V}O$ species and derivatives thereof, we have initiated a search into the little known rhenium chemistry [8,9] of azoheterocycles. An attractive feature of this class of ligands is their excellent π acidity [10–12] which could potentially influence the structure and reactivity of their complexes. Herein we report the successful chelation of $Re^{V}O$ by 2-(arylazo)-1-methylimidazoles.[10,13] In turn this has provided facile access to $Re^{V}(NR)$, $Re^{III}(OPPh_3)$ and $Re^{III}(PPh_3)$ species (R = aryl). The structure and properties of this interesting family are described in this work.

Results and discussion

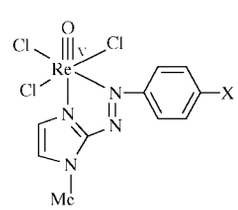
The ligands and complexes

Three 2-(arylazo)-1-methylimidazoles (L^1–L^3; general abbreviation, L) have been used as chelating ligands in the present work. The twelve complexes reported here belong to the four types **1**–**4**. The geometrical preference (meridional in **1**–**3** and facial in **4**) is strong and exclusive and in no case have isomers been observed.

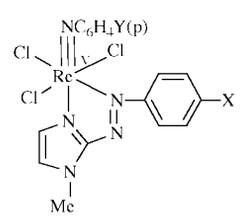


L^1 (X = H)
L^2 (X = Me)
L^3 (X = Cl)

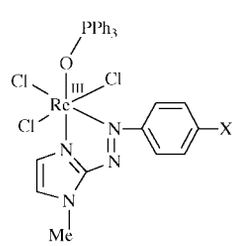
Synthesis. The reaction of $KReO_4$ with an excess of L in boiling concentrated hydrochloric acid affords the red oxo complex **1** in excellent yields. Here the metal is reduced from +7 to +5 state presumably by HCl; the reaction does not proceed in non-reducing acids such as glacial acetic acid. The species **2**–**4** have been prepared from **1** *via* the procedures outlined in Scheme 1 which also incorporates the conversions **3**, **4** ⟶ **2** and **3** ⟶ **4**. All the transformations are facile and proceed in excellent yields.



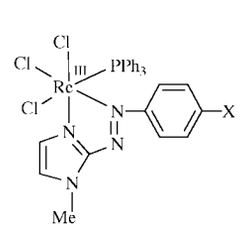
1a $[ReL^1(O)Cl_3]$
1b $[ReL^2(O)Cl_3]$
1c $[ReL^3(O)Cl_3]$



2a $[ReL^2(NC_6H_4Me)Cl_3]$
2b $[ReL^2(NC_6H_4Cl)Cl_3]$
2c $[ReL^3(NC_6H_4Me)Cl_3]$



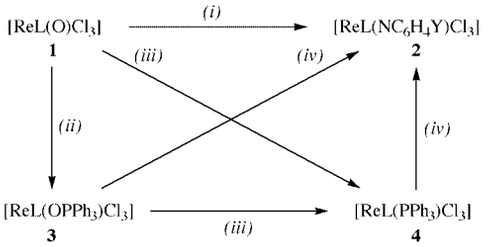
3a $[ReL^1(OPPh_3)Cl_3]$
3b $[ReL^2(OPPh_3)Cl_3]$
3c $[ReL^3(OPPh_3)Cl_3]$



4a $[ReL^1(PPh_3)Cl_3]$
4b $[ReL^2(PPh_3)Cl_3]$
4c $[ReL^3(PPh_3)Cl_3]$

The imido complex **2** is the most stable member among **1**–**4**, each of which can be irreversibly transformed to **2**, Scheme 1. Indeed **2** is formed in significant yields (up to ≈30%) upon boiling **1**, **3** or **4** in toluene even in the absence of the reagents

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3747/



Scheme 1 Synthetic conversions, reagents and conditions (solvent is toluene unless otherwise mentioned): (*i*) excess of *p*-$YC_6H_4NH_2$, boil for 10 min; (*ii*) stoichiometric PPh_3, stir for 5 min; (*iii*) excess of PPh_3 in benzene, boil for 1 h; (*iv*) excess of *p*-$YC_6H_4NH_2$, boil for 30 min in air.

indicated in Scheme 1. Under this condition the imido function evidently arises *via* splitting of the azo ligand.[8,14]

In the conversion **1** ⟶ **2**, eqn. (1), $Re^{V}O$ acts as a base and

$$\mathbf{1} + p\text{-}YC_6H_4NH_2 \longrightarrow \mathbf{2} + H_2O \qquad (1)$$

the oxo function is transferred formally as the oxide dianion which combines with the amine protons of *p*-$YC_6H_4NH_2$ generating the bound imide and free water. On the other hand, in the reaction **1** ⟶ **3**, $Re^{V}O$ is an oxidant transferring an oxygen atom to PPh_3. The phosphine oxide thus produced remains bonded to the reduced metal site in **3**, eqn. (2).

$$\mathbf{1} + PPh_3 \longrightarrow \mathbf{3} \qquad (2)$$

The oxygen atom transfer is believed to proceed *via* initial nucleophilic attack on the Re≡O π* orbital of complex **1** by PPh_3. The superior π acidity and electron withdrawing ability of the azo function facilitates the attack and reaction (2) proceeds much faster than that of pyridine-2-aldimine complexes of $Re^{V}O$.[1] Several instances of formation of phosphine oxides from $Re^{V}O$ and tertiary phosphines are known[1,15,16] but rarely does the phosphine oxide remain firmly bonded to the reduced metal centre[1,15] as in **3**.

