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Chemistry of monovalent and bivalent rhenium: synthesis, structure, isomer specificity and metal redox of azoheterocycle complexes

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The reaction of [Re^{V}O(OEt)X$_2$(PPh$_3$)$_2$] (X = Cl, Br, I) with 2-(arylazo)-1-methylimidazoles (aryl = Ph(L^1), C$_6$H$_4$Me-*p*(L^2) or C$_6$H$_4$Cl-*p*(L^3)) as well as 2-(*p*-tolylazo)-1-benzylimidazole (L^4) in toluene has afforded the orange coloured bis chelates of type [Re^{II}X$_2$(L)$_2$]. The green coloured tris chelates [Re^I(L)$_3$]ReO$_4$ are formed when the ligand is used in excess. Similar bis and tris chelates have also been synthesized by reacting [ReOCl$_3$(PPh$_3$)$_2$] with 2-(arylazo)pyridines (aryl = Ph(L^5), C$_6$H$_4$Cl-*p*(L^6)). Structure determination of [ReCl$_2$(L^2)$_2$], [ReI$_2$(L^4)$_2$] and [ReCl$_2$(L^6)$_2$] has revealed that the isomeric geometry for the XX–N^{h}N^h–N^{a}N^a donor sites (N^h, heterocyclic nitrogen; N^a, azo nitrogen) is uniformly *cis–trans–cis*. In the structure of [Re(L)$_3$]ReO$_4$ the tris chelate has facial geometry. The isomer preference of both families is exclusive, no other isomer having been observed in any of the preparations. The ^{1}H NMR spectra of the tris chelates are consistent with the facial geometry. The bis chelates are one-electron paramagnets and display well-resolved EPR sextets in fluid solutions. The cyclic voltammetric Re^{III}/Re^{II} response of [Re^{II}X$_2$(L)$_2$] occurs in the range 0.20–0.50 V *vs.* SCE in the case of the azoimidazole chelates and in the range 0.60–0.70 V in the case of the azopyridine chelates. In the case of [Re^I(L)$_3$]$^+$ the Re^{II}/Re^I couple is observed near 0.50 and 0.90 V for the azoimidazole and azopyridine species respectively. The average Re–N^a distance is generally shorter than the Re–N^h distance by ~0.1 Å and the average N–N length is longer by ~0.1 Å compared to that of uncoordinated azo function. Strong d(Re)–π*(azo) back-bonding characterize the present systems. Both back-bonding and steric factors stabilize the *cis–trans–cis* isomer of [ReX$_2$(L)$_2$]. In facial [Re(L$_3$)]$^+$ the net back-bonding is strong enough to offset the disadvantage of steric crowding.

Introduction

This work stems from our interest in variable valent rhenium chemistry[1] and deals specifically with the bivalent and monovalent states of the metal. Compared to trivalent osmium and to a lesser extent tetravalent iridium, bivalent rhenium is a rarely observed 5d^5 oxidation state.[2] Excluding metal–metal bonded species[3] most structurally characterized rhenium(II) complexes incorporate nitrosyl/thionitrosyl[4] or tertiary phosphine[5–7] binding. The only non-nitrosyl and non-phosphine species of known structure are the tris bipyridine[8] and trithiacyclononane chelates.[9,10] In case of rhenium(I), π-acidic ligands such as carbon monoxide, isonitriles, and tertiary phosphines are required for stabilization[2,11] and the chemistry of the [Re(CO)$_3$]$^+$ moiety is attracting significant activity.[12] In the design of rhenium containing radiopharmaceuticals, higher oxidation states (specially +5) of the metal are commonly employed, but the lower states (+1, +2) are receiving increasing attention.[10,13]

Our previous work on azoheterocycle complexes of rhenium[14–17] has prompted us to scrutinize the possible stabilization of bivalent and monovalent states by such ligands. Herein we report the synthesis and characterization of bis and tris chelates of the coordination types [Re^{II}X$_2$(NN)$_2$] (X = Cl, Br, I) and [Re^I(NN)$_3$]$^+$ which, to our knowledge, are unprecedented in rhenium chemistry. The structure, magnetism, and spectra of the two families are examined and the systematics of metal reduction potentials analyzed. A remarkable feature of each family is its exclusive occurrence in a single isomeric form. The origin of this geometrical selectivity is scrutinized.

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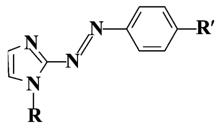
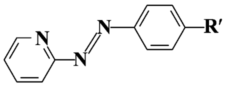
Results and discussion

Synthesis

The azoheterocycle ligands (general abbreviation, L) employed in the present work are imidazoles[14,18,19] L^1–L^4 and pyridines,[16] L^5 and L^6. Twelve bis chelates (types **1** and **2**) and five tris chelates (types **3** and **4**) have been synthesized. The lone benzyl complex **1j** is included in this study as it afforded single crystals unlike the other iodo species.



L^1 (R = Me, R′ = H)
L^2 (R = Me, R′ = Me)
L^3 (R = Me, R′ = Cl)
L^4 (R = CH$_2$Ph, R′ = Me)



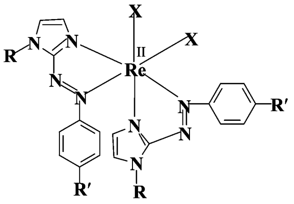
L^5 (R′ = H)
L^6 (R′ = Cl)

The orange coloured type **1** complexes are afforded in good yield upon reacting [Re^{V}O(OEt)X$_2$(PPh$_3$)$_2$] (X = Cl, Br, I) with L in 1 : 2.5 molar ratio in toluene followed by chromatographic workup of the reaction mixture. In this synthesis the initial reduction of the metal (Re^V ⟶ Re^{III}) occur *via* oxygen atom transfer from Re^{V}O to PPh$_3$, eqn. (1).

