Syntheses and structures of pyrazolylmethane complexes of rhenium(III), (IV) and (V)

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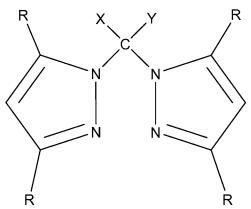
Reaction of $[ReOCl_3(PPh_3)_2]$ with $HCpz_3$ (pz = pyrazole) in dichloromethane leads to the formation of a new Re(IV) complex $[ReCl_3(HCpz_3)]X$ (X=Cl, $[ReO_4]$) with loss of the rhenium-oxo group. We also report a convenient, high-yield synthetic route to complexes of the type $[ReOX_n(L)]^{(3-n)+}$ (X=Cl, Br, $n = 2, 3$) by the reaction of bis(pyrazolylmethane) and bis(pyrazolylacetate) ligands with $[ReOCl_3(PPh_3)_2]$. Dinuclear complexes containing the O=Re–O–Re=O group were also isolated and structurally characterised. We have also investigated the reactions of these ligands with diazenide precursors and isolated and characterised complexes of the type $[ReCl_x(N_2Ph)(L)(PPh_3)]$ ($x = 1,2$). The potential applications of these complexes as radiopharmaeuticals is discussed.

Introduction

There is much interest in the development of new radiotherapeutic cancer agents based on rhenium.[1] There are two β-emitting isotopes of Re, ^{186}Re and ^{188}Re which have suitable nuclear properties for therapeutic applications. ^{188}Re is readily available from a generator by decay of ^{188}W and is obtained as a very dilute solution of $[ReO_4]^-$.[2,3] This can provide a useful source of sterilising β radiation if it can be targeted *in vivo.* Such targeting can be achieved by the incorporation of the metal atom in a coordination complex involving a bifunctional ligand. Ideally the ligand must form a highly stable complex and possess a point of further functionalisation that can allow the attachment of biologically active molecules[4] to provide specificity and selectivity *in vivo.*[5–8] The addition of a fluorescent probe to the complex would allow the biological targeting of the complex in living cells *in vitro*.

The majority of complexes that have been explored in this context to date have involved the use of linear tetradentate ligands with the Re(V) oxo-core giving generally neutral square pyramidal complexes of the general type [ReOL].[9] Tetradentate ligands with a tripodal framework have been relatively much less explored. Pyrazolylborate ligands are of potential use with rhenium and complexes of the type $[ReOX_2HBpz_3]$ (X_2 = Cl_2, Br_2, 1,2-$C_6H_4O_2$ 1,2-$C_6H_4S_2$ *etc.*,[10–14] pz = pyrazole) have been investigated extensively. Other complexes reported include the hexahydride $[ReH_6HBpz_3]$.[15] However degradation of the pyrazolylborate complexes is a frequent complicating side reaction when protic solvents are employed.[16] Pyrazolylmethane complexes are an attractive alternative due to the higher stability of the C–N bond over the B–N bond, but there have been comparatively few reports of their complexes with rhenium. A series of Re(I) carbonyl complexes of the type $[ReCl(CO)_3HCpz_3]$ and $[Re(CO)_3HCpz_3]^+$[17] together with analogous dimeric complexes of a binucleating variant of the $HCpz_3$ ligand 1,4-$C_6H_4(HOCH_2Cpz_3)_2$ and $[ReO_3HCpz_3]^+$ have been isolated.[18] There are a few isolated references to complexes of rhenium with heteroscorpionate ligands including the neutral species $[ReO_3O_2CCHpz_2]$ prepared from reaction of the so-called heteroscorpionate ligand with perrhenic acid.[18] During the course of this work rhenium complexes containing the O_2CCHpz_2 and CH_2pz_2 ligands were reported.[19] However not all the complexes have been fully identified and there is some uncertainty as to their structures. We have investigated the chemistry of a range of tripodal pyrazole-based ligands (Fig. 1) with rhenium, and we present a much more convenient method to prepare the rhenium(V) pyrazolato complexes using $[ReOCl_3(PPh_3)_2]$, and the synthesis of new Re(III) diazenide complexes by reacting $[ReCl_2(N_2Ph)(NCMe)(PPh_3)_2]$ with ligands HL^4 and L^7. The main objective of this work is a systematic study of the chemistry of pyrazolyl-ligands with rhenium in medium/high oxidation states in the context of possible radiopharmaceutical applications, with full characterisation of the products and a study of their redox and HPLC behaviour.



L^1, L^2 : X=pyrazole; Y=H; L^1, R=H, L^2, R=Me.
L^3 : X=pyrazole; Y=CH_2OH, R=H.
HL^4 to HL^6 : X=COOH; Y=H, HL^4, R=H, HL^5, R=Ph, HL^6, R=2-$MeOC_6H_4$.
L^7, L^8 : X=Y=H; R=H, L^7, R=Me, L^8.

Fig. 1 Pyrazole-based ligands investigated.

Results and discussion

Synthesis of ligands

The structures of the ligands used are summarised in Fig. 1. Ligands L^1 to L^8 were prepared by the literature routes or minor modifications thereof.[20,21] The synthesis of HL^6 and other related ligands will be described elsewhere.[22]

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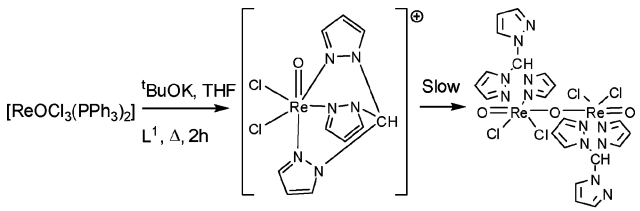
Complexes of the type $[ReOCl_2L^{1-2}]Cl$, (1), (2); and $[Re_2O_3Cl_4(L^1)_2]$ (3)

$[ReOCl_3(PPh_3)_2]$ is conveniently made from perrhenate in virtually quantitative yield and reacts rapidly with a range of $HC(pzR_2)_3$ type ligands (R_2 = H_2, L^1; 3,5-Me_2, L^2) in the presence of potassium tertiary butoxide in thf under reflux to give turquoise blue complexes $[ReOCl_2L^1]X$ **1** (Scheme 1) and $[ReOCl_2L^2]X$, **2** (X = Cl,) in isolated yields of 78%. The precise role of the added butoxide in these reactions is unclear but in its absence brown solutions in thf are formed. Infrared and ESMS(+) data on these complexes were consistent with the formation of the previously reported species formulated as $[ReCl_2(OPPh_3)(HC(PzR_2)_3)]$.[23] However the ^{1}H NMR for complex **1** in d_6-dmso differs from that reported previously[23] in $CDCl_3$, showing three resonances for protons 3-pz, 4-pz and 5-pz, implying that the three pyrazolyl rings are magnetically equivalent. This suggests that some exchange process may be occurring, or that the inequivalence generated by the different groups *trans* to the pyrazole nitrogens is too small to detect. The complexes **1** and **2** showed a characteristic IR band at about 990 cm^{-1}, assigned to the Re=O stretching frequency. The HPLC traces of isolated complexes **1** and **2** (isocratic elution with CH_3CN–H_2O, 80 : 20) show predominantly single species with retention times of 1.38 and 1.46 min, respectively, Fig. 2. Clearly the products of these reactions are highly dependent on the reaction solvent used and carefully controlled conditions are required to prevent formation of inseparable mixtures.[24]



1 **3**

Scheme 1

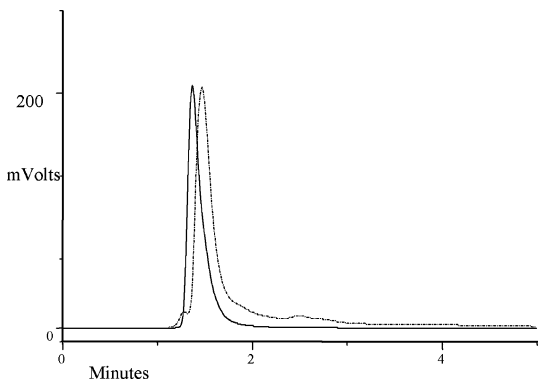


Fig. 2 HPLC traces for compounds **1** (——) and **2** (···), in dmso at 1.38 and 1.46 min respectively, with isocratic elution CH_3CN–H_2O, 80 : 20.