In the reactions (1) and (2) the meridional geometry is preserved. On the other hand, the conversion **1** ⟶ **4**, eqn. (3), is

$$\mathbf{1} + 2\ PPh_3 \longrightarrow \mathbf{4} + OPPh_3 \qquad (3)$$

attended with *mer*→*fac* isomerization of the co-ordination sphere. The reaction proceeds *via* the intermediacy of **3**, eqn. (2), which then reacts with more PPh_3 forming **4**, eqn. (4). The isomerization process occurs in the latter step.

$$\mathbf{3} + PPh_3 \longrightarrow \mathbf{4} + OPPh_3 \qquad (4)$$

Spectra and electrochemistry. Relevant data are listed in the Experimental section. All the compounds display two or three Re–Cl stretches (300–360 cm^{-1}) and one azo stretch (1300–1340 cm^{-1}) in the IR. Characteristic Re≡O, Ph_3P–O and PPh_3 vibrations occur near 990, 1120 and 690 cm^{-1} for **1**, **3**, and **4** respectively.

The electronic spectra of the complexes are of diagnostic value and four representative spectra are compared in Fig. 1. Complexes of type **1** and **2** display a relatively weak band near 700 nm. This transition is believed to have significant ligand field character ($5d_{xy} \longrightarrow d_{xz}, d_{yz}$).[1,8] The allowed bands near 500 nm of **1** and **2** and near 450 nm of **3** and **4** are tentatively assigned to LMCT and MLCT excitations respectively.

The type **1** and **2** complexes are diamagnetic ($5d_{xy}^2$) and display well resolved ^1H NMR spectra in the δ 2–8 region. The magnetic moments (≈2 μ_B) of the complexes of types **3** and **4** are lower than the spin-only value as is often the case for trivalent rhenium.[7,17] These display paramagnetically shifted ^1H NMR lines spreading over the wide range δ −25 to 30. The largest shifts occur to the imidazole protons (near δ −16, 19 for **3** and −23, 16 for **4**) and the *ortho* protons (near δ 28 for both **3** and **4**) of the pendant aryl group of L. The spectra were assigned on the basis of signal intensity, spin–spin structure and previous work.[7,8,18]

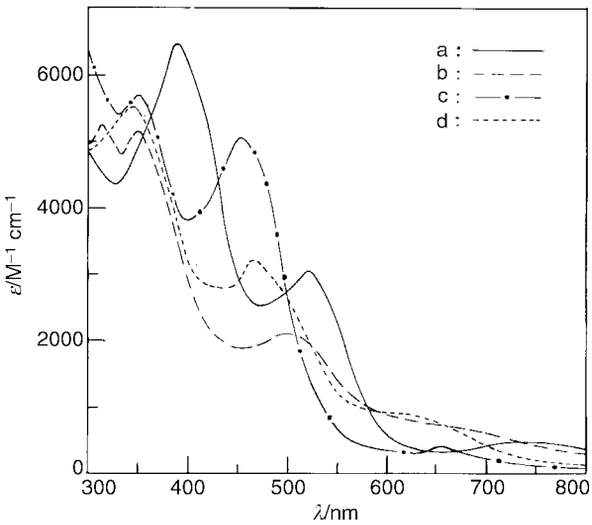


Fig. 1 Electronic spectra of (a) $[ReL^1(O)Cl_3]$ **1a**, (b) $[ReL^2(NC_6H_4Cl\text{-}p)Cl_3]$ **2b**, (c) $[ReL^2(OPPh_3)Cl_3]$ **3b** and (d) $[ReL^3(PPh_3)Cl_3]$ **4c** in CH_2Cl_2 solution.

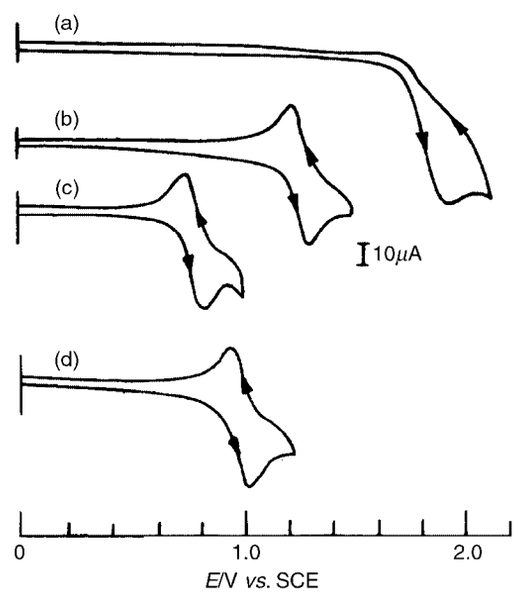


Fig. 2 Cyclic voltammograms of ≈10^{-3} mol dm^{-3} solutions of (a) $[ReL^3(O)Cl_3]$ **1c**, (b) $[ReL^3(NC_6H_4Me\text{-}p)Cl_3]$ **2c**, (c) $[ReL^1(OPPh_3)Cl_3]$ **3a** and (d) $[ReL^2(PPh_3)Cl_3]$ **4b** in acetonitrile solution (0.1 mol dm^{-3} Et_4NClO_4) at a platinum electrode (scan rate, 50 mV s^{-1}).

In acetonitrile solution the complexes generally display one-electron electroactivity at both metal and ligand sites. Approximate cyclic voltammetric reduction potentials are: **1**, 1.8 and −0.3; **2**, 1.2 and −0.7; **3**, 0.8 and −0.9; **4**, 1.0 and −0.5 V. The response at negative potential which is irreversible in all cases except **4** is assigned to azo reduction[10,11] consistent with the relatively low-lying nature of the azo-π* orbital which can thus participate in back bonding (see below). The couple at positive potentials corresponds to metal redox: Re^{VI}–Re^{V} in **1** (irreversible) and **2**; Re^{IV}–Re^{III} in **3** and **4**. Representative voltammograms are shown in Fig. 2. The imido ligand is a superior electron donor than the oxo ligand and hence the reduction potential order is **1** > **2**. The order **4** > **3** is consistent with the stabilization of metal t_2 electrons of **4** *via* Re^{III}–PPh_3 back bonding (see above).