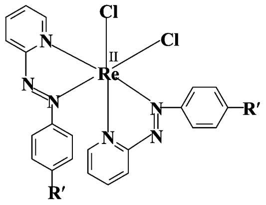
$$[\mathrm{Re^VO(OEt)X_2(PPh_3)_2}] + \mathrm{L} \longrightarrow [\mathrm{Re^{III}(OPPh_3)(OEt)X_2(L)}] + \mathrm{PPh_3} \quad (1)$$

Species of types [Re^{III}(OPPh$_3$)(OEt)X$_2$(L)] have been isolated as intermediates and these are found to react with L in presence of PPh$_3$ (reducing agent) furnishing **1**. Details of one case are given in the Experimental section. In the direct synthesis from [Re^{V}O(OEt)X$_2$(PPh$_3$)$_2$] it is not necessary to add PPh$_3$ because it is already present in the reaction mixture, eqn. (1). The green coloured tris chelates were isolated as perrhenate salts, **3**, by the reaction of [Re^{V}O(OEt)X$_2$(PPh$_3$)$_2$] (X = I affords the best yields) with excess (1 : 6) L in acetonitrile. It is unclear how the ReO$_4^-$ anion originate from the starting material but this behaviour has precedence.[4c,8] For the synthesis of the azopyridine chelates **2** and **4** the convenient starting material is [ReOCl$_3$(PPh$_3$)$_2$]. The chelation reactions were carried out in benzene for both bis and tris chelates.

The geometrical disposition of the XX–N^{h}N^h–N^{a}N^a donor sites (N^h is heterocyclic nitrogen and N^a is azo nitrogen) in both **1** and **2** is *cis–trans–cis* as proven by representative structure determination. The other possible geometrical isomers are *cis–cis–cis*, *trans–cis–cis*, *cis–cis–trans* and *trans–trans–trans*. Careful chromatographic experiments did not reveal the formation of any of these isomers in the synthetic methods developed here. Dihaloosmium(II)[20–22] and dihalo-ruthenium(II)[23–26] bis chelates of L are known to occur in isomeric forms: *cis–cis–cis* and/or *trans–cis–cis* in addition to *cis–trans–cis*.



1a [ReCl$_2$(L^1)$_2$]
1b [ReCl$_2$(L^2)$_2$]
1c [ReCl$_2$(L^3)$_2$]
1d [ReBr$_2$(L^1)$_2$]
1e [ReBr$_2$(L^2)$_2$]
1f [ReBr$_2$(L^3)$_2$]
1g [ReI$_2$(L^1)$_2$]
1h [ReI$_2$(L^2)$_2$]
1i [ReI$_2$(L^3)$_2$]
1j [ReI$_2$(L^4)$_2$]



2a [ReCl$_2$(L^5)$_2$]
2b [ReCl$_2$(L^6)$_2$]

In **3** and **4** the tris chelates geometry is exclusively facial as proven by structure determination and ^{1}H NMR results. The facial geometry has a potential threefold axis which can make the three chelate rings exactly equivalent. The meridional isomer which lacks such symmetry has not been observed either in the solid state or in solution. Osmium(II) is isoelectronic with rhenium(I) but tris chelates of type [Os(L)$_3$]$^{2+}$ occur predominantly in the meridional form.[20,27]

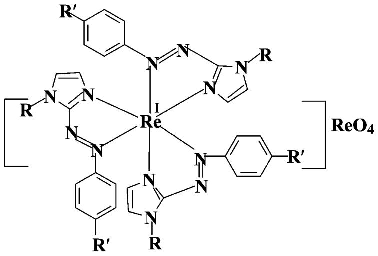
Spectra and magnetism

The bis chelates display a moderately intense band near 500 nm while the tris chelates display two such bands near 600 and 450 nm. These are presumably of MLCT origin. In IR an N=N stretch occurs near 1300 and 1230 cm^{-1} in the bis and tris chelates respectively. The latter shows a characteristic strong band near 910 cm^{-1} assigned to the ν_3 vibration of the ReO$_4^-$ anion.[28] Consistent with the *cis*-ReCl$_2$ disposition, the [ReCl$_2$(L)$_2$] species uniformly display two Re–Cl stretches near 320 and 330 cm^{-1}. In the case of [ReX$_2$(L^3)$_2$] the ReX$_2$ stretches were recorded for all three compounds. X = Cl (315, 335 cm^{-1}); X = Br (204, 227 cm^{-1}); X = I (174, 188 cm^{-1}).

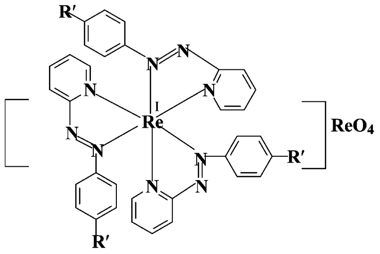
Table 1 Cyclic voltammetric formal potentials at 298 K in acetonitrile (0.1 M Et$_4$NClO$_4$) at a platinum electrode[a]

Compound	$E_{1/2}$/V (ΔE_p/mV)	Compound	$E_{1/2}$/V (ΔE_p/mV)
1a	0.46(80)	**2a**	0.61(160)
1b	0.44(80)	**2b**	0.70(160)
1c	0.48(80)		
1d	0.43(120)	**3a**	0.48(80)
1e	0.41(120)	**3b**	0.46(60)
1f	0.46(120)	**3c**	0.50(80)
1g	0.25(100)		
1h	0.20(60)	**4a**	0.93(60)
1i	0.27(60)	**4b**	0.95(80)
1j	0.21(100)		

[a] Re^{III}/Re^{II} couple for **1** and **2** and Re^{II}/Re^{I} couple for **3** and **4**. Scan rate 50mV s^{-1}. $E_{1/2} = \frac{1}{2}(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials respectively. $\Delta E_p = E_{pa} - E_{pc}$. Reference electrode, SCE.