On standing the solution of the reaction of L^1 with $[ReOCl_3(PPh_3)_2]$ in thf deposited a dark blue complex **3** (Scheme 1) in an isolated yield of 2–5% which showed an IR band at 980 cm^{-1} assigned to ν(Re=O). In the range 720–765 cm^{-1} the product showed a strong multi component ν(Re–O–Re) band. The results suggest that there is slow formation of the oxo bridged dimer on standing in solution (Scheme 1) probably due to the presence of adventitious water. The amounts formed in the fresh reaction mixture are too small to be detected by HPLC.

The ^{1}H NMR spectrum of complex **3** showed a complex series of peaks in the region for the pyrazolyl protons, consistent with one of the pyrazolyl groups being uncoordinated. Evidently the reaction to give the complexes of the type $[ReOCl_2L^{1-2}]^+$ is accompanied by the slow formation of the dimeric species.

Single crystals of **3** suitable for an X-ray structure determination were obtained from the reaction solution on standing for 3 days.

An ORTEP representation of the structure appears in Fig. 3. Complex **3** contains the well known linear Re_2O_3 unit comprising a bridging oxo-group with a *trans* oxo-group on each rhenium.[25] Each rhenium is pseudo octahedral with the trispyrazolylmethane ligands functioning in a bidentate manner.

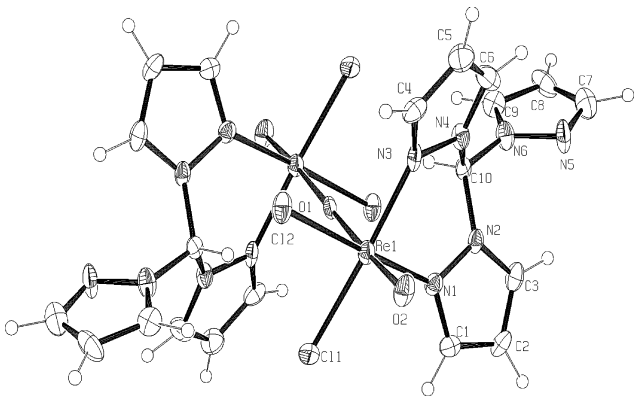


Fig. 3 ORTEP view of the dimeric structure of **3**; thermal ellipsoids are drawn at the 40% level.

As expected it is the pyrazole *trans* to the labilising oxo group that is replaced by the bridging oxo group. Previous reports of this complex had suggested that it was a chloro-bridged dimer.[23] This type of bidentate coordination has been observed previously for tetrakis(pyrazolylborate) ligands.[26] The pyrazolyl groups are arranged in an *anti* configuration to minimise steric interactions. The bond distances and angles are similar to those found for other complexes of the general type $[Re_2O_3Cl_4L_2]$ where L is a neutral bidentate ligand.[25]

Synthesis of $[ReCl_3L^1]X$ (X = Cl, $[ReO_4]$), 4

The reaction of $[ReOCl_3(PPh_3)_2]$ with L^1 in CH_2Cl_2 under reflux (Scheme 2) illustrates that the chemistry of the tris(pyrazolylmethane) ligands with Re(V) oxo precursors is far from straightforward. After 2 h a brown solution was obtained which on treatment with diethyl ether gave a brown-green precipitate. ESMS(+) of this solid showed two peaks, at m/z = 470.9871 (100%), $([M–Cl]^+$. $C_{10}H_{10}Cl_2N_6Re$ requires 470.9901) and at m/z = 749.0844 (60%) $([M + OPPh_3–Cl]^+$. $C_{28}H_{25}Cl_2N_6OPRe$ requires 749.0762). The product showed only very broad signals in the ^{1}H NMR spectrum in $CDCl_3$ consistent with the presence of a paramagnetic Re(IV) species. The IR spectrum showed a strong band at 917 cm^{-1} characteristic of the perrhenate anion. Recrystallisation gave brown crystals unambiguously identified as the Re(IV) cation

by an X-ray structure determination (see below). We assume that $[ReCl_3L^1]^+$ is generated in the mass spectrometer giving rise to the $[M–Cl]^+$ ion observed. The ESMS spectrum of the recrystallised product shows peaks at m/z = 470.9775 (100%), ($[M–Cl]^+$. $C_{10}H_{10}Cl_2N_6Re$ requires 470.9901) as well as m/z = 505.9508 (1%), (M^+. $C_{10}H_{10}Cl_3N_6Re$ requires 505.9569). The other species observed in the mass spectrum of the crude product has been reported as the product of the reaction of complex **1** with triphenylphosphine, but was not fully characterised.[23] Whatever its structure, it is removed in the recrystallisation process. Interestingly the same cationic Re(IV) complex was obtained when L^3 was reacted under the same conditions and the hydroxymethyl group is eliminated during the reaction. The formation of the Re(IV) cation requires disproportionation/oxidation to occur during the reaction, but the formation of the perrhenate anion is well documented in the chemistry of Re(V) oxo-complexes with non-reducing ligands.

Suitable crystals of **4** for an X-ray structure determination were obtained by slow evaporation from $CHCl_3$. An ORTEP representation of the structure appears in Fig. 4 and Table 1 details selected bond lengths and angles of the two crystallographically distinct molecules. The asymmetric unit contains two crystallographically distinct molecules of the cation, two molecules of the perrhenate anion, and four molecules of the solvent ($CHCl_3$). There are a number of H-bonding interactions between the hydrogens on the apical carbons and pyrazole rings and the perrhenate anion. The significance of H-bonding interactions in the solid state structures of pyrazolylmethane complexes has been discussed previously.[23] The geometry around the Re atom is distorted octahedral and the bond lengths and angles are similar to those reported for other Re complexes of L^1.[17,23] The bond distances and angles in the two independent molecules are very similar.

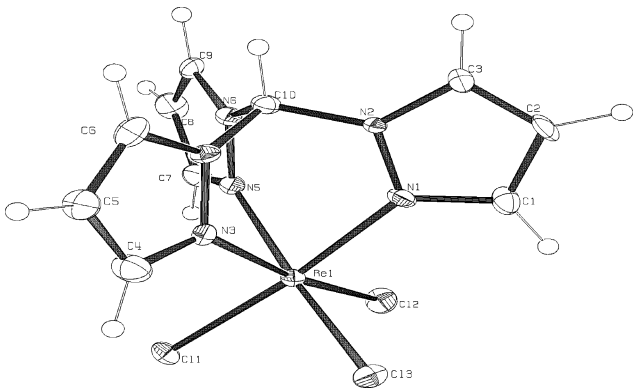
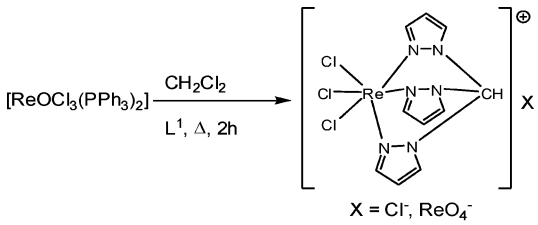


Fig. 4 ORTEP view of the Re(IV) cation $[ReCl_3L^1]^+$ **4**; thermal ellipsoids at 40% probability.