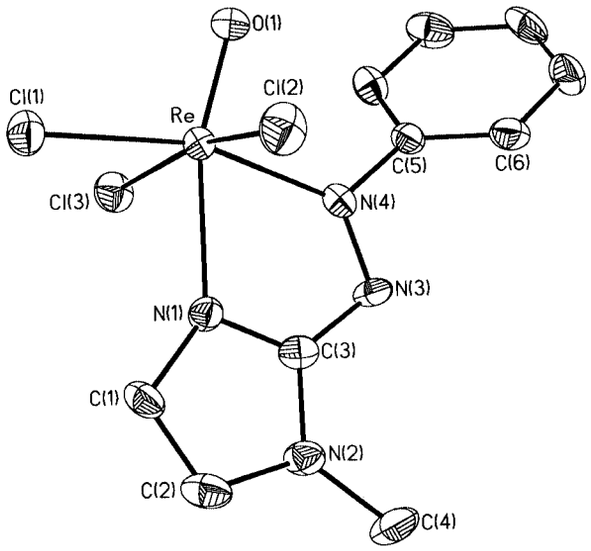


Fig. 3 A view of $[ReL^1(O)Cl_3]$ **1a**. The atoms are represented in all structures by their 30% thermal probability ellipsoids.

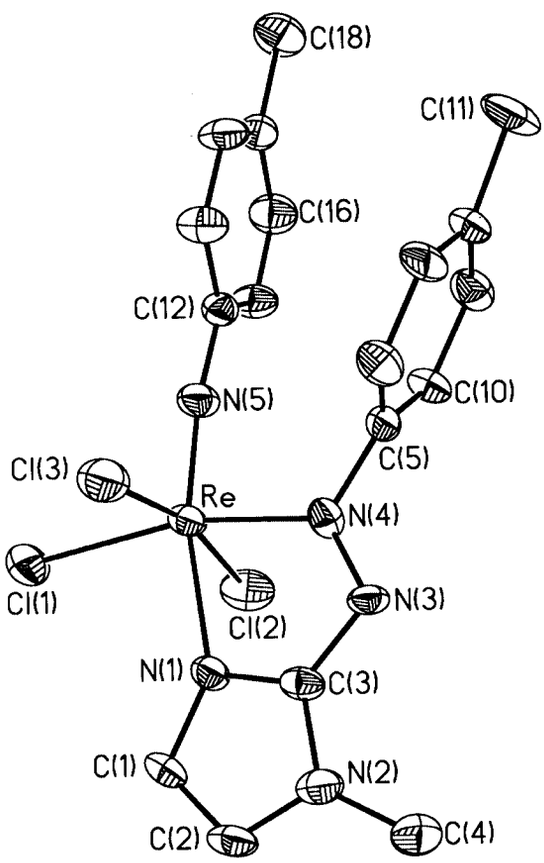


Fig. 4 A view of $[ReL^2(NC_6H_4Me\text{-}p)Cl_3]$ **2a**.

Structures of complexes 2, 3 and 4. The structure of one member of each group, **1a**, **2a**, **3c**, has been determined. Molecular views are shown in Figs. 3–5 and selected bond parameters are listed in Table 1. All the complexes have highly distorted octahedral geometry. The chelate ring along with the imidazole ring constitutes a good plane (mean deviation 0.02–0.03 Å) in each case. The $ReCl_3$ fragment is uniformly meridional.

The Cl(1), Cl(2), Cl(3) and N(4) atoms define a good equatorial plane in both complexes **1a** and **2a** (mean deviation, < 0.04 Å) from which the metal atom is displaced by 0.31 Å towards O(1) in **1a** and by 0.27 Å towards N(5) in **2a**. In **3c** the

Table 1 Selected bond lengths [Å] and angles [°] for complexes **1a**, **2a**·$\frac{1}{2}C_6H_6$ and **3c**

	1a	**2a**	**3c**
Re–O(1)	1.660(5)	—	2.039(11)
Re–N(5)	—	1.723(9)	—
Re–N(4)	2.086(6)	2.024(8)	1.978(15)
Re–N(1)	2.174(6)	2.140(8)	1.999(14)
Re–Cl(1)	2.307(2)	2.344(3)	2.369(6)
Re–Cl(2)	2.350(2)	2.371(3)	2.336(6)
Re–Cl(3)	2.359(2)	2.374(3)	2.363(5)
N(3)–N(4)	1.280(8)	1.319(10)	1.351(20)
O(1)–Re–N(4)	90.6(2)	—	99.0(6)
N(5)–Re–N(4)	—	93.7(4)	—
O(1)–Re–N(1)	162.4(2)	—	173.9(5)
N(5)–Re–N(1)	—	166.9(4)	—
N(4)–Re–N(1)	71.8(2)	73.9(3)	75.3(6)
O(1)–Re–Cl(1)	107.8(2)	—	93.3(4)
N(5)–Re–Cl(1)	—	102.5(3)	—
N(4)–Re–Cl(1)	161.5(2)	163.5(2)	167.5(5)
N(1)–Re–Cl(1)	89.8(2)	90.3(2)	92.4(5)
O(1)–Re–Cl(2)	97.0(2)	—	87.1(4)
N(5)–Re–Cl(2)	—	94.8(3)	—
N(4)–Re–Cl(2)	88.7(2)	95.0(3)	92.2(5)
N(1)–Re–Cl(2)	82.9(2)	82.5(2)	90.8(5)
Cl(1)–Re–Cl(2)	87.75(8)	87.09(14)	90.4(3)
O(1)–Re–Cl(3)	96.9(2)	—	88.6(4)
N(5)–Re–Cl(3)	—	97.2(3)	—
N(4)–Re–Cl(3)	92.7(2)	88.3(3)	89.7(4)
N(1)–Re–Cl(3)	84.4(2)	86.7(2)	93.6(4)
Cl(1)–Re–Cl(3)	86.47(8)	86.29(14)	88.7(2)
Cl(2)–Re–Cl(3)	166.04(8)	167.28(11)	175.5(2)
C(12)–N(5)–Re	—	172.4(8)	—