3a [Re(L^1)$_3$]ReO$_4$
3b [Re(L^2)$_3$]ReO$_4$
3c [Re(L^3)$_3$]ReO$_4$



4a [Re(L^5)$_3$]ReO$_4$
4b [Re(L^6)$_3$]ReO$_4$

The bis chelates are paramagnetic (t$_{2g}$ ^{5}, $S = \frac{1}{2}$) with room temperature (300 K) magnetic moments in the range 1.94–2.10 μ_B. In fluid solution (300 K) these display well-resolved EPR spectra with six hyperfine lines due to the $I = 5/2$ nuclei ^{185}Re and ^{187}Re. There is a systematic increase in the separation between the adjacent hyperfine lines in going towards higher fields due to second order effects[29] (range of variable separation, 200–400 G). Center field g values and the average hyperfine splitting A for the complexes span the ranges 2.05–2.13 and 240–315 G respectively (see Experimental section). Variable hyperfine spacing has been observed[1b,c] among Re^{VI}NAr(t$_{2g}$^{1}) chelates of picolinamides where the metal oxidation state is higher and the magnitude and span of A (300–700 G) are also larger. The [Re(L)$_3$]ReO$_4$ complexes are diamagnetic and display well-resolved ^{1}H NMR spectra. The three chelate rings are equivalent and give rise to a single set of resonances consistent with facial geometry (**3** and **4**).

Metal redox: chelate ring number and oxidation state

All the complexes are electroactive in acetonitrile solution (Table 1). The azoimidazole bis species display a quasireversible one-electron cyclic voltammetric oxidative response assignable to the Re^{III}/Re^{II} couple in the range 0.20–0.50 V *vs.* SCE. For a given X there is a small but systematic shift of the reduction potential to more positive values as the electron withdrawing power of the R′ substituent increases (Me < H < Cl). For a given R′ the potential decreases as the X ligand becomes softer and its ligand field strength decreases (Cl > Br > I), the effect being more pronounced between the bromo and iodo species. For azopyridine bis chelates the Re^{III}/Re^{II} reduction potentials is higher, 0.60–0.70 V. Attempted isolation of the oxidized species, $[Re^{III}X_2(L)_2]^+$, *via* coulometry has not succeeded so far because of their instability. In the tris azoimidazole chelates the oxidative Re^{II}/Re^{I} couple occur at ~ 0.5 V and is nearly reversible with peak-to-peak separation in the range 60–80 mV. Again the azopyridine species have significantly higher potentials ~0.9 V.

The $E_{1/2}$ value of a given Re^{Z+1}/Re^{Z} couple increases progressively with the number of L chelate rings present. Consequently variation of this number along with coligand control provides an excellent handle for stabilizing a range of oxidation states of rhenium under ambient conditions. With monochelation, rhenium(V) and rhenium(III) were found to be stabilized as in $[Re^{V}OCl_3(L)]$, $[Re^{V}(NAr)Cl_3(L)]$, $[Re^{III}(OPPh_3)Cl_3(L)]$ and $[Re^{III}(PPh_3)Cl_3(L)]$.[14,16] Bis and tris chelation are now shown to make the bivalent and monovalent states readily accessible in the form of $[Re^{II}X_2(L)_2]$ and $[Re^{I}(L)_3]ReO_4$, respectively.

Structures

Among bis chelates the structures of $[ReCl_2(L^2)_2]$, **1b**; $[ReI_2(L^4)_2]$, **1j** and $[ReCl_2(L^6)_2]$, **2b** have been determined. Perspective views are shown in Fig. 1–3 and selected bond parameters are listed in Tables 2 and 3.

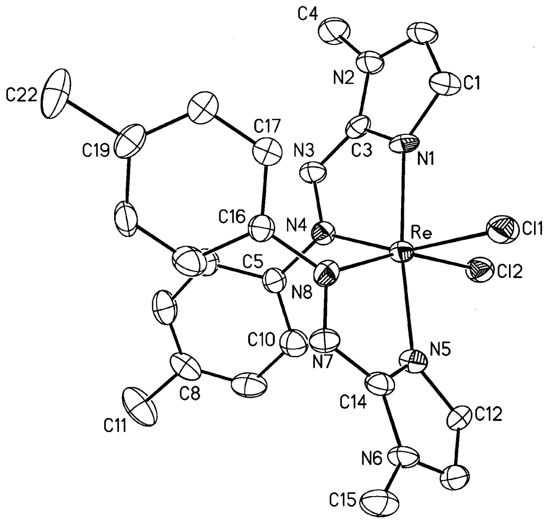


Fig. 1 A perspective view of $[ReCl_2(L^2)_2]$ **1b**. The atoms are represented by their 30% thermal probability ellipsoids.

The distorted octahedral ReX_2N_4 coordination spheres have *cis–trans–cis* geometry. Whereas the angular dimensions in **1b** and **1j** are similar, subtle differences related to halide bulk do occur. Thus, the X1–Re–X2 and N1–Re–N5 angles are 3–4° larger in **1j** than in **1b** resulting in associated changes in the other angles. In all three molecules the chelate ring along with the heterocyclic ring constitute a satisfactory plane.

Among tris chelates $[Re(L^5)_3]ReO_4$, **4a** afforded good single crystals. A perspective view is shown in Fig. 4 and selected bond parameters are listed in Table 4.

The ligands are facially disposed in the distorted octahedral ReN_6 coordination sphere. Each chelate ring along with the pyridine ring constitute a satisfactory plane. The three chelate rings are very closely similar although there is no formal crystallographic threefold axis. In mobile solution, the three chelate rings become exactly equivalent (^1H NMR). The complex $[Re(L^3)_3]ReO_4$, **3c** also afforded single crystals. The X-ray results revealed the overall connectivity and the facial geometry. However, the structure did not refine very well due to crystallographic complications.

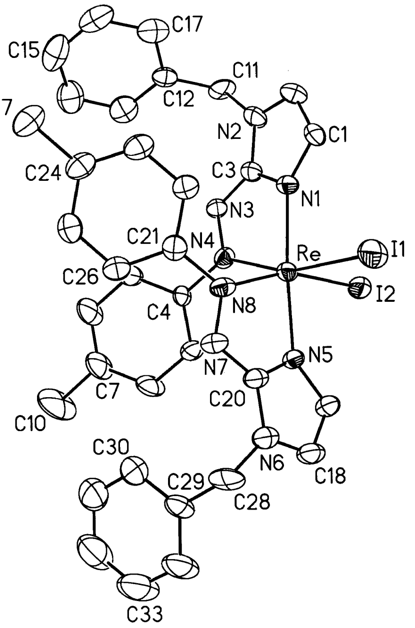


Fig. 2 A perspective view of $[ReI_2(L^4)_2]$ **1j**. The atoms are represented by their 30% thermal probability ellipsoids.