Table 1 Selected bond lengths (Å) and angles (°) for the two independent molecules of $[ReCl_3L^1]^+$

Bond lengths and angles	1	2
Re–N(1)	2.098(7)	2.108(6)
Re–N(3)	2.116(7)	2.119(6)
Re–N(5)	2.108(7)	2.113(6)
Re–Cl(1)	2.306(2)	2.308(2)
Re–Cl(2)	2.290(2)	2.296(2)
Re–Cl(3)	2.292(2)	2.285(2)
$N–Re–N_{av}$	82.5(3)	83.0(3)
$Cl–Re–Cl_{av}$	93.62(8)	93.81(8)



4

Scheme 2

The elemental analysis of the brown product was consistently low in C, H, N for the chloride salt, but higher than required for the perrhenate salt and the C, H, N ratios confirmed the presence of L^1. This is consistent with the presence of both $[ReO_4]^-$ and Cl^- anions. Investigation of another crystal from the same batch as that of the perrhenate salt above showed a chloride anion.

HPLC studies were carried out to monitor the reaction that leads to the loss of the rhenium-oxo group, Fig. 5. Samples of the reaction mixture were collected after 10, 30, and 60 min and examined by HPLC. In the first 10 min there are two major species present with retention times of 1.60 and 1.85 min in a ratio of 1 : 6. After 30 min the ratio of the two peaks changes to 1 : 1 whereas 60 min later formation of a single species with retention time 1.60 min is observed. This peak corresponds to the isolated Re(IV) cation as confirmed by HPLC measurements on the isolated product and shows that it is the major product of the reaction despite the evident complexity. We were unable to identify the intermediate species with a retention time of 1.85 min.

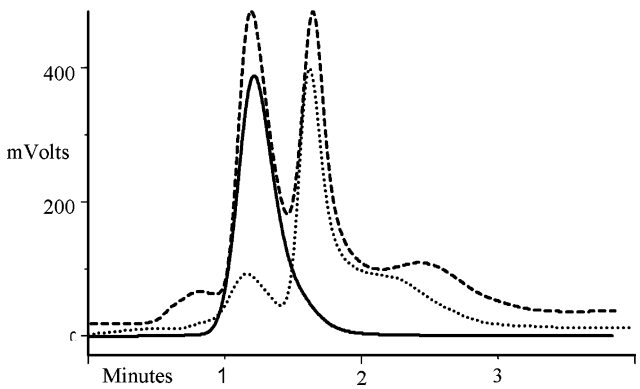


Fig. 5 HPLC studies of the reaction mixture leading to the formation of the cationic complex $[ReCl_3L^1]^+$ **4** in thf at 1.60 min with isocratic elution $CH_3CN–H_2O$ 80 : 20. 10 min (· · ·), 30 min (---), 60 min (——). Small impurity peaks are caused by the reaction solvent (thf).

Complexes of the type $[ReOX_2L^{4\text{-}6}]$ (HL^4, X = Cl), 5a; (HL^4, X = Br), 5b; (HL^5, X = Cl), 6; (HL^6, X = Cl), 7a; (HL^6, X = Br), 7b

The synthesis of the complex $[ReOCl_2(L^4)]$ **5a** from $[ReOCl_4]^-$ has previously been reported.[16] We now report a much more convenient method leading to complex **5a** from $[ReOCl_3(PPh_3)_2]$ by reaction with HL^4 and ^{t}BuOK in thf in 2 h under reflux. The complex is isolated as a turquoise blue solid in yields of 72–75%. The spectroscopic properties of the complex are identical to those previously described. Reaction of $[ReOX_3(PPh_3)_2]$ (X = Cl, Br) with HL^5 and HL^6 gave products **6**, **7a** and **7b** of the same

stoichiometry as for HL[4]. The HPLC retention times in Fig. 6 for **5a** 1.61 min, **6** 2.20 min, **7a** 5.76 min, show how substituents on the pyrazoles modulate the lipophilicity of the complexes. HPLC studies of the reaction solutions show that the complexes are formed in very high yields.

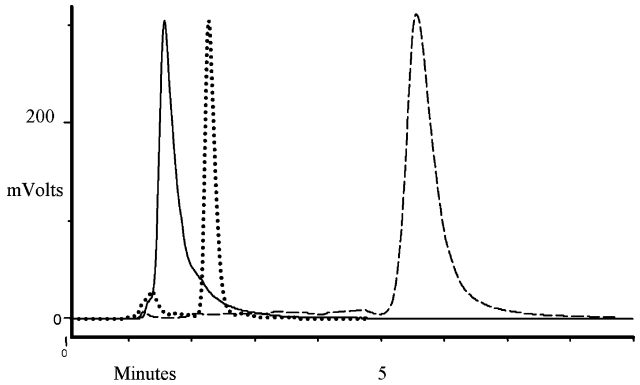


Fig. 6 HPLC traces for complexes **5a** (——), **6** (· · ·), **7a** (---) in CH_3CN at 1.61, 2.20 and 5.76 min respectively, with isocratic elution CH_3CN–H_2O 80 : 20.

Crystals of **7a** suitable for an X-ray structure determination were grown by slow evaporation of a solution in thf. This structure was investigated to assess the steric impact of the bulky substituents on the pyrazole rings and whether the methoxy groups interacted with the rhenium. An ORTEP representation of the structure is shown below in Fig. 7.

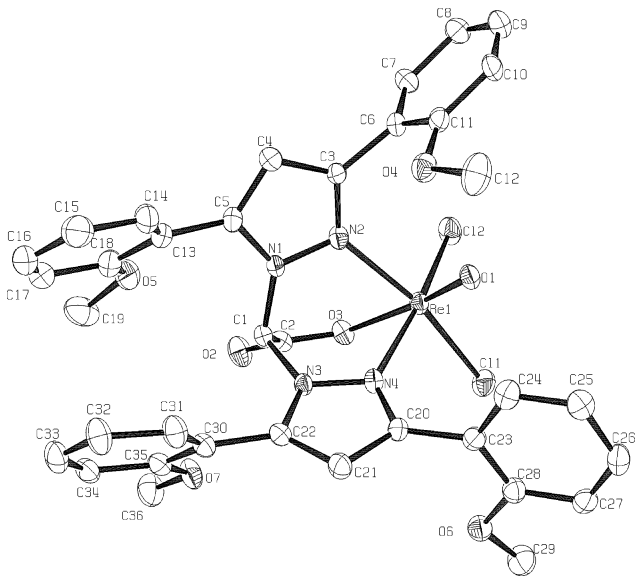


Fig. 7 ORTEP representation of the structure of complex **7a**; thermal ellipsoids at 40% probability.

The coordination about the rhenium atom is in the event directly comparable with that of complex **5a**[16] with pseudooctahedral geometry about the metal. The methoxy groups are oriented so that there are no bonding interactions with the rhenium and the aryl pyrazole substituents are twisted to minimise steric interactions between aromatic C–H hydrogens. Table 2 below makes a comparison between the structures of complexes **5a**[16] and **7a**.

Table 2 Selected bond distances (Å) and bond angles (°) for complexes **5a** and **7a**

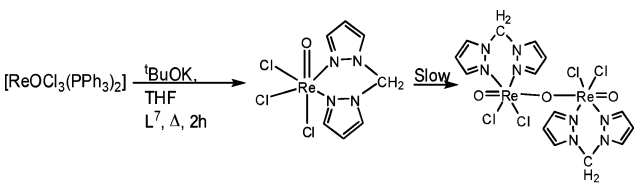
Bond lengths and angles	**5a**[a]	**7a**[a]
Re–Cl(1)	2.3480(13)	2.3335(12)
Re–Cl(2)	2.3415(14)	2.3432(12)
Re–O(1)	1.660(4)	1.666(3)
Re–N(1)	2.089(4)	2.159(4)
Re–N(2)	2.098(3)	2.146(6)
Re–O(2)	2.092(3)	2.069(3)
N(1)–Re–N(2)	88.50(17)	85.83(15)
N(1)–Re–Cl(1)	89.14(12)	90.34(11)
N(2)–Re–Cl(2)	88.78(13)	93.31(11)

[a] The numbering for complex **5a** differs from that of **7a** but comparable bond distances and angles have been selected.

