A novel series of rhenium-bipyrimidine complexes: synthesis, crystal structure and electrochemical properties†

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Four novel rhenium complexes of formula [ReCl$_4$(bpym)] (**1**), [ReBr$_4$(bpym)] (**2**) PPh$_4$[ReCl$_4$(bpym)] (**3**) and NBu$_4$[ReBr$_4$(bpym)] (**4**) (bpym = 2,2′-bipyrimidine, PPh$_4$ = tetraphenylphosphonium cation and NBu$_4$ = tetrabutylammonium cation), have been synthesized and their crystal structures determined by single-crystal X-ray diffraction. The structures of **1** and **2** consist of [ReX$_4$(bpym)] molecules held together by van der Waals forces. In both complexes the Re(IV) central atom is surrounded by four halide anions and two nitrogen atoms of a bpym bidentate ligand in a distorted octahedral environment. The structures of **3** and **4** consist of [ReX$_4$(bpym)]$^-$ anions and PPh$_4{}^+$ (**3**) or NBu$_4{}^+$ (**4**) cations. The coordination sphere of the Re(III) metal ion is the same as in **1** and **2**, respectively. However, whereas the Re–X bonds are longer the Re–N bonds are shorter than in **1** and **2**. This fact reveals that the bpym ligand forms a stronger bond with Re(III) than with Re(IV) resulting in a stabilisation of the lower oxidation state. [ReX$_4$(bpym)] complexes are easily reduced, chemically and electrochemically, to the corresponding [ReX$_4$(bpym)]$^-$ anions. A voltammetric study shows that the electron transference is a reversible process characterized by formal redox potentials of +0.19 V (**1**) and +0.32 V (**2**) *vs.* NHE, in acetonitrile as solvent.

Introduction

In the past few years we have devoted our efforts to the synthesis, through ligand substitution reactions of the [ReX$_6$]$^{2-}$ anions (X = Cl, Br), of rhenium(IV) complexes with potential bridging ligands and we have used them as reagents in the preparation of heteropolynuclear coordination compounds. In particular, we have explored the possibilities of Re(IV)-oxalate and Re(IV)-malonate complexes acting as ligands towards 3d metal ions. Following this approach numerous oxalato- and malonato-bridged bimetallic assemblies Re–M (M = Cu, Ni, Co, Fe, Mn) have been reported and their magnetic properties investigated.[1]

Recently we have embarked on a research program for the synthesis of rhenium(IV) complexes with nitrogen-donor ligands and we have focused our interest on exploring the possibilities of the use of 2,2′-bipyrimidine (bpym). This bis-chelating heterocyclic molecule has proven to be an efficient bridging ligand for the stepwise synthesis of polynuclear complexes and is capable of transmitting electronic and magnetic interactions between metal centers.[2]

Only a few rhenium complexes containing bpym as the ligand have been reported up to now. Among them, a number of rhenium(I) tricarbonyl complexes of general formula [Re(CO)$_3$(bpym)L]$^{n+}$ (L = CO, CH$_3$CN, pyridine, *N*-methyl-4,4′-bipyridinium ion; *n* = 0–2) have been synthesized and structurally characterized.[3] Also several bipyrimidine-bridged homo and heteropolynuclear complexes of Re(I) and different metal ions such as Ru(II), Rh(III), Ir(III) and Ln(III) (Ln = Yb, Er, Eu, Gd, Nd) have been prepared and their photophysical properties studied.[4] But the only example of higher valence rhenium bipyrimidine compounds described up until now is the oxorhenium(V) compound [ReO(CH$_3$)(edt)(bpym)] (edt = 1,2-ethanedithiolate).[5]

The chemistry of Re(IV) with *N*-heterocyclic ligands is scarcely developed compared with that of other oxidation states. In fact, very few complexes of Re(IV) containing this type of ligand are known. The compounds [ReCl$_4$(pzH)(PPh$_3$)] (pzH = pyrazole) and [ReCl$_4$(pyz)(PPh$_3$)] (pyz = pyrazine) were synthesized by ligand substitution onto [ReCl$_4$(PPh$_3$)$_2$] in chloroform.[6] On the other hand, [ReX$_4$(bpy)] (X = Cl, Br; bpy = 2,2′-bipyridine)[7] and other reported Re(IV) complexes with the substituted *N*-heterocyclic ligands dimethyladenine,[8] *N*–*p*-tolyl-2-picolinamida,[9] 2–[(6-benzothiazol-2-yl-pyridin-2-ylmethyl)-amino]-benzenethiol[10] and 2,9-dimethyl-1,10-phenantroline[11] have been prepared from Re(III) or Re(V) complexes. Finally, the compound *trans*-[ReCl$_4$(py)$_2$] (py = pyridine) has been obtained by reaction of (pyH)$_2$[ReCl$_6$] with pyridine in a sealed tube.[12]

Here we report the synthesis and crystal structure of four novel complexes, [ReCl$_4$(bpym)] (**1**), [ReBr$_4$(bpym)] (**2**),

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$(PPh_4)[ReCl_4(bpym)]$ (**3**) and $(NBu_4)[ReBr_4(bpym)]$ (**4**). An easy interconversion of the Re^{III}/Re^{IV} bpym complexes was notorious in the course of the synthesis of the complexes. With this in mind, we also investigated the electrochemical behavior of the chloro and bromo complexes in two solvents used during the preparation, namely, acetonitrile and dimethylformamide.