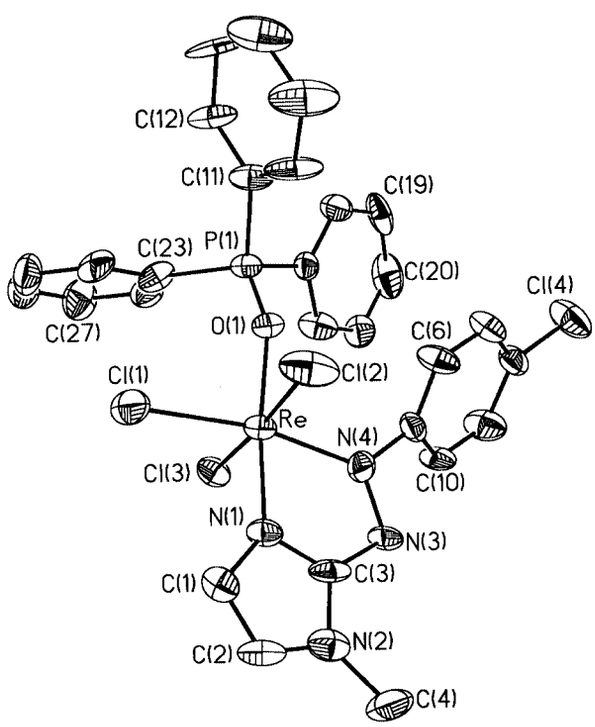


Fig. 5 A view of $[ReL^3(OPPh_3)Cl_3]$ **3c**.

equatorial atoms constitute only an approximate plane (mean deviation 0.16 Å) and the metal atom lies within this plane. The reaction $Re^{V}O \longrightarrow Re^{III}(OPPh_3)$ is thus associated with a descent of the metal atom on to the equator.

The phosphorus atom in complex **3c** is positioned at a distance of 2.82 Å from the centroid of the octahedral face defined by O(1), Cl(1) and Cl(3). The corresponding distances from the centroid of the other three faces having O(1) as the common vertex are systematically larger (3.01–3.21 Å). It is likely that

Table 2 Selected bond lengths [Å] and angles [°] for complex **4c**

Re–N(1)	1.997(8)	Re–N(4)	2.035(7)
Re–Cl(2)	2.338(2)	Re–Cl(3)	2.352(2)
Re–Cl(1)	2.399(3)	Re–P(1)	2.476(3)
N(3)–N(4)	1.337(10)		
N(1)–Re–N(4)	75.9(3)	N(1)–Re–Cl(2)	172.3(2)
N(4)–Re–Cl(2)	98.0(2)	N(1)–Re–Cl(3)	89.0(2)
N(4)–Re–Cl(3)	164.5(2)	Cl(2)–Re–Cl(3)	97.41(10)
N(1)–Re–Cl(1)	93.2(2)	N(4)–Re–Cl(1)	88.5(2)
Cl(2)–Re–Cl(1)	91.23(10)	Cl(3)–Re–Cl(1)	89.04(10)
N(1)–Re–P(1)	93.0(2)	N(4)–Re–P(1)	95.9(2)
Cl(2)–Re–P(1)	82.92(9)	Cl(3)–Re–P(1)	88.07(10)
Cl(1)–Re–P(1)	173.08(9)		

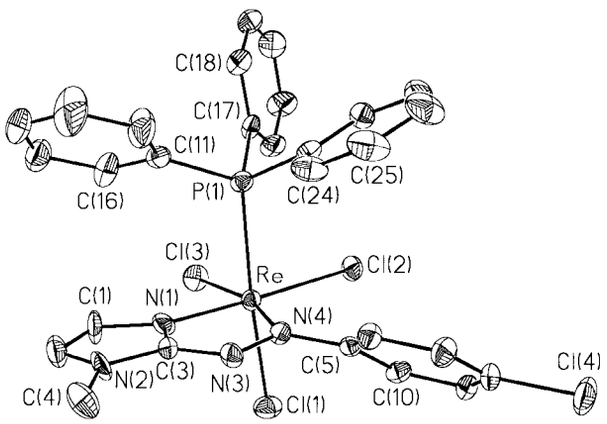


Fig. 6 A view of $[ReL^3(PPh_3)Cl_3]$ **4c**.

the initial nucleophilic attack by PPh_3 on $Re^{V}O$ of **1** occurs from the side of the O(1), Cl(1), Cl(3) face.

The Re–O(1) length in complex **1a**, 1.660(5) Å, lies within the range 1.68 ± 0.03 Å usually spanned by structurally characterized $Re^{V}O$ species.[1–3,19] Idealized $Re^{V}{\equiv}O$ and $Re^{V}{=}O$ distances are estimated to be 1.60,[19,20] and 1.75 Å [19,21] respectively. On this basis the Re–O(1) bond in **1a** is primarily triple in character and is therefore represented simply as Re≡O. Similarly the Re–N(5) bond in **2a**, 1.723(9) Å (Re–N(5)–C(12) angle, 172.4(8)) is approximately triple in nature.[6,8,22–24]

The imidazole nitrogen N(1) is co-ordinated *trans* to O(1) in complex **1a**, N(5) in **2a** and O(1) in **3c**. There is a significant decrease (≈ 0.15 Å) of the Re–N(1) length in going from **1a** and **2a** to **3c** even though the rhenium(III) atom is larger in size than the rhenium(V) atom. While this can be ascribed to the *trans* influence of the oxo and imido groups, the trend also reflects the variable position of the metal atom with respect to the equatorial plane (see above).