The only significant variation seen in the bond distances is the lengthening of the Re–N bond distances as the steric bulk of the ligands in **7a** forces the pyrazole ligands further from the rhenium. This is accompanied by a decrease in the N–Re–N angles. There is also as expected an increase in the N–Re–Cl angles, again to accommodate the larger aryl substituted pyrazole ligands.

Complexes of the type $[ReOCl_3L^{7-8}]$, 8; 9; and $[Re_2O_3Cl_4(L^7)_2]$, 10

$[ReOCl_3(PPh_3)_2]$ reacts with L^7 under reflux for 2 h in THF to give the previously reported[19] (made from $[ReOCl_4]^-$) neutral turquoise blue complex **8** in 74% yield (Scheme 3). However, beside the monomeric Re(v) oxo-complexes ESMS(+) also indicated the presence of small amounts of a dimeric species. The HPLC of **8** shows a single peak with a retention time of 1.6 min (Fig. 8). The dimeric species was not present in sufficient amounts to be detected in the reaction mixture by HPLC and as with complex **3** it is formed slowly on standing the reaction mixtures in air.



Scheme 3

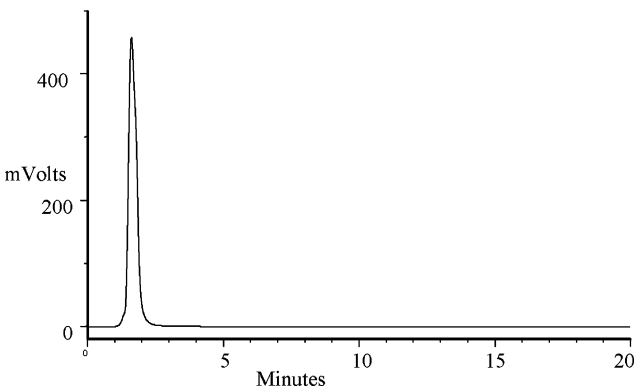


Fig. 8 HPLC trace for complex **8** in dmso at 1.6 min, with isocratic elution with CH_3CN–H_2O 80 : 20.

Table 3 Selected bond lengths (Å) and angles (°) for complexes **3** and **10**

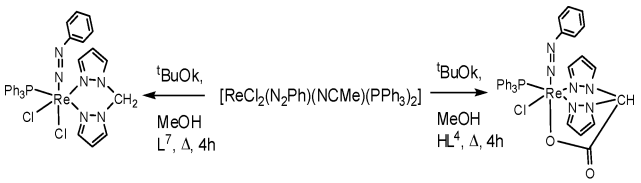
Bond lengths and angles	**3**	**10**
Re(1)–Cl(1)	2.396(2)	2.4025(11)
Re(1)–O(1)	1.9242(3)	1.9182(3)
Re(1)–O(2)	1.683(6)	1.692(5)
Re(1)–N(1)	2.105(7)	2.098(4)
Cl(1)–Re(1)–Cl(2)	90.62(8)	90.26(6)
Cl(1)–Re(1)–O(1)	88.22(6)	88.46(3)
Cl(1)–Re(1)–O(2)	95.0(2)	95.14(12)
Cl(1)–Re(1)–N(1)	90.3(2)	90.03f(11)
O(1)–Re(1)–N(1)	87.68(18)	85.85(11)
O(2)–Re(1)–N(1)	90.9(3)	90.51(16)
Re(1)–N(1)–N(2)	123.4(5)	123.7(3)

By slow evaporation of a solution of **8** from CH_3CN we were able to isolate two types of blue crystals. The pale blue crystals corresponded to the monomer **8**, whereas crystals of the dimer **10** were a dark blue colour. Crystals of **10** suitable for an X-ray structure determination confirmed its formulation as a dimer. For complex **10** selected bond lengths and angles are given in Table 3 with those for dimer **3** above included for comparison. As expected the two structures are very similar. An ORTEP representation is shown in Fig. 9. The dimer has been previously been reported but not structurally characterised.[19]

Complexes of the type [ReCl(NNPh)L^4(PPh$_3$)], 11; [ReCl$_2$(NNPh)L^7(PPh$_3$)], 12

Complexes with diazenide ligands are readily available from pertechnetate for radiopharmaceutical applications but optimal co-ligands have yet to be established. We have therefore investigated the potential use of pyrazole-based ligands. The diazenido complex [ReCl$_2$(N$_2$Ph)(NCMe)(PPh$_3$)$_2$] reacts with HL^4 and L^7 in MeOH in the presence of ^{t}BuOK to give the orange complexes [ReCl(N$_2$Ph)L^4(PPh$_3$)] (**11**) and [ReCl$_2$(N$_2$Ph)L^7(PPh$_3$)] (**12**) respectively in good yields (77–78%) (Scheme 4).

The ESMS(+) spectra show peaks at $m/z = 819.0914$ (M$^+$ + K. $C_{32}H_{27}ClKN_6O_2PRe$ requires 819.0816) for **11** and $m/z = 772.0672$ (M$^+$ + K. $C_{31}H_{28}Cl_2KN_6PRe$ requires 811.0685) for **12**. Both have appropriate isotope distribution patterns. ^{1}H NMR spectra for **11** and **12** are complex, with peaks corresponding to PPh$_3$, Ph–N$_2$ and 4-pz protons dominating at 7.5-7.1 ppm. In the IR spectra (KBr disc) of the complexes the bands assigned to ν(NN) of the diazenide ligands are observed in the 1650–1560 cm^{-1} range. The UV/vis spectra of the complexes remain unchanged in dmso solution over 24 h, suggesting the complexes are stable in solution. The HPLC traces for complexes **11** and **12** confirm the formation of single species with retention times of 4 and 4.2 min respectively, Fig. 10. The minor peaks correspond to the solvent (dmso) used to dissolve the complexes.



12 **11**

Scheme 4

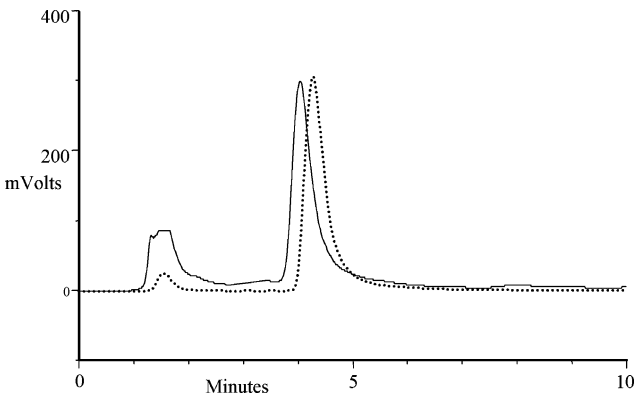


Fig. 10 HPLC traces for complexes **11** (——) and **12** (···) in dmso at 4.0 and 4.2 min respectively; dmso 1.75 min, with isocratic elution CH_3CN–H_2O, 80 : 20.

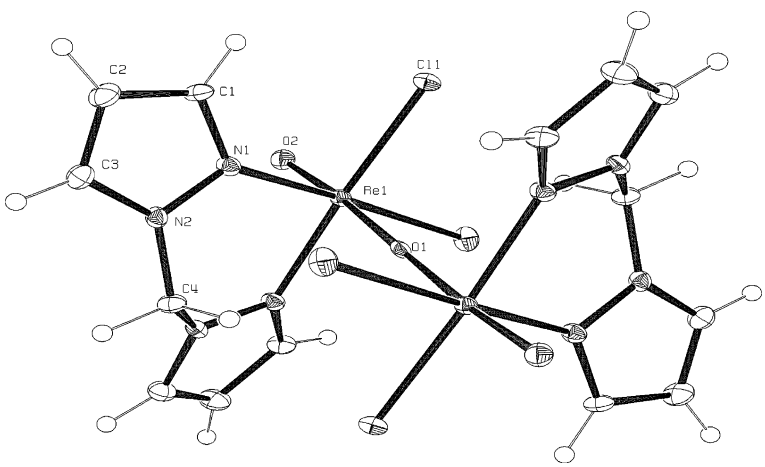


Fig. 9 ORTEP view of the dimeric complex **10**; thermal ellipsoids are drawn at the 40% probability level.