Results and discussion

Synthesis of the complexes

The reaction of $[ReX_6]^{2-}$ anions (X = Cl, Br) with bpym in hot dry *N*,*N*-dimethylformamide (DMF) gave rise after some work up to the monosubstituted complexes $[ReX_4(bpym)]$. Ligand substitution reactions of the inert hexahalorhenates in this solvent have been previously reported for the preparation of $[Re(CN)_7]^{3-}$[13] and a series of mono and bis(oxalato) complexes.[14] In the latter case, it was also noted that a complete halide substitution could not be achieved due to kinetic factors. The main reason for the choice of this solvent was its high boiling point, but the role of the DMF molecules in the reaction path may be important, as the isolation of the $[ReX_5(DMF)]^-$ anion suggests.[15]

Neutral compounds **1** and **2** are readily soluble in most organic solvents but insoluble in water. They can be crystallized as solvates, $[ReX_4(bpym)]\cdot S$ (S = solvent), from chloroform as well as benzene, ethyl acetate or acetone. The solvent molecules are lost slowly in the air at room temperature and more quickly by heating at 100 °C in the oven. Well-formed crystals without solvent molecules are isolated from chloroform solutions, provided that evaporation of solvent is slow enough.

Both Re(IV) complexes undergo easily an one-electron reduction, by reaction with ascorbic acid in ethanol solution for example, giving the $[ReX_4(bpym)]^-$ anions. The reaction is visually detected due to the intense dark violet colour of these Re(III) complexes. Solutions of $[ReX_4(bpym)]$ in alcohols and other solvents such as tetrahydrofuran evolve over time a violet colour, showing that the solvent can act as a reductant of Re(IV). We have found that these reactions, which are very slow at room temperature and usually require heating, are catalysed very effectively by activated alumina. This result was first observed accidentally during the attempts of purification of the rhenium(IV) complexes by column chromatography and it is the best procedure to synthesize the chloro complex **3**. The bromo analog **4** can be obtained in the same way. Although the synthesis of **3** needs the previous isolation of **1**, **4** can also be obtained by direct reaction of $(NBu_4)_2[ReBr_6]$ and bpym in isopropanol in an "one-pot" process (see Experimental).

The rhenium(III) complexes are stable in air as solids but in solution are slowly oxidised by O_2 giving a mixture of $[ReX_4(bpym)]$ and ReO_4^-.

Description of the structures of $[ReCl_4(bpym)]$ (1) and $[ReBr_4(bpym)]$ (2)

Compounds **1** and **2** are isostructural and consist of discrete $[ReX_4(bpym)]$ molecules held together by means of van der Waals interactions. A perspective drawing of the structure showing the atom numbering is depicted in Fig. 1, while selected bond lengths and angles are listed in Table 1. Each $[ReX_4(bpym)]$ unit contains a Re(IV) atom in a distorted octahedral geometry, being bonded to a bidentate bpym molecule and four chloride/bromide anions. The main distortion of the ideal octahedral geometry is due to the short bite angle of the bidentate bpym ligand [76.3(3) and 75.6(2)° for N(1)–Re–N(2) in **1** and **2**, respectively]. The average Re–X and Re–N bond distances [2.322(2) and 2.133(7) Å in **1** and 2.4595(7) and 2.145(4) Å in **2**] are in agreement with those found in the literature.[7,8,12,16] The Re–X bond lengths in *trans* position to the nitrogen donors are slightly shorter than those in *cis* positions. This effect is more evident in compound **2** [average value 2.311(3) and 2.333(2) Å in **1** and 2.4406(7) and 2.4634(6) Å in **2**]. The N(1), N(2), X(2), and X(3) set of atoms constitute the best equatorial plane around Re, the largest deviation from planarity being 0.009(3) Å for N(1) and 0.017(2) Å for N(2) in **1** and **2**, respectively. The Re atom is practically placed in this plane. The pyrimidyl rings are planar [largest deviation from the mean planes not greater than 0.038(6) Å for C(4) in **1** and 0.030(4) Å for C(3) in **2**] and the C–C and C–N bond lengths are as expected. On the contrary the bpym molecule as a whole shows evident deviation from planarity, largest deviations from the mean planes being 0.183(8) (**1**) and 0.209(6) (**2**) Å. There is an appreciable *tilt* between the two pyrimidyl rings, the dihedral angles between them being 16.0(3) and 16.8(2)° in **1** and **2**, respectively (Fig. S1†). This is probably the main reason for which both compounds crystallize in an acentric space group. The metal atom is −0.246(9) (**1**) and 0.264(5) Å (**2**), respectively, out of the mean plane of the whole bpym molecule. The dihedral angles between previous plane and mean equatorial one are 6.9(2) (**1**) and 8.7(2)° (**2**).

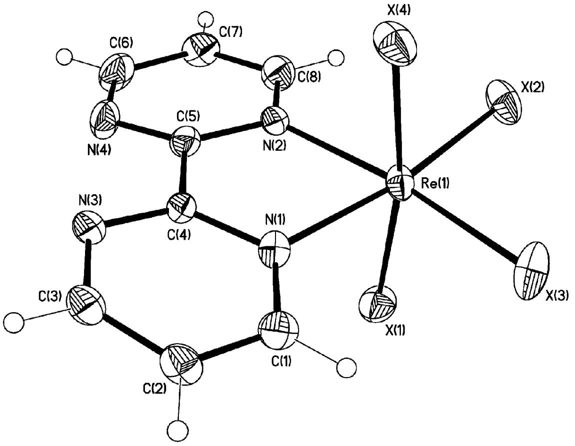

Fig. 1 Perspective drawing of the structure of $[ReX_4(bpym)]$ [X = Cl (**1**) and Br (**2**)] showing the atom numbering scheme. Thermal ellipsoids are drawn at 30% of probability level.