A notable feature of the structures is the lengthening of the azo N=N distance to 1.28–1.35 Å from the normal value, 1.25 Å.[25] This is ascribed to electron flow to the azo(π*) orbital *via* the $O \longrightarrow Re^{V} \longrightarrow$ azo(π*) route in complex **1a** and the more potent $RN \longrightarrow Re^{V} \longrightarrow$ azo(π*) route in **2a**.[1,6,8] In **3c** the direct back bonding by the trivalent metal,[1,9] $Re^{III} \longrightarrow$ azo(π*), is strong and the N=N lengthening is also more pronounced.

Structure of complex 4. The structure of **4c** has been determined and a view is shown in Fig. 6 and relevant bond parameters are given in Table 2. Here the $ReCl_3$ fragment is facially disposed and so are the phosphine and L ligands resulting in a severely distorted $ReCl_3N_2P$ co-ordination sphere. The metal atom along with Cl(2), Cl(3), N(1) and N(4) constitute a satisfactory plane (mean deviation 0.05 Å) to which the P(1)–Re–Cl(1) axis defines a perpendicular. The chelate ring along with the imidazole ring constitute a nearly perfect plane (mean deviation 0.01 Å) with which the pendant aryl ring of L^3 makes a dihedral angle of 39.1°.

The Re–N(1) length, 1.997(8) Å, is virtually the same as that of complex **3c** but the Re–N(4) length, 2.035(7) Å, is longer (see below). The Re–Cl(1) bond lying *trans* to the Re–P(1) bond is ≈0.05 Å longer than the other two Re–Cl bonds. The azo N=N bond, 1.337(10) Å, is weakened due to $Re^{III} \longrightarrow$ azo (π*) back bonding.

Origin of isomeric variation. Steric and electrostatic factors alone would favour the meridional over the facial configuration. The oxo, imido and $OPPh_3$ ligands are pure donors and their interaction with the metal including those[1,8] of the $O \longrightarrow Re \longrightarrow$ azo (π*) and $RN \longrightarrow Re \longrightarrow$ azo (π*) types (see above) is well suited to the meridional configuration and this is the observed geometry in the species of types **1**–**3**.

In the presence of PPh_3 the electronic situation is affected by its π acidity, the concerned orbital being a mixture of $3d_\pi$ and P–C σ* components.[26,27] We thus have two good π acceptors in complex **4**, the azo function and PPh_3, co-ordinated to rhenium(III). The back-bonding effect is maximized in the facial disposition which ensures minimum competition between the two ligands for identical metal orbitals. It is significant that the Re–N(4) distance in **4c** is actually ≈0.04 Å longer than that in **3c** where the azo ligand alone is available for back bonding.

We have here the second example of the present kind of geometrical control by PPh_3 among rhenium(III) chelates of unsaturated nitrogenous ligands. The first example reported recently is the facial 2-pyridylmethanimine (L′) complex $[ReL'(PPh_3)Cl_3]$.[7] Even though the π*(aldimine) orbital in L′ is a less potent acceptor than the π*(azo) orbital of L,[28] it is still sufficiently π-acidic to stabilize the facial geometry. We are searching for more examples of the π acidity–geometry relationship in rhenium(III) structural chemistry.

Conclusion

The synthesis and structural characterization of a hitherto unknown family of rhenium complexes incorporating 2-(arylazo)-1-methylimidazole (L) chelation have been successfully achieved. The parent oxo system $[Re^{V}L(O)Cl_3]$ prepared by the reaction of L with $KReO_4$ in hydrochloric acid has meridional geometry. It undergoes facile and stereoretentive oxygen transfer affording the systems $[Re^{V}L(NR)Cl_3]$ and $[Re^{III}L(OPPh_3)Cl_3]$. The latter in turn has furnished the phosphine system $[Re^{III}L(PPh_3)Cl_3]$ which assumes facial geometry reflecting the maximization of Re^{III}–L and Re^{III}–PPh_3 back-bonding interactions. All the species display electrochemical electron transfer processes involving metal-t_2 and azo-π* orbitals. The low-lying nature of the latter orbital significantly affects the structure and reactivity of the family.

Experimental

Materials

Ligands of type 2-(arylazo)-1-methylimidazole were prepared by a reported method.[13] The purification and drying of dichloromethane and acetonitrile for synthesis as well as for electrochemical and spectral work were done as before.[29] Toluene and benzene were distilled over sodium before use. All other chemicals and solvents were of reagent grade used as received.

Physical measurements

Spectral measurements were carried out with Perkin-Elmer 783 (IR; KBr disc) and Hitachi 330 (UV-vis, CH_2Cl_2 solution) spectrophotometers. Proton NMR spectra ($CDCl_3$ solvent, standard $SiMe_4$) were recorded on a Bruker FT 300 MHz spectrometer. The numbering scheme used for ^1H NMR is the same as in crystallography. Spin–spin structures are abbreviated as:

s, singlet; d, doublet; t, triplet and m, multiplet. Electrochemical measurements were performed (acetonitrile solution) on a PAR model 370–4 electrochemistry system as described elsewhere[27] using a platinum working electrode under a dinitrogen atmosphere. The supporting electrolyte was tetraethylammonium perchlorate and potentials are referenced to the saturated calomel electrode (SCE) without junction correction. Magnetic susceptibilities were measured on a PAR 155 vibrating-sample magnetometer and microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 Series II elemental analyzer.