Electrochemistry

The cyclic voltammograms of complexes **1** and **5–12** were recorded at room temperature in dmso and for complex **4** in CH_3CN solutions, at a glassy carbon working electrode with 0.2 M $[Bu^n_4N][BF_4]$ as the supporting electrolyte at a scan rate of 400 mV s^{-1}. Potentials are quoted relative to the ferrocene–ferrocenium couple taken as 0.38 V in CH_3CN. Complexes **1** and **5–10** exhibit an irreversible one electron Re^{V}/Re^{VI} oxidation near 1.2 V (*vs* SCE) and several other irreversible reduction processes at rather negative potentials, suggesting that both the oxidised Re(VI) and reduced Re(IV) species are not stable in solution. The potential values observed show that the complexes are unlikely to undergo reduction *in vivo.*. Complex **4** shows a one electron reversible (i_p *vs* (scan rate)$^{1/2}$ straight line) oxidation process at $E_{1/2}$ = + 0.017 V *vs* Fe/Fe^+, ($E_{1/2}$ = + 0.397 V *vs* SCE) corresponding to the formation of a Re(V) complex, Fig. 11a. This was confirmed to be an oxidation process by linear sweep voltammetry in a stirred solution. On reduction only an irreversible process is observed at *ca.* −0.9 V. The failure to observe a reduction to Re(III) but oxidation to Re(V) is surprising and suggests that the carboxypyrazolylmethane ligand is more effective at stabilising higher oxidation states. This electrochemical behaviour contrasts with that of the very recently reported complex formulated as $[ReCl_3L^1]$ which was quoted as having a single irreversible oxidation process at *ca.* +1.2 V.[24] Cyclic voltammetry measurements on **11** and **12** in dmso (Fig. 11b) show that the mono-diazenide species undergo a fully reversible oxidation assigned to the Re(III)/Re(IV) couple at 0.39 and 0.41 V (*vs* SCE) respectively. The precursor diazenido complexes show analogous reversible oxidation processes.

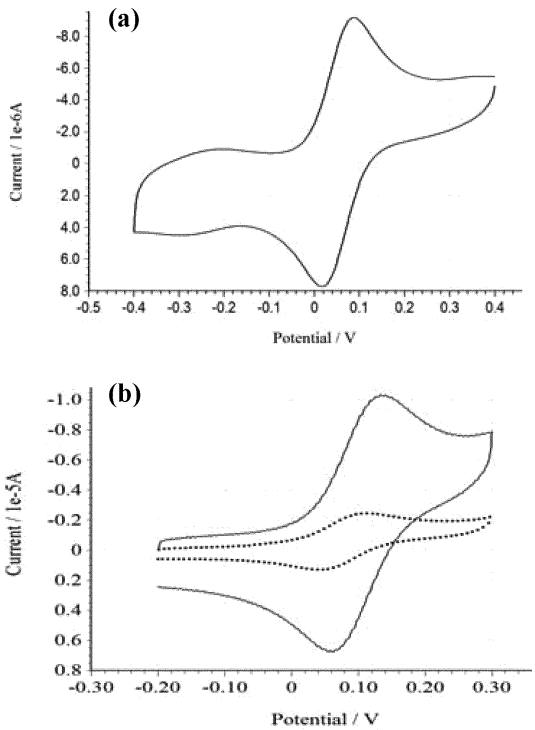


Fig. 11 Cyclic voltammograms of complexes (a) **4** in CH_3CN solution, (b) **11** (——) and **12** (· · ·) in dmso, recorded at a scan rate of 400 mV s^{-1}. Scale relative to Ag wire pseudoreference electrode.

Conclusions

A simple synthetic route to the rhenium (V) complexes of the type $[ReOCl_2(L^{1-8})]^{n+}$ (n = 0,1) has been established by reaction of L^1 and HL^4 ligands with $[ReOCl_3(PPh_3)_2]$ in thf in the presence of potassium tertiary butoxide. There appears to be a labile equilibrium involving dissociation of the pyrazolyl group *trans* to the oxo-group and the monomeric complexes are slowly converted to dimeric complexes with bidentate tris(pyrazolylmethane) ligands and an Re_2O_3 core on standing in solution. The reaction of the rhenium-oxo precursor with L^1 in CH_2Cl_2 in the absence of base leads to loss of the oxo group from the rhenium starting material and to the formation of a Re(IV) complex $[ReCl_3L^1]^+$. The formation of these Re(IV) cationic complexes, which is interestingly observed in the reaction with L^3 with the loss of the $HOCH_2$ group, appears to be accompanied by the formation of perrhenate anion in varying amounts. These complex equilibria with rhenium in high oxidation states strongly suggest that this class of ligand is not appropriate for use in a radiopharmaceutical context with Re=O cores. However, HPLC studies of the reactions of the bis(pyrazolyl)acetates shows that single complexes are formed in high yield in solution. HPLC studies of the isolated complexes also demonstrate their high purity and give information on the lipophilicities of the compounds. UV/vis studies of the neutral complexes also confirm that they are stable in solution for at least 24 h. In view of the relatively facile derivatisation of these ligands at the capping carbon, these complexes show some promise as the basis of future rhenium radiopharmaceuticals with both oxo- and diazenido-cores. The aryl-substituted pyrazolylmethane complexes are also strongly fluoresecent and the optical properties of these complexes and studies of their cellular uptake will be reported elsewhere.

Experimental

Precursors

The L^1,[20] and L^3,[20] ligands used were prepared using standard literature methods. The ligand HL^6 was prepared by a new route to be described elsewhere.[22] $[ReOCl_3(PPh_3)_2]$ and $[ReCl_2(NNPh)(MeCN)(PPh_3)_2]$ were prepared according to the literature.[27,28] Reactions were carried out under nitrogen using reagent grade solvents.

Physical measurements

Elemental analyses were performed by the microanalysis service of the department at the University of Oxford. NMR spectra were recorded on either a Varian Mercury VX300 spectrometer, (^1H 300 MHz, $^{13}C\{^1H\}$ at 75.5 MHz) or a Varian Unity 500 MHz spectrometer, (^1H 499.9 MHz, $^{13}C\{^1H\}$ at 125.7 MHz) using the residual solvent signal as an internal reference. Mass spectra were recorded on a Micromass LCT time of flight mass spectrometer using positive ion electrospray (ES^+), solid probe electron impact (EI) or field ionisation (FI^+) techniques. Where possible accurate masses are reported to four decimal places using tetraoctylammonium bromide (466.5352 Da) as an internal reference. UV/vis spectra were recorded on a Cintra 10 UV/vis spectrometer. High performance liquid chromatography (HPLC) was conducted using a Gilson HPLC machine with a Hamilton PRP-1 reverse

phase column and UV/vis detection at 254 nm. Retention times, R_t/min, using a water–acetonitrile gradient elution method are presented for all compounds. For the cyclic voltammetry tests a CH Instruments Electrochemical Analyser was used. Cyclic voltammograms of 0.1 M solutions of complexes in 10 mL of dmso or CH_3CN with tetrabutylammonium tetrafluoroborate as support electrolyte were recorded using a glassy carbon stationary working electrode, a platinum wire counter/auxiliary electrode and a silver/silver ion pseudoreference electrode at scan rates of 100–600 mV s^{-1}. Nitrogen was bubbled through the solutions before the electrochemical test to remove oxygen. Ferrocene was used as an internal reference for which the one-electron redox process occurs at $E_{1/2} = +0.53$ V (dmf) *vs.* SCE. All electrochemical measurements were carried out at 25 °C.