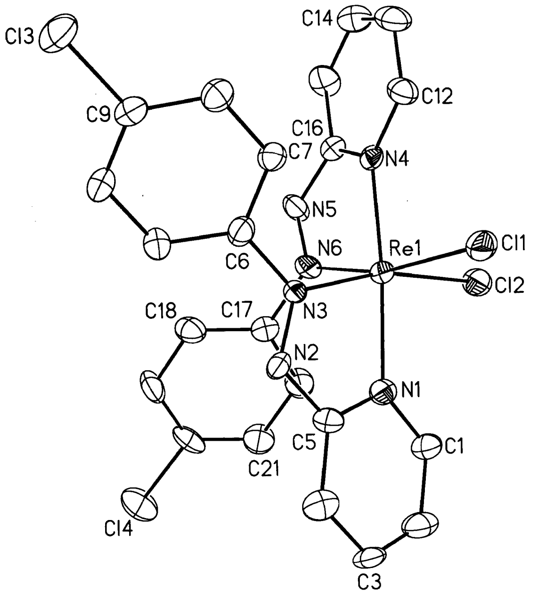


Fig. 3 A perspective view of $[ReCl_2(L^6)_2]$ **2b**. The atoms are represented by their 30% thermal probability ellipsoids.

Bond length, back-bonding and isomer specificity

The average $Re–N^a$ distance is significantly shorter (by 0.05–0.1 Å) than the $Re–N^h$ distance in all the four structures. On the other hand the average N–N length is uniformly longer (by 0.07–0.1 Å) than that (1.25 Å)[30] in uncoordinated azo compounds. Clearly strong d(Re)–π*(azo) back-bonding characterizes the present compounds. The excellent π-acceptor character of azoheterocycles originates from low lying π*(azo) orbitals.[14,16,20,30–32] The average Re–Cl length in **1b** and **2b** is 2.39 Å which is significantly shorter than that (2.42 Å) in compounds of type *trans*-$[ReCl_2(diphosphine)_2]$.[7]

Table 2 Selected bond distances (Å) and angles (°) for compounds **1b** and **1j**

	1b	**1j**
Re–N1	2.057(7)	2.065(8)
Re–N4	2.007(8)	2.041(8)
Re–N5	2.046(8)	2.053(8)
Re–N8	1.999(8)	2.000(9)
Re–X1	2.381(3)	2.7214(10)
Re–X2	2.398(3)	2.7412(12)
N4–N3	1.328(11)	1.339(10)
N8–N7	1.345(11)	1.366(11)
N8–Re–N4	89.4(3)	85.7(3)
N4–Re–N5	112.0(3)	109.7(3)
N4–Re–N1	74.5(3)	74.4(3)
N8–Re–X1	93.6(3)	93.8(2)
N5–Re–X1	87.8(2)	87.6(2)
N8–Re–X2	160.4(2)	160.6(2)
N5–Re–X2	86.3(2)	88.0(3)
X1–Re–X2	92.04(12)	95.75(4)
N8–Re–N5	75.2(3)	75.6(3)
N8–Re–N1	109.0(3)	106.8(3)
N5–Re–N1	172.6(3)	175.5(3)
N4–Re–X1	160.1(2)	161.8(2)
N1–Re–X1	85.9(2)	88.4(2)
N4–Re–X2	91.7(2)	90.4(2)
N1–Re–X2	90.1(2)	90.3(2)

Table 3 Selected bond distances (Å) and angles (°) for compound **2b**

Re1–N1	2.069(11)	Re1–Cl1	2.382(4)
Re1–N3	2.006(11)	Re1–Cl2	2.380(4)
Re1–N4	2.066(10)	N2–N3	1.319(14)
Re1–N6	1.964(12)	N5–N6	1.33(2)
N6–Re1–N3	91.3(4)	N6–Re1–N4	74.1(4)
N3–Re1–N4	104.5(4)	N6–Re1–N1	100.4(4)
N3–Re1–N1	74.1(4)	N4–Re1–N1	174.4(4)
N6–Re1–Cl2	89.1(3)	N3–Re1–Cl2	166.4(3)
N4–Re1–Cl2	88.7(3)	N1–Re1–Cl2	92.5(4)
N6–Re1–Cl1	166.5(3)	N3–Re1–Cl1	92.3(3)
N4–Re1–Cl1	92.4(3)	N1–Re1–Cl1	93.1(3)
Cl2–Re1–Cl1	90.5(2)		

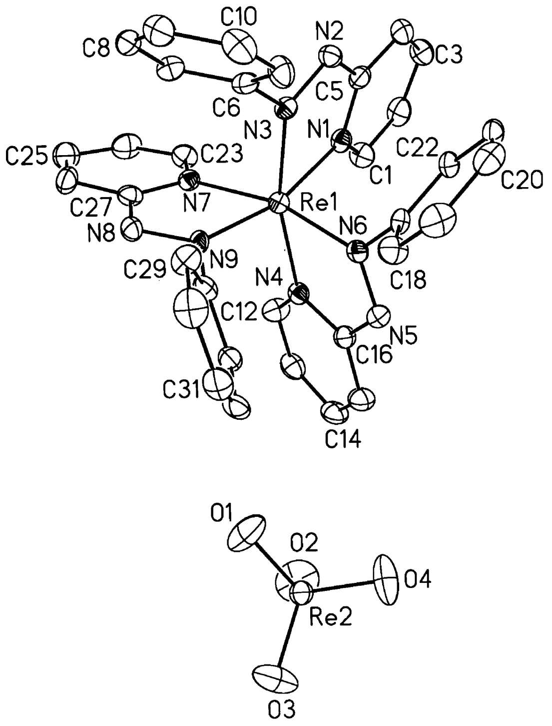


Fig. 4 A perspective view of [Re(L^5)$_3$]ReO$_4$ **4a**. The atoms are represented by their 30% thermal probability ellipsoids.