$[ReX_4(bpym)]$ molecules are packed through weak forces, even if there are aromatic groups no π–π interactions are present. It is possible to define different planes of rhenium atoms in the crystal packing: pair of parallel planes, with shortest Re · · · Re distance between them of 6.766 in **1** and 6.886 Å in **2** [Re(1) · · · Re(1a); a = $x - 1/2, -y + 1/2, -z$], spaced by other planes forming a dihedral angle with previous pair of sheets of 37.2 and 39.2° in **1** and **2**, respectively, giving rise to a herringbone motif (Fig. S2†). The shortest Re · · · Re distances between the two not parallel planes are 6.550 and 6.728 Å [Re(1) · · · Re(1b); b = $-x + 1/2 + 1, -y, z - 1/2$].

Table 1 Selected bond lengths (Å) and angles (°) for compounds **1–4**[a]

	1 (X = Cl)	**2** (X = Br)	**3** (X = Cl)	**4** (X = Br)
Re(1)–N(1)	2.134(7)	2.147(4)	2.0545(14)	2.08(2)
Re(1)–N(2)	2.131(7)	2.144(4)	2.0438(15)	2.08(2)
Re(1)–X(1)	2.344(2)	2.4964(7)	2.3717(5)	2.514(3)
Re(1)–X(2)	2.317(2)	2.4418(6)	2.3766(6)	2.523(3)
Re(1)–X(3)	2.306(3)	2.4394(7)	2.3780(5)	2.531(3)
Re(1)–X(4)	2.322(2)	2.4604(6)	2.3711(5)	2.536(3)
Re(2)–N(5)				2.07(2)
Re(2)–N(6)				2.09(2)
Re(2)–X(5)				2.520(2)
Re(2)–X(6)				2.519(2)
Re(2)–X(7)				2.540(2)
Re(2)–X(8)				2.521(2)
N(1)–Re(1)–N(2)	76.3(3)	75.6(2)	76.90(6)	74.9(7)
N(1)–Re(1)–X(1)	85.8(2)	85.1(1)	171.2(4)	92.6(5)
N(2)–Re(1)–X(1)	87.2(2)	87.1(1)	94.29(4)	90.5(5)
N(1)–Re(1)–X(3)	95.0(2)	96. 0(1)	89.80(5)	169.1(5)
N(2)–Re(1)–X(3)	171.3(2)	171.5(1)	91.73(4)	94.7(5)
N(1)–Re(1)–X(2)	170.2(2)	170.3(1)	94.60(5)	97.0(5)
N(2)–Re(1)–X(2)	93.9(2)	94.7(1)	171.16(4)	171.8(5)
X(1)–Re(1)–X(2)	93.9(2)	93.88(2)	94.16(2)	91.2(1)
X(1)–Re(1)–X(3)	92.6(1)	93.20(3)	89.80(5)	90.8(1)
X(1)–Re(1)–X(4)	170.5(1)	169.23(2)	90.62(2)	177.4(1)
X(2)–Re(1)–X(3)	94.8(1)	93.69(3)	90.68(2)	93.3(1)
X(2)–Re(1)–X(4)	93.4(1)	94.14(2)	89.92(2)	89.6(1)
X(3)–Re(1)–X(4)	93.5(1)	93.43(3)	178.06(2)	91.6(1)
N(1)–Re(1)–X(4)	86.4(2)	85.8(1)	88.32(5)	84.9(5)
N(2)–Re(1)–X(4)	85.7(2)	93.88(2)	87.41(4)	88.3(5)
N(5)–Re(2)–N(6)				75.7(8)
N(5)–Re(2)–X(5)				88.4(5)
N(5)–Re(2)–X(6)				94.8(5)
N(5)–Re(2)–X(7)				172.3(6)
N(5)–Re(2)–X(8)				92.5(5)
N(6)–Re(2)–X(5)				89.4(5)
N(6)–Re(2)–X(6)				170.3(5)
N(6)–Re(2)–X(7)				97.0(5)
N(6)–Re(2)–X(8)				86.2(5)
X(5)–Re(2)–X(7)				89.12(8)
X(6)–Re(2)–X(7)				92.60(8)
X(6)–Re(2)–X(8)				92.37(8)
X(5)–Re(2)–X(6)				92.32(8)
X(5)–M(1)–X(8)				175.14(9)
X(7)–M(1)–X(8)				89.40(8)

[a] Estimated standard deviations in the last significant digits are given in parentheses.

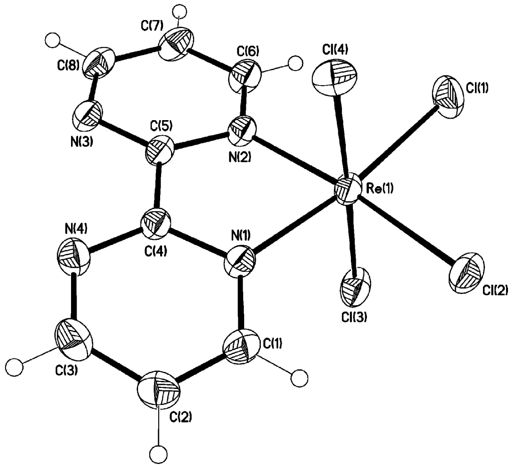

Fig. 2 Perspective drawing of the $[ReCl_4(bpym)]^-$ anions in **3** showing the atom numbering scheme. Thermal ellipsoids are drawn at 30% of probability level.