Syntheses

***mer*-[ReL(O)Cl_3] 1.** The complexes were prepared by the same general methods. Details are given for **1c** (L = L^3).

To a hot suspension of $KReO_4$ (250 mg, 0.86 mmol) in concentrated hydrochloric acid (10 cm^3) 760 mg (3.4 mmol) of L^3 were added. The resulting mass was stirred magnetically and heated to reflux for 30 min. It was then cooled to room temperature, extracted with toluene and evaporated to dryness. The residue thus obtained was dissolved in a small amount of dichloromethane and subjected to chromatography on a silica gel column (20 × 1 cm, 60–120 mesh, BDH) prepared in toluene. Upon elution with toluene–acetonitrile (25 : 1) red complex **1c** was isolated. Yield: 365 mg (80%) (Found: C, 22.79; H, 1.79; N, 10.67. Calc. for $C_{10}H_9Cl_4N_4ORe$: C, 22.68; H, 1.70; N, 10.58%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 738(500), 525(4180) and 375(6600). IR (cm^{-1}): 320, 330, 360 (Re–Cl), 990 (Re=O), 1335 (N=N). ^{1}H NMR [δ (*J*/Hz)]: MeC_3N_2, 6.42 (d, 1.5, H(1)), 7.12 (d, 1.5, H(2)) and 4.3 (s, N–Me); C_6H_4Cl, 7.90 (d, 9.0, H(6), H(10)) and 7.49 (d, 8.7, H(7), H(9)). E_{pa} (Re^{VI}–Re^{V} couple) 1.88 V, E_{pc} (N=N/N···N) −0.22 V.

[$ReL^1(O)Cl_3$] **1a** (Found: C, 24.32; H, 2.10; N, 11.39. Calc. for $C_{10}H_{10}Cl_3N_4ORe$: C, 24.25; H, 2.02; N, 11.31%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 738(490), 526(3295) and 391(6780). IR (cm^{-1}): 320, 330, 360 (Re–Cl), 990 (Re=O), 1330 (N=N). ^{1}H NMR [δ (*J*/Hz)]: MeC_3N_2, 6.43 (d, ill resolved, H(1)), 7.12 (d, ill resolved, H(2)) and 4.30 (s, N–Me); C_6H_5, 7.93 (d, 7.5, H(6), H(10)), 7.50 (t, 6.9, H(7), H(9)) and 7.65 (t, 8.1, H(8)). E_{pa} (Re^{VI}–Re^{V} couple) 1.84 V, E_{pc} (N=N/N···N) −0.34 V.

[$ReL^2(O)Cl_3$] **1b** (Found: C, 26.06; H, 2.42; N, 11.32. Calc. for $C_{11}H_{12}Cl_3N_4ORe$: C, 25.95; H, 2.35; N, 11.01%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 739(450), 520(2960) and 392(6530). IR (cm^{-1}): 320, 330, 360 (Re–Cl), 980 (Re=O), 1335 (N=N). ^{1}H NMR [δ (*J*/Hz)]: MeC_3N_2, 6.42 (d, 1.5, H(1)), 7.09 (d, ill resolved, H(2)) and 4.27 (s, N–Me); C_6H_4Me, 7.85 (d, 8.4, H(6), H(10)), 7.30 (d, 8.4, H(7), H(9)) and 2.45 (s, C(8)–Me). E_{pa} (Re^{VI}–Re^{V} couple) 1.82 V, E_{pc} (N=N/N···N) −0.30 V.

***mer*-[ReL(NC_6H_4Y-*p*)Cl_3] 2.** The same general methods were used for all the complexes. The case of **2c** is detailed below.

To a warm solution of complex **1c** (100 mg, 0.19 mmol) in toluene (10 cm^3) was added an excess of *p*–toluidine (101 mg, 0.95 mmol) and the mixture heated to reflux for 1 h affording a violet solution. The solvent was then removed under reduced pressure and the solid thus obtained subjected to column chromatography. A pink-violet band was eluted using benzene–acetonitrile (20 : 1) and from the eluate **2c** was obtained in ≈80% yield by slow evaporation (Found: C, 33.16; H, 2.66; N, 11.37. Calc. for $C_{17}H_{16}Cl_4N_5Re$: C, 33.00; H, 2.58; N, 11.32%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 680(540), 500(2840) and 325(6300). IR (cm^{-1}): 305, 320, 340 (Re–Cl), 1300 (N=N). ^{1}H NMR [δ (*J*/Hz)]: MeC_3N_2, 6.46 (d, 1.5, H(1)), 7.31 (d, 1.2, H(2)) and 4.19 (s, N–Me); C_6H_4Me, C_6H_4Cl, 7.38 (d, 8.4, H(6), H(10)), 7.13 (complex multiplet, H(7), H(9), H(13), H(15)), 6.97 (d, 8.1, H(12), H(16)) and 2.27 (s, C(14)–Me). $E_{1/2}$ (Re^{VI}–Re^{V} couple) 1.24 V (ΔE_p = 80 mV), E_p (N=N/N···N) −0.66 V.