Table 4 Selected bond distances (Å) and angles (°) for compound **4a**

Re1–N1	2.111(7)	N5–N6	1.313(10)
Re1–N3	1.979(7)	N8–N9	1.321(10)
Re1–N4	2.092(7)	Re2–O1	1.705(9)
Re1–N6	1.991(8)	Re2–O2	1.702(8)
Re1–N7	2.103(7)	Re2–O3	1.709(9)
Re1–N9	1.986(7)	Re2–O4	1.702(8)
N2–N3	1.337(10)		
N3–Re1–N9	96.7(3)	N3–Re1–N6	96.5(3)
N9–Re1–N6	96.7(3)	N3–Re1–N4	165.2(3)
N9–Re1–N4	95.8(3)	N6–Re1–N4	74.1(3)
N3–Re1–N7	96.5(3)	N9–Re1–N7	73.9(3)
N6–Re1–N7	164.7(3)	N4–Re1–N7	94.6(3)
N3–Re1–N1	74.3(3)	N9–Re1–N1	164.7(3)
N6–Re1–N1	96.6(3)	N4–Re1–N1	95.1(3)
N7–Re1–N1	94.5(3)	O4–Re2–O2	109.0(5)
O4–Re2–O1	109.9(6)	O2–Re2–O1	109.4(6)
O4–Re2–O3	109.7(6)	O2–Re2–O3	109.5(6)
O1–Re2–O3	109.3(5)		

The *cis* (as opposed to *trans*) disposition of two N^a donor sites ensures lack of competition between them for the same metal d-orbital thus maximizing back-bonding. This happens in the *cis–trans–cis* geometry of **1** and **2**. This geometry is also sterically more favourable than the other two possible but unobserved isomers (*cis–cis–cis* and *trans–cis–cis*) having the *cis* ReN^{a}N^a disposition. The various isomers of [OsX$_2$(L)$_2$][20–22] and [RuX$_2$(L)$_2$][23–26] undergo spontaneous thermal conversion to the thermodynamically most stable *cis–trans–cis* form.[23b,26,33] In the case of [ReX$_2$(L)$_2$] this happens to be the only isomer observed.

In facial [Re(L)$_3$]$^+$ the three N^a atoms are mutually *cis* to one another representing a model situation for back-bonding (three *cis* ReN^{a}N^a interactions). This geometry is, however, more crowded (pendant aryl groups) than the unobserved meridional form which can have only two ReN^{a}N^a interactions. Evidently the strong back-bonding more than offsets the steric disadvantage of the facial form which alone is observed for [Re(L)$_3$]$^+$.

A comparison of isoelectronic [Re(L)$_3$]$^+$ and [Os(L)$_3$]$^{2+}$ is in order. The latter occurs primarily in the meridional form.[20] That back-bonding is significantly weaker in Os^{II}–N^a than in Re^I–N^a can be indirectly inferred from bond parameter data of bis chelates. In *cis–trans–cis* [OsCl$_2$(L^2)$_2$] the average N–N distance is 1.32 Å[22] as compared to 1.35 Å in [ReCl$_2$(L^2)$_2$], **1b**. Similarly the N–N distances in azopyridine bis chelates are 1.31[20] and 1.33 Å respectively. The π-basicity order is thus Os^{II} < Re^{II} which in turn implies the order Os^{II} << Re^I.

Concluding remarks

The synthesis and structural characterization of the hitherto unreported bivalent and monovalent rhenium coordination types [Re^{II}X$_2$(NN)$_2$] and [Re^I(NN)$_3$]ReO$_4$ have been successfully achieved. An increase in the number of azoheterocycle chelate rings causes a relatively large increase in metal reduction potentials, thus stabilizing lower oxidation states: bis chelation affords rhenium(II) and tris chelation rhenium(I).

The bis and tris chelates occur exclusively in the *cis–trans–cis* and facial isomeric forms respectively. The presence of strong d(Re)–π*(azo) back-bonding in both families is revealed by bond distance data. In the bis chelates the *cis–trans–cis* isomer has the advantage of both maximized back-bonding and minimized steric crowding. In the tris chelates the net back-bonding is strong enough to offset the disadvantage of steric crowding in the facial geometry. The high π-acidity of azoheterocycles is neatly revealed by the present work.

Experimental

[ReOCl$_3$(PPh$_3$)$_2$],[34] [ReO(OEt)X$_2$(PPh$_3$)$_2$],[35] 2-(arylazo)imidazoles[14,18,19] and 2-(arylazo)pyridines[16] were prepared by reported methods. For electrochemical work HPLC grade acetonitrile was used. All other chemicals and solvents were of reagent grade and were used as received. Spectral measurements were made with following equipment: UV-vis, Shimadzu UV-1601 PC spectrophotometer; IR (KBr and polyethylene disk), Nicolet Magna IR 750 Series II and 550 FAR IR spectrometers; ^{1}H NMR, Bruker 300 MHz FT spectrometer (proton numbering scheme used is the same as in crystallography); X-band EPR, Varian E-109C spectrometer. Electrochemical measurements were performed under nitrogen atmosphere using a PAR 370–4 electrochemistry system with platinum working electrode.[36] The supporting electrolyte was tetraethylammonium perchlorate (TEAP), 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 the microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 Series II elemental analyzer.

Synthesis of complexes

Synthesis of azoimidazole $[ReX_2(L)_2]$ 1 complexes

These complexes were prepared by the same general procedure based on the reaction of $[ReO(OEt)X_2(PPh_3)_2]$ with L in toluene. Details are given below for a representative case.