Synthesis of complexes

[$ReOCl_2L^1$]X (X = Cl), 1. A solution of L^1 (0.025 g, 0.12 mmol) and potassium *tert*-butoxide (0.013 g, 0.12 mmol) in thf (30 mL) was stirred for 10 min at room temperature. [$ReOCl_3(PPh_3)_2$] (0.100 g, 0.12 mmol) was added and the mixture was heated under reflux for 2 h. During this time the colour of the brown-green suspension changed to turquoise blue. The precipitated blue product was filtered off, washed with Et_2O (2 × 30 mL) and dried *in vacuo* (78%) (Found: C, 22.90; H, 2.12; N, 16.19. $C_{10}H_{10}N_6OCl_3Re$ requires C, 22.97; H, 1.93; N, 16.08%); IR ν_{max}/cm^{-1} (KBr) 1319 (m), 1307 (m), 1234 (m), 1103 (m) 1073 (s), 1038 (w), 995 (m, Re=O), 950 (w), 821 (m), 765 (s), 722 (s), 633 (m); δ_H (300 MHz; ppm; d_6-dmso; Me_4Si) 8.72 (3H, d, pz-5), 8.45 (3H, d, pz-3), 8.08 (1H, s, CH), 7.02 (3H, t, pz-4); $\delta_{13C\{1H\}}$ (75.5 MHz; ppm; d_6-dmso; Me_4Si) 148.2 (C-3pz), 139.4 (C-5pz), 111.6 (C-4pz), 71.2 (CH); *m/z* (ESMS)(+) 486.9452 ([(M–Cl]$^+$. $C_{10}H_{10}N_6OCl_2Re$ requires 486.9851); HPLC, **1** (dissolved in dmso), (gradient elution CH_3CN/H_2O) 9.7 min.

$ReOCl_2(L^2)$]X (X = Cl), 2. Prepared in an analogous manner to **1**.

[$Re_2O_3Cl_4(L^1)_2$], 3. Complex **3** formed when **1** dissolved in CH_3CN (1 mL). The pale blue filtrate was allowed to stand at room temperature. Single crystals suitable for X-ray structure determination were obtained by slow evaporation of a solution in thf.

[$ReCl_3L^1$]X (X = Cl, [ReO_4]$^-$), 4. A solution of L^1 (0.077 g, 0.36 mmol) and [$ReOCl_3(PPh_3)_2$] (0.300 g, 0.36 mmol) was heated under reflux in CH_2Cl_2 (50 mL) for 2 h. During this time the colour of the brown-green suspension changed to dark brown. The precipitated product was filtered off, washed with Et_2O (2 × 50 mL) and dried *in vacuo* (87%). Suitable crystals for X-ray structure analysis were obtained from a solution in $CHCl_3$ by slow evaporation. UV-vis (CH_2Cl_2; 1 mM) 380 nm; IR ν_{max}/cm^{-1} (KBr): 1464 (s), 1386 (s), 1094 (m), 880 (m), 752 (m), 721 (m); *m/z* (ESMS)(+) 470.9871 ([M–Cl]$^+$. $C_{10}H_{10}Cl_2N_6Re$ requires 470.9902), 100 (%), 749.0844 (M^+–Cl + $OPPh_3$), (60), 263.0984 (PPh_3) (30); 505.9508 (1%), (M^+. $C_{10}H_{10}Cl_3N_6Re$ requires 505.9569). HPLC, **4** (reaction mixture in thf), (isocratic elution CH_3CN–H_2O, 80 : 20) 1.60 min.

[$ReOCl_2L^4$], 5a. A solution of HL^4 (0.138 g, 0.72 mmol) and potassium *tert*-butoxide (0.081 g, 0.72 mmol) in thf (50 mL) was stirred for 10 min at ambient temperature. [$ReOCl_3(PPh_3)_2$] (0.600 g, 0.72 mmol) was added and the mixture was heated under reflux for 2 h. The precipitated turquoise blue product was filtered off, washed with thf (2 × 50 mL) and dried *in vacuo* (74%). Suitable crystals for X-ray structure analysis were obtained from a solution in CH_3CN by slow evaporation. (Found: C, 19.50; H, 1.53; N, 11.38. $C_8H_7Cl_3N_4O_3Re$ requires C, 20.14; H, 1.41; N, 11.92%); UV-vis (dmso, 1 mM) 345 nm, 680 nm; IR ν_{max}/cm^{-1} (Nujol) 3119 (w), (CH), 1719 (s), 1703s (C=O), 1513 (m) (C=C + C=N), 1462 (s), 1380 (m), 1287 (m), 1082 (w), 1004 (w), 940s (Re=O), 761 (m); δ_H (300 MHz; ppm; d_6-dmso; Me_4Si) 8.72 (d, 2H, 3-pz), 8.45 (d, 2H, 5-pz), 7.02 (t, 2H, 4-pz), 8.09 (s, 1H, CH); $\delta_{13C\{1H\}}$ (75.5 MHz; ppm; d_6-dmso; Me_4Si) 160.3 (C=O), 148.1 (C-3pz), 139.5 (C-5pz), 106.4 (C-4pz), 71.3 (CH); (ESMS)(+) 502.9051 ([M + K]$^+$. $C_8H_7Cl_2KN_4O_3Re$ requires 502.9090); HPLC, **5a** (dissolved in CH_3CN), (isocratic elution CH_3CN–H_2O, 80 : 20) 1.61 min.

[$ReOBr_2L^4$)], 5b. Prepared in an analogous manner to **5a** in 75% yield. (Found: C, 17.12; H, 1.16; N, 9.88. $C_8H_7Br_2N_4O_3Re$ requires C, 17.37; H, 1.28; N, 10.13%); IR ν_{max}/cm^{-1} (KBr) cm^{-1} 3418 (b), 3151 (w), 3118 (s), 3021 (w), 2989 (w), 2368 (w), 1712 (s), 1520 (m), 1458 (m), 1412 (s), 1288 (s), 1254 (s), 1108 (w), 1074 (s), 1000 (s), 938 (s), 858 (s), 780 (s), 756 (s), 683 (w), 650 (s), 598 (m), 554 (w), 420 (s); δ_H (300 MHz; ppm; d_6-dmso; Me_4Si) 8.69 (2H, d, 3-pz), 8.52 (2H, d, 5-pz), 8.03 (1H, s, CH), 7.01 (2H, t, 4-pz); $\delta_{13C\{1H\}}$ (75.5 MHz; ppm; d_6-dmso; Me_4Si) 160.2 (C=O), 148.4 (C-3pz), 138.3 (C-5pz), 111.5 (C-4pz), 71.4 (CH); *m/z* (ESMS)(+) 590.8346 ([M + K]$^+$. $C_8H_7Br_2KN_4O_3Re$ requires 590.8079); HPLC, **5b** (dissolved in dmso), (gradient elution CH_3CN–H_2O) 10.65 min.

[$ReOCl_2L^5$], 6. Prepared in an analogous manner to **5a** in 74% yield. (Found: C, 49.76; H, 2.91; N, 7.22. $C_{32}H_{23}Cl_2N_4O_3Re$ requires C, 50.00; H, 3.02; N, 7.29%); *m/z* (ESMS)(+) 807.0893 ([M + K]$^+$. $C_{32}H_{23}Cl_2N_4O_3Re$ requires 807.0342); HPLC, **6** (dissolved in CH_3CN), (isocratic elution CH_3CN–H_2O, 80 : 20) 2.20 min.