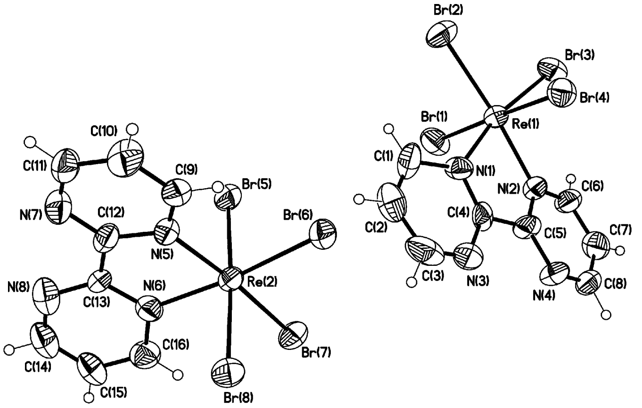

Fig. 3 Perspective drawing of the $[ReBr_4(bpym)]^-$ anions of the asymmetric unit in **4** showing the atom numbering scheme. Thermal ellipsoids are drawn at 30% of probability level.

Description of the structures of $(PPh_4)[ReCl_4(bpym)]$ (3) and $(NBu_4)[ReBr_4(bpym)]$ (4)

The structure of compounds **3** and **4** consists of discrete $[ReX_4(bpym)]^-$ anions and tetraphenylphosphonium (**3**) or tetrabutylammonium (**4**) cations. Two crystallographically inequivalent complex anions are present in the asymmetric units of compound **4**. A perspective drawing of the structures showing the atom numbering is depicted in Fig. 2 and 3, and selected bond lengths and angles are summarized in Table 1. Each $[ReX_4(bpym)]$ unit contains a Re(III) atom in the same environment of **1** and **2**, being bonded to a bidentate bpym molecule and four chloride/bromide anions in a distorted octahedral geometry. As in all compounds with chelating ligands, the main distortion of the ideal octahedral geometry is due to the short bite angle of the bidentate bpym ligand [76.90(6) in **3** and 75.0(6) and 75.7(7)° in **4**]. The average Re–X and Re–N bond distances [2.374(1) and 2.049(1) Å in **3** and 2.526(2) and 2.07(2) Å in **4**] are in agreement with those found in the literature for compounds containing rhenium(III),[17,18] and it can be noted that while Re–X bond distances enlarge, Re–N bond distances shorten in **3** and **4** when compared to **1** and **2**. Shorter Re–N bond distances indicate that a stronger bond occurs in compounds **3** and **4** where rhenium atom is in a lower oxidation state, evidencing a higher affinity of Re(III) respect to Re(IV) for bpym, and reflecting the π-accepting ability of this heterocyclic ligand.

Unlike structures **1** and **2**, no significant variations in the Re–X bond lengths in *trans* and *cis* positions to the nitrogen donors were observed in **3** and **4**. As in compounds **1** and **2**, the best equatorial plane around the Re atom contains the nitrogen atoms of bpym ligands [the largest deviation from planarity being 0.018(1) for N(2) and 0.047(8) Å for N(5) in **3** and **4**, respectively] and forms a dihedral angle with the mean plane of the bpym molecule of 12.0(1) in **3** and 11.2(5) and 7.6(6)° in **4**. The Re atom is practically placed in this plane. The pyrimidyl rings are planar [largest deviation from the mean planes not greater than 0.033(1) Å for C(4) in **3** and 0.04(1) Å for N(2) in **4**] and the C–C and C–N bond lengths are as expected. As found in the structures of **1** and **2**, the bpym molecule as a whole shows evident deviation from planarity, largest deviations from the mean planes being 0.217(2) (**3**) and 0.15(2) Å (**4**) and again there is an appreciable *tilt* between the two pyrimidyl rings, the dihedral angles between them being 16.0(1) in **3** and 13(1) and 14(1)° in **4**.

The metal atom is 0.425(2) Å out of the mean plane of the whole bpym molecule in **3** and 0.37(2) and 0.28(2) Å out of the previous plane, respectively, for Re(1) and Re(2) in **4**.

$[ReX_4(bpym)]^-$ anions are well separated by the bulky PPh_4^+ (**3**) or NBu_4^+ (**4**) cations in the resulting three-dimensional ionic lattices. The values of the shortest interionic Re···Re distances are 8.412(1) (**3**) [Re(1)···Re(2a); (a) = $1 - x, 2 - y, 2 - z$] and 8.974 (1) Å (**4**) [Re(1)···Re(2a); (a) = $1 + x, y, z$].

The PPh_4^+ cation in **3** shows the expected tetrahedral shape and its bond lengths and bond angles are in agreement with those previously reported in other compounds.[19–22] Each cation is involved in a *parallel-fourfoldphenyl-embrace* (P4PE), in which two phenyl rings are approximately parallel and the motif comprises one offset-face-to-face (off) and two edge-to-face (ef) attractive phenyl interactions.[23] The N–C and C–C distances and the N–C–C and C–C–C angles of each tetrahedral NBu_4^+ cation in **4** are affected by same scatterings. This doubtless arises from the considerable thermal motion, which is quite a common feature observed in most of the crystals containing this organic cation.