$[ReCl_2(L^1)_2]$ 1a. To a suspension of $[ReO(OEt)Cl_2(PPh_3)_2]$ (100 mg, 0.119 mmol) in 25 cm^3 of toluene was added 56 mg (0.298 mmol) of L^1. The resulting mixture was heated to reflux for 45 min affording a reddish orange solution. The solvent was then removed under reduced pressure, and the mass thus obtained was dissolved in minimum amount of dichloromethane and subjected to chromatography on a silica gel column (20 × 1 cm, 60–120 mesh). Following elution with pure toluene, reddish orange band was eluted out with toluene–acetonitrile (50 : 3) mixture. Solvent removal from the eluate under reduced pressure afforded $[ReCl_2(L^1)_2]$ in pure form which was dried under *vacuo* over fused calcium chloride. Yield: 52 mg (70%). (Found: C, 38.21; H, 3.25; N, 17.76. Calc. for $C_{20}H_{20}N_8Cl_2Re$: C, 38.16; H, 3.20; N, 17.80.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2 solution]: 484 (5600) and 373 (10200). IR (cm^{-1}): 320, 330 (Re–Cl), 1300 (N=N). μ_{eff}/μ_B, 2.09; *g*(center), 2.053; A_{av}/G, 312.

$[ReCl_2(L^2)_2]$ 1b. (Found: C, 40.24; H, 3.60; N, 17.09. Calc. for $C_{22}H_{24}N_8Cl_2Re$: C, 40.18; H, 3.68; N, 17.04.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2 solution]: 486 (7300), and 345 (12000). IR (cm^{-1}): 317, 320 (Re–Cl), 1300 (N=N). μ_{eff}/μ_B, 2.10; g(center), 2.078; A_{av}/G, 304.

$[ReCl_2(L^3)_2]$ 1c. (Found; C, 34.49; H, 2.57; N, 16.12. Calc. for $C_{20}H_{18}N_8Cl_4Re$: C, 34.39; H, 2.60; N, 16.04.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2 solution]: 489 (5700) and 337 (9300). IR (cm^{-1}): 315, 335 (Re–Cl), 1310 (N=N). μ_{eff}/μ_B, 2.10; g (center), 2.066; A_{av}/G, 315.

$[ReBr_2(L^1)_2]$ 1d. The dibromo complexes were synthesized by the same general procedure as described for **1a**. Only $[ReO(OEt)Cl_2(PPh_3)_2]$ was replaced by $[ReO(OEt)Br_2(PPh_3)_2]$ in the above synthesis. (Found: C, 33.39; H, 2.73; N, 15.70. Calc. for $C_{20}H_{20}N_8Br_2Re$: C, 33.44; H, 2.81; N, 15.60.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2 solution]: 464 (3400) and 352 (6700) IR (cm^{-1}): 1300 (N=N). μ_{eff}/μ_B, 2.02; *g*(center), 2.103; A_{av}/G, 273.

$[ReBr_2(L^2)_2]$ 1e. (Found: C, 33.50; H, 3.29; N, 15.09. Calc. for $C_{22}H_{24}N_8Br_2Re$: C, 35.40; H, 3.24; N, 15.01.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2 solution]: 477 (3500) and 342 (6300). IR (cm^{-1}): 1290 (N=N). μ_{eff}/μ_B, 1.98; *g*(center), 2.116; A_{av}/G, 295.

$[ReBr_2(L^3)_2]$ 1f. (Found: C, 30.46; H, 2.27; N, 14.30. Calc. for $C_{20}H_{18}N_8Cl_2Br_2Re$: C, 30.51; H, 2.30; N, 14.23.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2 solution]: 485 (3700) and 347 (7900). IR (cm^{-1}): 204, 227 (Re–Br), 1300 (N=N). μ_{eff}/μ_B, 1.96; *g*(center), 2.098; A_{av}/G, 285.

$[ReI_2(L^1)_2]$ 1g. The diiodo complexes were synthesized by the same general procedure as described for **1a**. Only $[ReO(OEt)Cl_2(PPh_3)_2]$ was replaced by $[ReO(OEt)I_2(PPh_3)_2]$ for the above synthesis. (Found: C, 29.67; H, 2.58; N, 13.70. Calc. for $C_{20}H_{20}N_8I_2Re$: C, 29.57; H, 2.48; N, 13.79.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2 solution]: 525 (3600) and 374 (7600). IR (cm^{-1}): 1290 (N=N). μ_{eff}/μ_B, 1.95; *g* (center), 2.117; A_{av}/G, 254.

$[ReI_2(L^2)_2]$ 1h. (Found: C, 31.35; H, 2.83; N, 13.40. Calc. for $C_{22}H_{24}N_8I_2Re$: C, 31.44; H, 2.88; N, 13.33.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2 solution]: 533 (1900) and 355 (7500). IR (cm^{-1}): 1290 (N=N). μ_{eff}/μ_B, 1.94; *g*(center), 2.131; A_{av}/G, 248.

$[ReI_2(L^3)_2]$ 1i. (Found: C, 27.17; H, 2.10; N, 12.80. Calc. for $C_{20}H_{18}N_8Cl_2I_2Re$: C, 27.26; H, 2.06; N, 12.71.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2 solution]: 516 (2000) and 353 (7200). IR (cm^{-1}): 174, 188 (Re–I), 1300 (N=N). μ_{eff}/μ_B, 1.94; *g*(center), 2.117; A_{av}/G, 255.

$[ReI_2(L^4)_2]$ 1j. (Found: C, 41.22; H, 3.35; N, 11.18. Calc. for $C_{34}H_{32}N_8I_2Re$: C, 41.14; H, 3.25; N, 11.29.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2 solution]: 489 (7000) and 351 (12400). IR (cm^{-1}): 1280 (N=N). μ_{eff}/μ_B, 1.95; *g*(center), 2.110; A_{av}/G, 253.