[$ReL^2(NC_6H_4Me$-*p*)Cl_3] **2a** (Found: C, 36.29; H, 3.27; N, 11.83. Calc. for $C_{18}H_{19}Cl_3N_5Re$: C, 36.15; H, 3.18; N, 11.71%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 678 (sh) (505), 510(2400) and 330(5600). IR (cm^{-1}): 310, 320, 340 (Re–Cl), 1300 (N=N). ^{1}H NMR [δ (*J*/Hz)]: MeC_3N_2, 6.50 (d, 3.3, H(1)), 7.06 (d, ill resolved, H(2)) and 4.17 (s, N–Me); C_6H_4Me, C_6H_4Me, 7.37 (d, 6.9, H(6), H(10)), 7.06 (d, 8.4, H(7), H(9)), 6.98 (d, 9.0. H(13), H(17)), 6.94 (d, 9.0, H(14), H(16)), 2.24 (s, C(15)–Me) and 2.40 (s, C(8)–Me)). $E_{1/2}$ (Re^{VI}–Re^{V} couple) 1.23 V (ΔE_p = 60 mV), E_{pc} (N=N/N···N) −0.66 V.

[$ReL^2(NC_6H_4Cl$-*p*)Cl_3] **2b** (Found: C, 33.14; H, 2.69; N, 11.41. Calc. for $C_{17}H_{16}Cl_4N_5Re$: C, 33.00; H, 2.58; N, 11.32%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 681 (sh) (555), 505(2100), 350(5150) and 315(5240). IR (cm^{-1}): 310, 320, 340 (Re–Cl), 1310 (N=N). ^{1}H NMR [δ (*J*/Hz)]: MeC_3N_2, 6.54 (d, ill resolved, H(1)), 7.04 (d, ill resolved, H(2)) and 4.12 (s, N–Me); C_6H_4Cl, C_6H_4Me, 7.33 (d, 7.0, H(6), H(10)), 7.18 (d, 8.60, H(7), H(9)), 6.96 (d, 9.0, H(12), H(16)), 6.90 (d, 9.0, H(13), H(15)) and 2.10 (s, C(8)–Me)). $E_{1/2}$ (Re^{VI}–Re^{V} couple) 1.21 V (ΔE_p = 70 mV), E_{pc} (N=N/N···N) −0.66 V.

***mer*-[ReL($OPPh_3$)Cl_3] 3.** The same general methods were used for all the complexes. The case of **3c** is detailed below.

To a solution of complex **1c** (100 mg, 0.19 mmol) in dichloromethane (10 cm^3) was added 250 mg (0.96 mmol) of PPh_3. The red solution turned brown instantly and was stirred for 5 min at room temperature. The solvent was then removed under reduced pressure. The golden brown crystalline solid was washed several times with hexane and finally dried *in vacuo* over P_4O_{10}. Yield: 120 mg (80%) (Found: C, 42.60; H, 3.11; N, 7.14. Calc. for $C_{28}H_{24}Cl_4N_4OPRe$: C, 42.46; H, 3.03; N, 7.07%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 655 (sh) (350), 450(3770) and 345(4710). IR (cm^{-1}): 320, 330 (Re–Cl), 1120 ($OPPh_3$), 1335 (N=N). ^{1}H NMR [δ (*J*/Hz)]: MeC_3N_2, −15.64 (d, ill resolved, H(1)), 18.74 (d, ill resolved, H(2)) and −16.08 (s, N–Me); C_6H_4Cl, 28.28 (d, 9.0, H(6), H(10)) and 10.88 (d, 8.4, H(7), H(9)); PPh_3, 1.60 (d, ill resolved, H(*o*)), 6.89 (t, 7.25, H(*m*)) and 6.39 (t, 7.35, H(*p*)). $E_{1/2}$ (Re^{IV}–Re^{III} couple) 0.82 V (ΔE_p = 80 mV), E_{pc} (N=N/N···N) −0.76 V.

[$ReL^1(OPPh_3)Cl_3$] **3a** (Found: C, 44.53; H, 3.41; N, 7.49. Calc. for $C_{28}H_{25}Cl_3N_4OPRe$: C, 44.41; H, 3.30; N, 7.40%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 650 (sh) (365), 457(5580) and 342(6760). IR (cm^{-1}): 320, 330 (Re–Cl), 1120 ($OPPh_3$), 1335 (N=N). ^{1}H NMR [δ (*J*/Hz)]: MeC_3N_2, −15.65 (d, ill resolved, H(1)), 18.76 (d, ill resolved, H(2)) and −16.07 (s, N–Me); C_6H_5, 28.28 (d, 6.0, H(6), H(10)), 11.23 (t, 7.5, H(7), H(9)) and 11.09 (t, 7.2, H(8)); PPh_3, 1.49 (d, ill resolved, H(*o*)), 6.84 (t, 9.15, H(*m*)) and 6.35 (t, 7.50, H(*p*)). $E_{1/2}$ (Re^{IV}–Re^{III} couple) 0.80 V (ΔE_p = 100 mV), E_{pc} (N=N/N···N) −0.86 V.

[$ReL^2(OPPh_3)Cl_3$] **3b** (Found: C, 45.28; H, 3.59; N, 7.37. Calc. for $C_{29}H_{27}Cl_3N_4OPRe$: C, 45.16; H, 3.50; N, 7.26%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 655(380), 455(5126) and 350(5790). IR (cm^{-1}): 320, 330 (Re–Cl), 1120 ($OPPh_3$), 1335 (N=N). ^{1}H NMR [δ (*J*/Hz)]: MeC_3N_2, −15.75 (d, ill resolved, H(1)), 17.61 (d, ill resolved, H(2)) and −17.47 (s, N–Me); C_6H_4Me, 27.76 (d, 7.8, H(6), H(10)), 10.82 (d, 7.5, H(7), H(9)) and 2.99 (s, C(8)–Me); PPh_3, 1.54 (d, 9.0, H(*o*)), 6.76 (t, 7.5, H(*m*)) and 6.27 (t, 7.50, H(*p*)). $E_{1/2}$ (Re^{IV}–Re^{III} couple) +0.74 V (ΔE_p = 120 mV), E_{pc} (N=N/N···N) −0.88 V.