[$ReOCl_2L^6$], 7a. Prepared in an analogous manner to **5a** in 72% yield. (Found: C, 48.31; H, 3.40; N, 6.15. $C_{36}H_{31}Cl_2N_4O_3Re$ requires C, 48.65; H, 3.52; N, 6.30%); δ_H (300 MHz; ppm; d_6-dmso; Me_4Si) 7.51 (2H, dd, o-Ph) 7.47-7.45 (2H, m, p-Ph), 7.45-7.42 (2H, m, m-Ph), 7.40 (2H, t), 7.17 (2H, d), 7.15 (2H, d), 7.1 (2H, d), 7.02 (1H, s), 6.97–6.87 (4H, m), 3.8 (6H, s, CH_3), 3.7 (6H, s, CH_3); $\delta_{13C\{1H\}}$ (75.5 MHz; ppm; d_6-dmso; Me_4Si) 159.1 (Cquat), 156.8 (Cquat), 155.5 (Cquat), 145.6 (Cquat), 131.2 (Cquat), 131.1 (CH), 128.5 (CH), 128.3 (CH), 120.6 (Cquat), 119.1 (CH), 117.8 (CH), 112.9 (Cquat), 112.5 (CH), 111.2 (CH), 110.7 (CH), 67.8 (CH), 55.3 (CH_3), 55.1 (CH_3); *m/z* (ESMS)(+) 927.0798 ([M + K]$^+$. $C_{36}H_{31}Cl_2KN_4O_7Re$ requires 927.0764); HPLC, **7a** (dissolved in dmso), (gradient elution CH_3CN–H_2O) 17.8 min, (dissolved in CH_3CN), (isocratic elution CH_3CN–H_2O, 80 : 20) 5.8 min.

[$ReOBr_2L^6$], 7b. Prepared in an analogous manner to **5a** in 75% yield. (Found: C, 44.42; H, 3.31; N, 5.88. $C_{36}H_{31}Br_2N_4O_7Re$ requires C, 44.23; H, 3.20; N, 5.73%); UV-vis (dmso; 1 mM) 684 nm; IR ν_{max}/cm^{-1} (KBr) 3406 (b), 3138 (w), 3062 (w), 2940 (w), 2832 (w), 2366 (w), 2334 (w), 2044 (w), 1911 (w), 1732 (s), 1610 (s, C=N), 1583 (s, C=N), 1556 (w), 1516 (w), 1490 (s), 1474 (s), 1440 (s), 1370 (s), 1228 (w), 1253 (s), 1198 (w), 1182 (w), 1168 (w), 1124 (s), 1087 (m), 1052 (m), 1024 (s), 1002 (w), 948 (m, Re=O), 908 (m), 860 (w), 796 (m), 758 (s), 730 (s), 694 (m), 582 (w), 548 (s), 444 (w); δ_H (300 MHz; ppm, d_6-dmso; Me_4Si) 7.82 (2H,

dd, o-Ph), 7.64-7.53 (2H, m, p-Ph), 6.80 (2H, m, m-Ph), 7.0 (2H, s, 4-pz), 6.66 (1H, s, CH), 6.64 (d, 2H), 6.62 (d, 2H), 6.54 (s), 6.42 (s), 3.8 (3H, s, CH_3), 3.7 (3H, s, CH_3); $\delta_{13C\{1H\}}$ (75.5 MHz; ppm; d_6-dmso; Me_4Si) 165.9 (COO), 159.2–155.7 (o-Ph), 147.5–141.6 (5-pz), 133.8–131.2 (p-Ph), 129.5–128.4 (o-Ph), 121.9–119.9 (m-Ph), 118.9–117.7 (C–Ph), 113.7–111.4 (m-Ph), 108.7 (4-pz), 68.2 (CH), 56.1 (CH_3), 55.1 (CH_3); *m/z* (ESMS)(+) 999.0072 ([M + Na]$^+$. $C_{36}H_{31}Br_2N_4O_7Re$ requires 999.0015); HPLC, **7b** (dissolved in dmso), (gradient elution CH_3CN–H_2O) 18.5 min.

[ReOCl$_3$L^7], 8. Prepared in an analogous manner to **5a** in 74% yield. (Found: C, 18.78; H, 1.72; N, 12.14. $C_7H_8Cl_3N_4ORe$ requires C, 18.41; H, 1.77; N, 12.27%); UV-vis (dmso; 1 mM) 363 nm, 534 nm; IR ν_{max}/cm^{-1} (KBr) cm^{-1} 1614 (w), 1462 (s), 1384 (s), 1278 (s), 1101 (m), 1093 (s), 954 (s, Re=O), 838, (w), 758 (s), 706 (m); UV-vis 363 nm and 534 nm; δ_H (300 MHz; ppm; d_6-dmso; Me_4Si) 8.68 (2H, d, 3-pz), 8.47 (2H, d, 5-pz), 7.93 (2H, s, CH_2), 7.03 (2H, t, 4-pz); $\delta_{13C\{1H\}}$ (75.5 MHz; ppm; d_6-dmso; Me_4Si) 147.8 (C-3pz), 138.1 (C-5pz), 110.6 (C-4pz), 70.86 (CH); (*m/z* (ESMS)(+) 455.9351 (M$^+$. $C_7H_8Cl_3N_4ORe$ requires 455.9321); HPLC, **8** (dissolved in dmso), (isocratic elution CH_3CN–H_2O, 80 : 20) 1.7 min, (gradient elution CH_3CN–H_2O) 9.73 min.

[ReOCl$_3$L^8], 9. Prepared in an analogous procedure to that used for **5a** in 73% yield. (Found: C, 25.79; H, 3.22; N, 11.01. $C_{11}H_{16}Cl_3N_4ORe$ requires C, 25.76; H, 3.14; N, 10.92%); δ_H (300 MHz; ppm; d_6-dmso; Me_4Si) 3.70 (s, 6H); 3.77 (s, 6H); 6.41 (s, 1H); 6.89 (t, 2H); 7.07–7.10 (m, 2H); 7.14–1.16, (m, 2H); 7.06, (s, 2H); 7.43 (dd, 2H); 7.61 (d, 2H); *m/z* (ESMS)(+) 511.9971 (M$^+$. $C_{11}H_{16}Cl_3N_4ORe$ requires 511.9947); HPLC **9** (dissolved in dmso), (gradient elution CH_3CN–H_2O) 9.72 min.

[Re$_2$O$_3$Cl$_4$(L^7)$_2$], 10. Complex **10** formed when compound **8** was dissolved in CH_3CN (1 mL). Single crystals suitable for X-ray structure determination were obtained by slow evaporation of the CH_3CN solution.

[ReCl(N$_2$Ph)L^4(PPh$_3$)], 11. In a round bottom flask (250 mL), potassium *tert*-butoxide (0.036 g, 0.32 mmol), HL^4 (0.062 g, 0.32 mmol) and [$ReCl_2(N_2Ph)(NCMe)(PPh_3)_2$] (0.300 g, 0.32 mmol) were heated under reflux in MeOH (60 mL) for 4 h. The orange precipitate formed was filtered off and washed with copious amounts of MeOH and dried (78%). (Found: C, 49.12; H, 3.21; N, 10.56. $C_{32}H_{27}ClN_6O_2PRe$ requires C, 49.26; H, 3.49; N, 10.77%); UV-vis (dmso; 1 mM) 450 nm; IR ν_{max}/cm^{-1} (KBr) 3454 (b), 3116 (w), 3057 (w), 2989 (w), 2368 (w), 2338 (w), 1978 (w), 1702 (s), 1678 (s, *ν*NN), 1622 (s), 1562 (s, *ν*NN), 1486 (s), 1466 (s), 1404 (s), 1306 (m), 1288 (m), 1243 (m), 1187 (s), 1166 (m), 1096 (s), 1066 (w), 1027 (w), 996 (s,), 944 (m), 861 (m), 762 (s), 692 (s), 600 (w), 525 (s), 436 (w); δ_H (300 MHz; ppm; d_6-dmso; Me_4Si) 7.8–7.5 (m, 14H, Ph), 7.4 (d, 2H, 5-pz), 7.3–7.1 (m, 6H, Ph), 7.0 (d, 2H, 3-pz), 6.4 (s, 1H, CH), 6.2 (dd, 2H, 4-pz); $\delta_{13C\{1H\}}$ (75.5 MHz; ppm; d_6-dmso; Me_4Si) 163.3 (C=O), 146.5 (PPh_3), 143.1 (PPh_3), 136.8 (PPh_3), 135.2 (C-3pz), 134.4 (PPh_3), 130.1 (PhNN), 129.6 (PhNN), 128.3 (PhNN), 125.4 (PhNN), 121.7 (C-5pz), 109.2 (C-4pz), 73.4 (CH); $\delta_{31P\{1H\}}$ (ppm; d_6-dmso; H_3PO_4) 10.0; *m/z* (ESMS)(+) 819.0914 ([M + K]$^+$. $C_{32}H_{27}ClKN_6O_2PRe$ requires 819.0816); HPLC **11** (dissolved in dmso), (isocratic elution CH_3CN–H_2O, 80 : 20) 4.0 min.