Electrochemistry

Fig. 4 shows the voltammetric profile of Au-*pc* in 1 mM solution of $[ReCl_4(bpym)]$ in acetonitrile obtained at $v = 0.050\ Vs^{-1}$. Three remarkable redox couples can be detected. Couple **I** is a reversible, one electron process located at $E'^0 = +0.19$ V, with $\Delta E_p = 0.06$ V, and $i_{pa}/i_{pc} = 1$, where i_{pa} and i_{pc} denote the intensities of the anodic and cathodic current peaks respectively, ΔE_p represents the anodic to cathodic peak separation ($E_{pa} - E_{pc}$), and E'^0 corresponds to the formal redox potential of the couple calculated as $(E_{pa} + E_{pc})/2$. This couple can be assigned to a Re(III)/Re(IV) pair, due to the alternating appearance and disappearance of the red–purple coloration of the Re(III)-complex on the surface of the gold electrode.

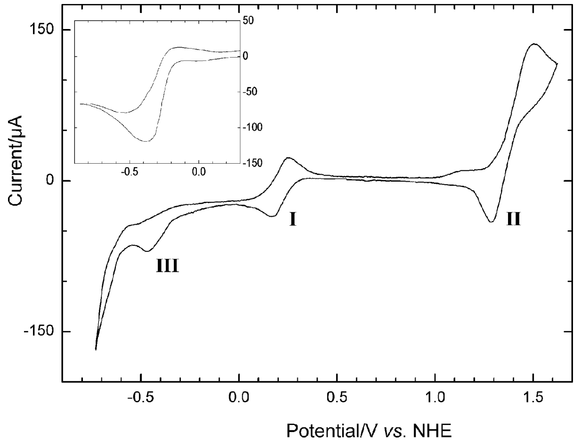

Fig. 4 Voltammetric profile of Au-*pc* in 1 mM $[ReCl_4(bpym)]$ in 0.04 M tetraethylammonium perchlorate in acetonitrile. Voltammetric profile of Au-*pc* in 1 mM 2,2′-bipyrimidine in 0.04 M tetraethylammonium perchlorate in acetonitrile (inset). $T = 25$ °C, $v = 0.050\ V\ s^{-1}$.

Irreversible couple **II** appears at $E'^0 = +1.35$ V, with $\Delta E_p = 0.18$ V, and $i_{pa}/i_{pc} < 1$, and is assigned to a Re(IV)/Re(V) pair. This process is controlled by the slow transference of the electron, according to the linear dependence between E_{pa} and ln v (slope 29 mV decade^{-1}). Both oxidation processes (couples **I** and **II**) involve electroactive species diffusing onto the electrode, as assessed by a linear plot for anodic current peak *versus* the square root of the scan rates.

The third signal (couple **III**) has a noticeable cathodic contribution detected at −0.47 V with a small anodic counterpart at −0.33 V ($i_{pa}/i_{pc} \ll 1$). A comparison with the profile of Au-*pc* in 1 mM bpym solution in acetonitrile (Fig. 4, inset) allows us to assign these waves to a redox process involving the ligand, superimposed to the reduction of the supporting electrolyte.

Fig. 5a shows the voltammetric profile of Au-*pc* in 1 mM solution of $[ReBr_4(bpym)]$ in acetonitrile, obtained at $v = 0.050\ Vs^{-1}$ for the first potential scan (solid line). At first sight, this profile presents more complexity when compared to the chloro analogue. However, it is possible to recognize couples **I** and **II**, corresponding to the successive oxidations Re(III) → Re(IV) and Re(IV) → Re(V). The reversible first couple is located at $E'^0 = +0.32$ V ($\Delta E_p = 0.06$ V), and irreversible couple **II** has an $E_a = +1.25$ V and $E_c = +0.95$ V. Contributions originated in the system ligand–supporting electrolyte–solvent are also present.

Fig. 5a also shows some other new contributions that did not appear in the first potential scan, but from recording the profile after some minutes of work, cycling between −0.10 V and + 0.90 V at the same scan rate (dashed line). The new peaks are labeled $\mathbf{IV}_a$ (+0.43 V), $\mathbf{V}_a$ (+0.67 V), $\mathbf{VI}_c$ (+0.26 V) and $\mathbf{VII}_c$ (0.05 V). As can be seen in Fig. 5b, after 1 h of work, the couple **I** is still detected, but anodic current peaks $\mathbf{IV}_a$ and $\mathbf{V}_a$ predominate. These anodic contributions that were not detected during the first cycles of the potential scan, arose during the working time and their intensity current peaks reached a maximum when couple **I** disappeared. Irreversible oxidations waves $\mathbf{IV}_a$ and $\mathbf{V}_a$ correspond to the formation of ReO_4^- from adsorbed ReO_2 monolayers or multilayers, respectively, while the cathodic peaks $\mathbf{VI}_c$ and $\mathbf{VII}_c$ are consequences of the formation of ReO_2 from ReO_4^- and subsequent steps of reduction to species such $[Re^{III}O]^+$ and ReO.[24] In order to confirm these assignments, the working electrode was then rinsed with acetonitrile and stored without further cleaning in a solution of the supporting electrolyte, and the voltammetric profile recorded again. This is shown in Fig. 5c, which shows only the characteristic signals corresponding to the formation of soluble perrhenate from ReO_2 deposited on the electrode.