Synthesis of the intermediate $[Re(OPPh_3)(OEt)Cl_2(L^3)]$. To a suspension of $[ReO(OEt)Cl_2(PPh_3)_2]$ (100 mg, 0.119 mmol) in 25 cm^3 of toluene was added 26 mg (0.119 mmol) of L^3. The resulting mixture was stirred magnetically for 1 h at room temperature, affording an yellowish orange solution. The solvent was then removed under reduced pressure, and the mass thus obtained was dissolved in a minimum amount of dichloromethane and subjected to chromatography on a silica gel column (20 × 1 cm, 60–120 mesh) in the same manner as in the case of **1a**. Solvent removal from the eluate under reduced pressure afforded $[Re(OPPh_3)(OEt)Cl_2(L^3)]$ in pure form which was dried under *vacuo* over fused calcium chloride. Yield: 62 mg (65%). (Found: C, 44.87; H, 3.60; N, 7.11. Calc. for $C_{30}H_{29}N_4Cl_3O_2PRe$: C, 44.96; H, 3.65; N, 7.00.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2 solution]: 659 (370), 459 (4500) and 343 (6200). IR (cm^{-1}): 1125 (O–P), 924 (O–Et), 1437 (N=N).

Conversion to $[ReCl_2(L^3)_2]$ 1c. To a solution of $[Re(OPPh_3)(OEt)Cl_2(L^3)]$ (50 mg, 0.062 mmol) in 25 cm^3 of toluene was added 21 mg (0.093 mmol) of L^3 and 3 mg (0.011 mmol) of PPh_3. The resulting mixture was heated to reflux for 30 min affording a reddish orange solution. The solvent was then removed under reduced pressure and chromatographic work up in the same manner as described for **1a** afforded $[ReCl_2(L^3)_2]$ in pure form which was dried under *vacuo* over fused calcium chloride. Yield: 27 mg (60%).

Synthesis of azopyridine $[ReCl_2(L)_2]$ 2 complexes

These complexes were synthesized by the same general procedure based on the reaction of $[ReOCl_3(PPh_3)_2]$ with L in benzene. Details are given below for a representative case.

$[ReCl_2(L^5)_2]$ 2a. To a suspension of $[ReOCl_3(PPh_3)_2]$ (100 mg, 0.120 mmol) in 25 cm^3 of benzene was added 55 mg (0.300 mmol) of L^5. The resulting mixture was warmed at 60°C for 10

Table 5 Crystal data for complexes **1b**, **1j**, **2b** and **4a**

Complex	**1b**	**1j**	**2b**	**4a**
Formula	$C_{22}H_{24}Cl_2N_8Re$	$C_{34}H_{32}I_2N_8Re$	$C_{22}H_{16}Cl_4N_6Re$	$C_{33}H_{27}N_9O_4Re_2$
M	657.59	992.68	692.41	986.04
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/n$	C_c
a/Å	28.74(2)	10.946(2)	8.532(6)	12.876(10)
b/Å	13.454(4)	18.790(4)	22.793(8)	22.313(10)
c/Å	13.427(5)	17.394(4)	12.417(3)	10.938(6)
α/°	90	90	90	90
β/°	110.86(4)	99.60(3)	100.22(4)	90.08(6)
γ/°	90	90	90	90
U/Å^3	4852(4)	3527.4(12)	2377(2)	3143(3)
Z	8	4	4	4
D/mg m^{-3}	1.801	1.869	1.935	2.084
T/K	293	293	293	293
μ/mm^{-1}	5.257	5.231	5.587	7.752
Unique reflections	3604	5257	4165	3733
R_{int}	0.0476	0.0376	0.0658	0.0435
Observed reflections [$I > 2\sigma(I)$]	2718	3631	2829	3106
R_1, wR_2 [$I > 2\sigma(I)$]	0.0399, 0.1049	0.0483, 0.0955	0.0616, 0.1386	0.0243, 0.0557
All data	0.0642, 0.1297	0.0876, 0.1206	0.1040, 0.1687	0.0388, 0.1160

min affording a reddish orange solution. The solvent was then quickly removed under reduced pressure and the solid mass 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). Following elution with pure benzene, a reddish orange band was eluted out with benzene–acetonitrile (25 : 2) mixture. Solvent removal from the elute under reduced pressure afforded [ReCl$_2$(L^5)$_2$] in pure form which was dried under *vacuo* over fused calcium chloride. Yield: 47 mg (62%). (Found: C, 42.41; H, 2.85; N, 13.41. Calc. for $C_{22}H_{18}Cl_2N_6Re$: C, 42.38; H, 2.90; N, 13.48.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2 solution]: 509 (7400). IR (cm^{-1}): 320, 330 (Re–Cl), 1310 (N=N). μ_{eff}/μ_B, 2.10; g(center), 2.104; A_{av}/G, 250.

[ReCl$_2$(L^6)$_2$] 2b. (Found: C, 38.21; H, 2.29; N, 12.17. Calc. for $C_{22}H_{16}Cl_4N_6Re$: C, 38.16; H, 2.33; N, 12.14.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2 solution]: 507 (7800). IR (cm^{-1}): 315, 330 (Re–Cl), 1300 (N=N). μ_{eff}/μ_B, 2.09; g(center), 2.079; A_{av}/G, 248.

Synthesis of azoimidazole [Re(L)$_3$]ReO$_4$ 3 complexes

These complexes were prepared by the same general procedure based on the reaction of [ReO(OEt)I$_2$(PPh$_3$)$_2$] with excess L in acetonitrile solution. Details are given below for a representative case.

[Re(L^1)$_3$]ReO$_4$ 3a. To a solution of [ReO(OEt)I$_2$(PPh$_3$)$_2$] (100 mg, 0.097 mmol) in 15 cm^3 of acetonitrile was added 108 mg (0.582 mmol) of L^1. The resulting mixture was heated to reflux for 8 h, affording a brownish green solution. The solvent was then removed under reduced pressure, and the mass thus obtained was dissolved in minimum amount of dichloromethane and subjected to chromatography on a silica gel column (20 × 1 cm, 60–120 mesh). A deep green band was eluted out with a toluene–acetonitrile (1 : 1) mixture. The solid obtained after solvent removal from the eluate under reduced pressure was again dissolved in small amount of dichloromethane and the above chromatographic procedure was repeated followed by a second repeat. After solvent removal from the final eluate [Re(L^1)$_3$]ReO$_4$ was afforded in pure form. It was dried under *vacuo* over fused calcium chloride. Yield: 58 mg (60%). (Found: C, 36.27; H, 3.09; N, 16.80. Calc. for $C_{30}H_{30}N_{12}O_4Re_2$: C, 36.21; H, 3.04; N, 16.89.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) CH_2Cl_2 solution]: 575 (6800), 448 (11300), 393 (7800) and 313 (9900). IR (cm^{-1}): 1235 (N=N), 910(Re–O, ReO$_4^-$), ^{1}H NMR [δ (J/Hz), $CDCl_3$ solution]: MeC$_3$N$_2$, 7.28 (d, 1.8, H1), 6.57 (d, 1.8, H2) and 4.01 (s, N–Me); C$_6$H$_5$, 7.20 (multiplet, H7, H9), 5.96 (d, 6.8, H6, H10) and 7.20 (multiplet, H8).