[ReCl$_2$(N$_2$Ph)L^7(PPh$_3$)], 12. Prepared in an analogous procedure to that used for **11** (77%). (Found: C, 48.35; H, 3.72; N, 10.91. $C_{31}H_{28}Cl_2N_6PRe$ requires C, 48.19; H, 3.65; N, 10.88%); UV-vis (dmso; 1 mM) 458 nm; IR ν_{max}/cm^{-1} (KBr) cm^{-1} 3452 (b), 3122 (w), 3056 (w), 3014 (w), 2372 (w), 2238 (w), 1646 (s, *ν*NN), 1614 (m), 1564 (s, *ν*NN), 1488 (s), 1436 (s), 1404 (m), 1339 (w), 1279 (s), 1226 (m), 1164 (m), 1100 (s), 1068 (w), 992 (m), 922 (s), 762 (s), 698 (s), 604 (w), 525 (s), 432 (w); δ_H (300 MHz; ppm; d_6-dmso; Me_4Si) 6.6 (4H, NNC_6H_4), 7.2 (18H, *meta*- and *para*-ArH PPh_3), 7.6 (12H, m *ortho*-ArHPPh_3), 6.9 (d, 2H, 3-pz), 6.8 (d, 2H, 5-pz), 6.4 (s, 2H, CH_2), 6.2 (dd, 2H, 4-pz); $\delta_{13C\{1H\}}$ (75.5 MHz; ppm; d_6-dmso; Me_4Si) 143.7 (C-3pz), 135.1 (PPh_3), 134.6 (PPh_3), 134.1 (PPh_3), 130.3 (PPh_3), 129.3 (PhNN), 128.4 (PhNN), 124.6 (PhNN), 121.0 (C-5pz), 108.9 (C-4pz), 72.8 (CH); $\delta_{31P\{1H\}}$ (ppm; d_6-dmso; H_3PO_4) 4.0; *m/z* (ESMS)(+) 811.0672 (M. $C_{31}H_{28}Cl_2N_6PRe$ requires 811.0685); HPLC, **12** (dissolved in dmso), (isocratic elution CH_3CN–H_2O, 80 : 20) 4.2 min.

X-Ray structure determinations

Single crystals of **3**, **4**, **7a** and **10** were mounted on glass fibres using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N_2 using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package.[29] The structures were solved using the direct-methods program SIR92,[30] which located all non-hydrogen atoms. Subsequent full matrix least squares refinement was carried out using the CRYSTALS program suite.[31] Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. ORTEP-3 was employed to represent the structures.[32]

CCDC reference numbers 629316–629319.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617549j

Crystal structure determination of complex 3

Single crystals of [$Re_2O_3Cl_4(L^1)_2$] **3** were obtained from a thf solution by slow evaporation in air.

Crystal data. $C_{20}H_{20}Cl_4N_{12}O_3Re_2$, M = 990.67, T = 150 K, λ = 0.71073 Å, monoclinic, $P\,2_1/n$, a = 9.7300(3), b = 13.4343(5), c = 10.8514(4) Å, β = 95.9521(16)°, cell volume = 1410.80(9) Å^3, Z = 2, ρ = 2.332 Mg m^{-3}, μ = 9 mm^{-1}, 10 485 reflections measured, 3329 unique, (R_{int} = 0.076, R = 0.0312, R_w = 0.0311).

The complex is located on a site with a crystallographic centre of inversion, and consequently the Re–O–Re bridge is exactly linear.

Crystal structure determination of complex 4

Single crystals of [$ReCl_3L^1$]X (X = Cl, [ReO_4]) **4** were obtained from chloroform by slow evaporation.

Crystal data. $C_{12}H_{12}Cl_9N_6O_4Re_2$, M = 995.74, T = 150 K, λ = 0.71073 Å, monoclinic, $P\,2_1/c$, a = 15.7338(2), b = 15.8808(2), c = 22.0122(3) Å, β = 06.5516(7)°, cell volume = 5272.18(12) Å^3, Z = 8, ρ = 2.509 Mg m^{-3}, μ = 10.12 mm^{-1}, 52 740 reflections measured, 12 405 unique, (R_{int} = 0.075, R = 0.0415, R_w = 0.0489).

A difference Fourier map showed there were a number of peaks of apparent residual electron density, but these could not be meaningfully assigned, and their positions suggested they were artefact arising from the presence of highly scattering atoms in the unit cell. The asymmetric unit contains two crystallographically distinct molecules of the cation, two molecules of the perrhenate anion and four molecules of solvent chloroform. The cations are related by a non-crystallographic translation as are the anions. There are a number of interactions between the anion oxygen atoms and the methane hydrogens, indicative of weak hydrogen bonding.

Crystal structure determination of complex 7a

Single crystals of $[ReOCl_2L^7]X$ (X = Cl) **7a** were derived from a thf solution by slow evaporation.

Crystal data. $C_{36}H_{31}Cl_2N_4O_7Re$, $M = 888.77$, $T = 150$ K, $\lambda = 0.71073$ Å, monoclinic, $P\,2_1/n$, $a = 11.7127(2)$, $b = 16.3000(3)$, $c = 18.0939(3)$ Å, $\beta = 98.4918(7)°$, cell volume = 3416.56(10) Å^3, $Z = 4$, $\rho = 1.728$ Mg m^{-3}, $\mu = 3.769$ mm^{-1}, 30 866 reflections measured, 8039 unique, ($R_{int} = 0.056$, $R = 0.0324$, $R_w = 0.0369$).

Crystal structure determination of complex 10

Single crystals of $[Re_2O_3Cl_4(L^7)_2]$ **10** were obtained from an acetonitrile solution by slow evaporation.

Crystal data. $C_{18}H_{22}Cl_4N_{10}O_3Re_2$, $M = 940.65$, $T = 150$ K, $\lambda = 0.71073$ Å, monoclinic, $C\,2/m$, $a = 15.2625(5)$, $b = 10.7896(4)$, $c = 8.5400(3)$ Å, $\beta = 95.1189(17)°$, cell volume = 1400.74(9) Å^3, $Z = 2$, $\rho = 2.23$ Mg m^{-3}, $\mu = 9.056$ mm^{-1}, 4815 reflections measured, 1671 unique, (R_{int}=0.037, $R = 0.0261$, $R_w = 0.0290$).

The Re complex is located on a site of crystallographic symmetry $2/m$ (D_{2d}) and as a consequence the Re–O–Re bridge is obligately linear. The molecule of MeCN solvent is also located on the mirror plane, accounting for the observed 2 : 1 stoichiometry. One of the methylene hydrogens projects towards the midpoint of the two Cl ligands of the second molecule of complex. The C···Cl distances are relatively short (C(4)···Cl(1′) = 3.415(6) Å, suggesting the presence of a bifurcated C–H···Cl hydrogen bonding interaction.

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