A second set of experiments was performed in DMF as solvent. The voltammetric profile of complex **1** is not so well resolved in DMF as in acetonitrile (Fig. S3†). In any case, couple **I** is clearly located at $E'^0 = +0.10$ V ($\Delta E_p = 0.10$ V, $i_{pa}/i_{pc} < 1$). For this couple, peak potential values are not dependant on the scan rate, indicating a fast electron exchange. The process involves the electroactive species diffusing onto the electrode, according to the i_p *versus* $v^{1/2}$ linear adjustment. Couple **I** is partially overlapped to the redox contributions ascribed to electron exchanges of the system ligand–supporting electrolyte–solvent. Couple **II**, corresponding to the Re(IV)/Re(V) pair, is poorly defined having an anodic contribution at +1.30 V, and a cathodic one at *ca.* +0.8 V.

The profile of complex **2** in DMF (Fig. S4†) shows a quasi reversible couple **I** located at $E'^0 = +0.22$ V ($\Delta E_p = 0.08$ V, $i_{pa}/i_{pc} = 1$

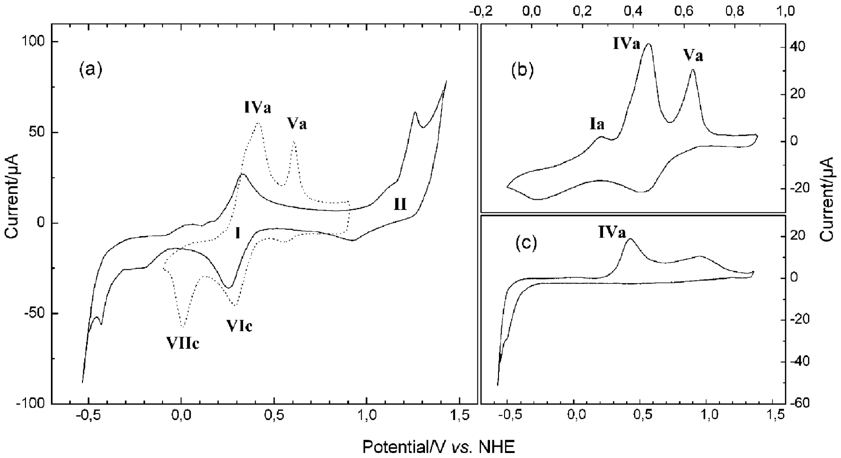

Fig. 5 Voltammetric profile of Au-*pc* in 1 mM $[ReBr_4(bpym)]$ in 0.04 M tetraethylammonium perchlorate in acetonitrile. (a) Profile for the first potential scan recorded at $v = 0.050$ V s^{-1}(solid line) and profile obtained after some minutes of work at the same potential scan rate (dashed line). (b) Profile after 1 h of work, recorded at low potential scan rates ($v = 0.025$ V s^{-1}). (c) Voltammetric profile of Au-*pc* in 0.04 M tetraethylammonium perchlorate in acetonitrile: electrode stored 24 h without cleaning.

at $v = 0.050$ V s^{-1}). This process is also diffusion controlled, as i_p adjusts linearly with $v^{1/2}$. It is possible to detect the couple **II**, with an anodic current peak at +1.15 V, and a cathodic contribution at *ca.* + 0.8 V. The potential peak value for the anodic wave is independent of v and i_{pa} adjusted linearly with $v^{1/2}$, involving the diffusion of the electroactive species. Other redox contributions from the ligand and/or the supporting electrolyte are not observed, probably due to overlap by the Re(III)/Re(IV) couple.

Conclusions

We have reported on the synthesis of the first examples of Re(IV)-bpym complexes, **1** and **2**, by ligand substitution onto $[ReX_6]^{2-}$ anions in DMF, and Re(III)-bpym complexes, **3** and **4**, by reduction of the former compounds.

Rhenium–nitrogen bond distances shorter in **3** and **4** than in **1** and **2**, respectively, indicate a stronger bond in the lower oxidation state, which can be explained on the basis of the π-acceptor character of bpym. The higher affinity of Re(III) for bpym stabilizes oxidation state III relative to IV, and then complexes **1** and **2** can be easily reduced, chemically and electrochemically.

Electrochemical reduction of **1** to **3** is reversible in acetonitrile; reduction of **2** to **4** is reversible in acetonitrile and quasi reversible in DMF. Complex **2** evidences a notorious instability in acetonitrile towards formation of rhenium dioxide and perrhenate. Voltammograms also show that **1** and **2** could be oxidized, but these processes are not reversible, probably due to the expected high reactivity of the Re(V) species. It can be noted that for the oxidation process Re(IV) → Re(V), the anodic peak is less positive for **2** than for **1** in both solvents, so **2** can be more easily oxidized than **1**. On the contrary, the bromine complex **2** is *ca.* 0.12 V easier to reduce to Re(III) than the chlorine complex **1** in acetonitrile and DMF, that suggests that bromo ligands contribute to stabilizing the oxidation state III with respect to IV better than chloro ligands. For both complexes, E'° values in CH_3CN are *ca.* 0.10 V more positive than the related potential values in DMF, and ΔE_p are smaller in CH_3CN than in DMF, due to a faster electron transfer.

Experimental

Preparation of compounds

All reagents, metal salts and ligands were used as received from commercial sources. Ammonium hexachlororhenate and potassium hexabromorhenate were prepared from the corresponding perrhenate salts following literature procedures.[25] The $K_2[ReBr_6]$ was transformed into the *n*-tetrabutylammonium salt by metathetic reaction in cold 0.5 M HBr. Solvents were dried by standard methods when necessary. *N*,*N*-Dimethylformamide (water content 0.1%) was stored with Linde type 4 Å molecular sieves.