[Re(L^2)$_3$]ReO$_4$ 3b. (Found: C, 38.28; H, 3.40; N, 16.13. Calc. for $C_{33}H_{36}N_{12}O_4Re_2$: C, 38.22; H, 3.50; N, 16.21.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2 solution]: 579(8830), 445 (14800), 398 (10500) and 311 (13000). IR (cm^{-1}): 1233 (N=N), 909 (Re–O, ReO$_4^-$). ^{1}H NMR [δ (J/Hz), $CDCl_3$ solution]: MeC$_3$N$_2$, 7.23 (d, 1.6, H1), 6.50 (d, 1.7, H2) and 3.98 (s, N–Me); C$_6$H$_4$Me, 6.97 (d, 8.1, H7, H9), 6.01 (d, 8.2, H6, H10) and 2.35 (s, p-Me).

[Re(L^3)$_3$]ReO$_4$ 3c. (Found: C, 32.77; H, 2.53; N, 15.22. Calc. for $C_{30}H_{27}N_{12}Cl_3O_4Re_2$: C, 32.80; H, 2.48; N, 15.30.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2 solution]: 573 (7530), 447 (12700), 396 (8900) and 315 (11000). IR (cm^{-1}): 1232 (N=N), 910 (Re–O, ReO$_4^-$). ^{1}H NMR [δ (J/Hz), $CDCl_3$ solution]: MeC$_3$N$_2$, 7.29 (d, 1.6, H1), 6.51 (d, 1.7, H2) and 4.01 (s, N–Me); C$_6$H$_4$Cl, 7.20 (d, 7.0, H7, H9) and 6.15 (d, 7.0, H6, H10).

Synthesis of azopyridine [Re(L)$_3$]ReO$_4$, 4 complexes

These complexes were prepared by the same general procedure based on the reaction of [ReOCl$_3$(PPh$_3$)$_2$] with excess L in benzene solution. Details are given below for a representative case.

[Re(L^5)$_3$]ReO$_4$ 4a. To suspension of [ReOCl$_3$(PPh$_3$)$_2$] (100 mg, 0.120 mmol) in 15 cm^3 of benzene was added 132 mg (0.720 mmol) of L^5. The resulting mixture was warmed at 60°C for 15 min, affording a brownish green solution. The solvent was then removed under reduced pressure, and the mass thus obtained dissolved in a small amount of dichloromethane and subjected to chromatography on a silica gel column (20 × 1 cm, 60–120 mesh). A deep green band was eluted out with a benzene–acetonitrile (1 : 1) mixture. After solvent removal from the eluate [Re(L^5)$_3$]ReO$_4$ was afforded in pure form. It was finally dried under *vacuo* over fused calcium chloride. Yield: 62 mg (52%). (Found: C, 40.25; H, 2.72; N, 12.81. Calc. for $C_{33}H_{27}N_9O_4Re_2$: C, 40.20; H, 2.76; N, 12.78.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2 solution]: 596 (6750), 456 (10050) and 314 (17200). IR (cm^{-1}): 1230 (N=N), 910 (Re–O, ReO$_4^-$). ^{1}H NMR [δ (J/Hz), $CDCl_3$ solution]: C$_5$N, 8.07 (d, 8.1, H1), 7.52 (t, 8.0, H2), 7.99 (t, 7.6, H3), and 7.81 (d, 5.9, H4); C$_6$H$_5$, 5.84 (d, 4.0, H7, H11), 7.30 (t, 7.2, H8, H10) and 7.19 (t, 7.7, H9).

[Re(L^6)$_3$]ReO$_4$ 4b. (Found: C, 36.33; H, 2.18; N, 11.61. Calc. for $C_{33}H_{24}N_9Cl_3O_4Re_2$: C, 36.38; H, 2.22; N, 11.57.) UV-vis [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2 solution]: 610 (8000), 459

(11800) and 315 (20200). IR (cm^{-1}): 1226 (N=N), 907 (Re–O, ReO_4^-). ^1H NMR [δ (J/Hz), $CDCl_3$ solution]: C_5N, 8.06 (d, 8.1, H1), 7.62 (t, 6.5, H2), 7.97 (multiplet, H3) and 7.97 (multiplet, H4); C_6H_4Cl, 6.04 (d, 8.7, H7, H11) and 7.23 (d, 8.7, H8, H10).

Crystallography. Single crystals of the complexes **1b**, **1j**, **2b**, and **4a** were grown by slow diffusion of hexane into dichloromethane solutions of the respective compounds. Data were collected on a Nicolet R3m/V four circle diffractometer with graphite monochromated Mo–Kα radiation (λ = 0.71073 Å) by the ω-scan technique in the range $3 \le 2\theta/° \le 47$ for complexes **1b** and **1j** and $3 \le 2\theta/° \le 50$ for **2b** and $3 \le 2\theta/° \le 55$ for **4a**. All the data were corrected for Lorentz-polarization and absorption.[37] 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[38] program package. Significant crystal data are listed in Table 5.

CCDC reference numbers 192365 (**1b**), 192366 (**1j**), 192367 (**2b**) and 192368 (**4a**).

See http://www.rsc.org/suppdata/dt/b2/b208338h/ for crystallographic data in CIF or other electronic format.

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