***fac*-[ReL(PPh_3)Cl_3] 4.** The complexes were prepared by the same general method. Details are given for **4c**.

To a solution of complex **3c** (100 mg, 0.12 mmol) in benzene (15 cm^3), PPh_3 (170 mg, 0.64 mmol) was added and the solution refluxed for 1 h. The resulting solution was evaporated to dryness and the solid mass thus obtained subjected to chromatography. Upon elution with toluene–acetonitrile (15 : 1) golden brown **4c** was obtained. Yield: 73 mg (75%) (Found: C, 43.45; H, 3.16; N, 7.29. Calc. for $C_{28}H_{24}Cl_4N_4PRe$: C, 43.34; H, 3.09; N, 7.22%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 630 (sh) (970), 465(3230) and 345(5590). IR (cm^{-1}): 330, 320 (Re–Cl), 690, 500 (PPh_3), 1330 (N=N). ^{1}H NMR [δ (*J*/Hz)]:

Table 3 Crystal data for complexes **1a**, **2a**·½C_6H_6, **3c** and **4c**

Complex	**1a**	**2a**·½C_6H_6	**3c**	**4c**
Formula	$C_{10}H_{10}Cl_3N_4ORe$	$C_{21}H_{22}Cl_3N_5Re$	$C_{28}H_{24}Cl_4N_4OPRe$	$C_{28}H_{24}Cl_4N_4PRe$
M	494.77	636.99	791.48	775.48
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group (no.)	$P2_1/c$ (14)	$Pbcn$ (60)	$P2_1/n$ (14)	$P2_1/n$ (14)
a/Å	14.231(7)	28.204(6)	11.588(6)	9.785(2)
b/Å	7.716(3)	11.364(2)	15.007(5)	21.183(8)
c/Å	13.409(6)	14.954(3)	17.661(8)	14.937(5)
β/°	101.41(4)	—	96.52(4)	109.00(2)
U/Å^3	1443.3(11)	4793(2)	3052(2)	2927(2)
Z	4	8	4	4
μ(Mo-Kα)/mm^{-1}	8.97	5.42	4.414	4.596
T/K	296	296	296	296
Total reflections	2477	3613	5194	5561
Independent reflections (R_{int})	2287 (0.016)	3539 (0.053)	4774 (0.096)	5138 (0.037)
Observed reflections [$I > 2\sigma(I)$]	1881	2274	2611	3719
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0301, 0.0637	0.0434, 0.0948	0.0658, 0.1582	0.0477, 0.1063
(all data)	0.0450, 0.0693	0.0852, 0.1192	0.1354, 0.2205	0.0824, 0.1332

MeC_3N_2, −22.56 (d, ill resolved, H(1)), 16.10 (d, ill resolved, H(2)) and −17.66 (s, N–Me); C_6H_4Cl, 27.97 (d, 7.5, H(6), H(10)) and 12.52 (9.00, H(7), H(9)); PPh_3, 13.98 (d, ill resolved, H(*o*)), 9.08 (t, 7.35, H(*m*)) and 8.50 (t, 7.50, H(*p*)). $E_{1/2}$ (Re^{IV}–Re^{III} couple) 1.08 V (ΔE_p = 60 mV), $E_{1/2}$ (N=N/N···N) −0.54 V (ΔE_p = 60 mV).

[$ReL^1(PPh_3)Cl_3$] **4a** (Found: C, 45.49; H, 3.46; N, 7.63. Calc. for $C_{28}H_{25}Cl_3N_4PRe$: C, 45.37; H, 3.37; N, 7.56%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 618 (sh) (925), 463(3310) and 374(5220). IR (cm^{-1}): 330, 320 (Re–Cl), 700, 510 (PPh_3); 1330 (N=N). $E_{1/2}$ (Re^{IV}–Re^{III} couple) 1.06 V (ΔE_p = 80 mV), $E_{1/2}$ (N=N/N···N) −0.50 V (ΔE_p = 80 mV).

[$ReL^2(PPh_3)Cl_3$] **4b** (Found: C, 46.24; H, 3.64; N, 7.50. Calc. for $C_{29}H_{27}Cl_3N_4PRe$: C, 46.12; H, 3.57; N, 7.42%). UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 625 (sh) (940), 460(3210) and 370(5120). IR (cm^{-1}): 330, 320 (Re–Cl), 700, 510 (PPh_3); 1330 (N=N). $E_{1/2}$ (Re^{IV}–Re^{III} couple) 1.02 V (ΔE_p = 80 mV), $E_{1/2}$ (N=N/N···N) −0.52 V (ΔE_p = 80 mV).

Crystallography

Single crystals of complexes **1a**, **2a**, **3c** and **4c** were grown by slow diffusion of hexane into benzene solutions of the respective complexes. Complex **2a** crystallized as **2a**·½C_6H_6, the solvent lying on a special position.

Data were collected by the ω-scan technique in the range $3 \leq 2\theta \leq 50°$ for complexes **1a** and **4c**, $3 \leq 2\theta \leq 47°$ for **2a** and $3 \leq 2\theta \leq 48°$ for **3c** on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). All data were corrected for Lorentz-polarization and absorption.[30] The metal atoms were located from Patterson maps and the rest of the non-hydrogen atoms emerged from successive Fourier syntheses. The structures were then refined by a full-matrix least-squares procedure on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions. Calculations were performed using the SHELXTL™ V 5.03[31] Program package. Significant crystal data are listed in Table 3.

CCDC reference number 186/1656.

See http://www.rsc.org/suppdata/dt/1999/3747/ for crystallographic files in .cif format.

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