$[ReCl_4(bpym)]$ 1. Ammonium hexachlororhenate (0.65 g, 1.5 mmol) and bpym (0.36 g, 2.25 mmol) were stirred in DMF (4 mL) for 4 h at 110 °C. After cooling the dark brown solution was filtered and evaporated at 60 °C until the complete elimination of solvent. The brown residue was washed with acidified H_2O (3 × 15 mL H_2O with 2–3 drops of 0.5 M HCl) and left to dry in the air. This solid was then shaken with CH_2Cl_2 (50 mL) for 30 min and the resulting solution was filtered and the insoluble residue was discarded. The filtrate was washed several times with portions of H_2O (25 mL) in a separation funnel until the aqueous layer became almost colourless. The dark orange dichloromethane layer was then dried and the solvent evaporated under reduced pressure to leave an orange–yellow microcrystalline solid which was finally dried at 110 °C. Yield: 20%. If all the pink aqueous fractions are collected and left to stand in air, the Re(III) complex is reoxidized to Re(IV) and a further crop of crystals of **1** can be obtained, increasing the yield by up to 25% (Found: C, 19.6; H, 1.23; N, 11.1. $C_8H_6N_4Cl_4Re$ requires C, 19.8; H, 1.24; N, 11.5%); λ_{max}/nm (CH_3CN) 240 (ε/dm^3 mol^{-1} cm^{-1} 20 300), 273sh, 290 (12000), 660sh, 719 (31) and 769 (36); IR bands associated with coordinated bpym at v_{max}(KBr disc)/cm^{-1} 1579vs, 1547m, 1406vs, 819m, 746s and 667m. Golden crystals of **1** suitable for X-ray determination were grown from a solution in $CHCl_3$ by very slow evaporation at room temperature.

$[ReBr_4(bpym)]$ 2. Potassium hexabromorhenate (223 mg, 0.3 mmol) and bpym (47.4 mg, 0.3 mmol) were mixed in DMF

(1 mL) and heated at 90 °C over 2 h with continuous stirring. The resulting dark brown solution was evaporated at 60 °C until complete elimination of DMF. The residue was extracted with $CHCl_3$ to give a reddish brown solution which was filtered and evaporated to dryness. The last residue was then extracted with dry methanol, filtered and evaporated to dryness again. The crude product was finally dried at 100 °C to give **2** as a dark powder. Yield: 40% (Found: C, 14.3; H, 1.05; N, 8.40. $C_8H_6N_4Br_4Re$ requires C, 14.5; H, 0.91; N, 8.44%); λ_{max}/nm (CH_3CN) 227 (ε/dm^3 mol^{-1} cm^{-1} 16100), 245 (16100), 308sh, 356 (4600), 688 (110), 741 (110) and 822 (110); IR bands associated with coordinated bpym at ν_{max}(KBr disc)/cm^{-1} 1576vs, 1544m, 1404vs, 814m, 743s and 665m. Red crystals of **2** suitable for X-ray determination were grown from a solution in $CHCl_3$ by very slow evaporation at room temperature.

(PPh$_4$)[ReCl$_4$(bpym)] 3. Complex **1** (48.6 mg, 0.1 mmol) was dissolved in the minimum amount of acetonitrile and the resulting yellow solution was loaded onto an alumina column partly deactivated with 10% water. At once, a colour change from yellow to violet was observed at the top of the column. The sample was then eluted with tetraphenylphosphonium chloride 0.013 M in acetonitrile, and the violet fraction was collected. The solvent was then evaporated to dryness at room temperature to give a mixture of an almost black crystalline solid (**3**) and a large excess of PPh_4Cl. The latter was dissolved by the addition of water and the insoluble crystals of **3** filtered, washed with water and dried in air. Yield: >80% (Found: C, 46.4; H, 3.11; N, 6.30. $C_{32}H_{26}N_4Cl_4PRe$ requires C, 46.6; H, 3.17; N, 6.78%); λ_{max}/nm (CH_3CN) 431 (ε/dm^3 mol^{-1} cm^{-1} 3400), 521 (6000), 592sh and 798 (2300); IR bands associated with coordinated bpym at ν_{max}(KBr disc)/cm^{-1}: 1387vs, 1179s, 997s. Better crystals of **3** for crystallographic studies could be obtained by a second procedure: A slurry of complex **1** (10 mg, 0.02 mmol) in absolute ethanol under inert atmosphere was treated with ascorbic acid (50 mg, 0.28 mmol). The colour changed slowly from yellow to violet as the rhenium(IV) complex was dissolved. Then an excess of tetraphenylphosphonium chloride (150 mg, 0,33 mmol) was added. The solution was filtered and left to evaporate slowly in an inert atmosphere. Small polyhedric crystals of **3** appeared after a few days.

(NBu$_4$)[ReBr$_4$(bpym)] 4. Tetrabutylammonium hexabromorhenate (230 mg, 0.2 mmol) and bpym (64 mg, 0.4 mmol) were refluxed in 2-propanol : acetone 10 : 1 (20 mL) for 1 h. After cooling, the solution was filtered and allowed to stand, producing well-formed dark red–purple crystals of complex **4** in 15% yield after 3 days. Alternatively, if the mentioned solution was first shaken with ascorbic acid (176 mg, 1.0 mmol) for 24 h and then filtered and allowed to stand for a few days, the yield rose to up to 30% (Found: C, 31.85; H, 4.72; N, 7.67. $C_{24}H_{42}N_5Br_4Re$ requires C, 31.80; H, 4.67; N, 7.73%); λ_{max}/nm (CH_3CN) 240 (ε/dm^3 mol^{-1} cm^{-1} 20 600), 352 (7200), 390sh, 524 (4500) and 786 (2400); IR bands associated with coordinated bpym at ν_{max}(KBr disc)/cm^{-1}: 1571m, 1392vs, 1170s, 999s, 734m.

Crystallography

X-Ray diffraction data were collected using a Bruker R3m/V automatic four-circle for compounds **1**, **4** and a Bruker-Nonius X8APEXII CCD area detector diffractometer for the complexes **2**, **3**. Graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) was used in both cases. Lorentz-polarization and empirical absorption corrections through the ψ-scan program[26] was applied for compound **4**, whereas the data of compound **1** was corrected by the XABS program.[27] The maximum and minimum transmission factors were 0.0931 and 0.1965 for **1**, and 0.1919 and 0.1267 for **4**. The data for compounds **2**, **3** were processed through the SAINT[28]

Table 2 Crystal data and structure refinement for [ReX$_4$(bpym)] where X = Cl (**1**) and X = Br (**2**), P(C_6H_5)$_4$[ReCl$_4$(bpym)] (**3**) and N(C_4H_9)$_4$[ReBr$_4$(bpym)] (**4**)[a]

Compound	**1**	**2**	**3**	**4**
Formula	$C_8H_6Cl_4N_4Re$	$C_8H_6Br_4N_4Re$	$C_{32}H_{26}Cl_4N_4PRe$	$C_{48}H_{84}Br_8N_{10}Re_2$
Formula weight	486.17	664.01	1651.08	1812.93
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$	$P2_1$
Z	4	4	2	2
a/Å	9.154(2)	9.6216(9)	9.0661(9)	16.227(3)
b/Å	10.703(3)	10.8583(10)	12.6350(12)	11.094(2)
c/Å	13.401(2)	13.4431(11)	14.2539(13)	18.502(4)
α/°	90.0	90.0	89.361(2)	90.0
β/°	90.0	90.0	86.606(2)	105.87(3)
γ/°	90.0	90.0	82.236(2)	90.0
V/Å^3	1313.0(5)	1404.5(2)	1615.0(3)	3203.8(11)
D_c/g cm^{-3}	2.459	3.140	1.698	1.879
F(000)	900	1188	808	1744
μ/cm^{-1}	100.49	200.15	41.72	88.02
refln. collected/obs.	4577/3835	17330/4872	20306/10366	6237/5992
Goodness-of-fit on F^2	1.058	0.989	1.027	0.892
R_1 [$I > 2\sigma(I)$][b]	0.0422	0.0299	0.0200	0.0501
Absolute structure parameter	0.008(15)	−0.030(14)		0.03(2)
wR_2[c,d]	0.1059	0.0646	0.0473	0.1143
Largest diff. peak and hole/e Å^{-3})	1.362 and −1.844	1.551 and −1.140	0.851 and −0.660	1.485 and −1.762

[a] Details in common: $T = 293(2)$ K. [b] $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [c] $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2]/[(w(F_o^2)^2]\}^{1/2}$. [d] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = [F_o^2 + 2F_c^2]/3$, $a = 0.0656$ (**1**), 0.0289 (**2**), 0.0226 (**3**) and 0.0720 (**4**), $b = 4.6686$ (**1**), 0.3058 (**3**) and 0 (**2**, **4**).

reduction and SADABS[29] absorption software. The unit cell parameters, which are listed in Table 2 together with a summary of the structure refinement data, in **1** and **4** were determined from least-squares refinement of the setting angles of 25 reflections in the 2θ range 15–30°, while in **2** and **3**, were based upon least-squares refinement of 8317 (**2**) and 6489 (**3**) reflections. The structures were solved by Patterson methods and subsequently completed by Fourier recycling using the SHELXTL software package.[30] Non-hydrogen atoms were refined anisotropically except the side chain carbon atoms C(21)–C(22)–C(23)–C(24) of the *n*-butyl in compound **4** that are affected by a large thermal motion, therefore were set on ΔF map and not refined. Hydrogen atoms were set in calculated positions and refined as riding atoms. Full-matrix least-squares refinements on F^2, carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, reached convergence with values of the discrepancy indices given in Table 2. The final geometrical calculations were carried out with the PARST program.[31] The graphical manipulations were performed using the XP utility of the SHELXTL system.

Testing the two enantiomeric models of the crystal **1**, **2** and **4** with a final refined Flack parameter of 0.01(1), 0.03(1), and 0.03(2), respectively, shows that the handedness was uniquely determined. CCDC reference numbers are 623923–623926 for complexes **1**–**4**, respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615136a

Other measurements

Electronic absorption spectra were recorded with a Shimadzu UV-1603 spectrophotometer. Infrared spectra (KBr pellets) were obtained on a Perkin-Elmer 1750 FT-IR spectrometer. Elemental analyses for carbon, hydrogen and nitrogen were carried out in a Carlo Erba EA1108 elemental analyzer.

The voltammetric profile of the systems were evaluated in acetonitrile or DMF with tetraethylammonium perchlorate (0.04 M) as supporting electrolyte, at potential scan rates v varying between $0.01\ \mathrm{V\ s^{-1}} \leq v \leq 0.10\ \mathrm{V\ s^{-1}}$. Measurements were carried out in a one compartment conic cell, using a polycrystalline (*pc*) Au disc (3 mm diameter) as working electrode, a Pt sheet as counter electrode and Ag/AgNO$_3$ 0.1 M in the supporting electrolyte ($E = 0.60$ V *vs.* NHE) as the reference. All potentials in the text are referenced to the NHE.

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