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Synthesis and characterisation of phosphorescent rhenium(I) complexes of hydroxy- and methoxy-substituted imidazo[4,5-*f*]-1,10-phenanthroline ligands

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ABSTRACT

Eight new fluorescent ligands (**L1**-**L8**) derived from the fused imidazo[4,5-*f*]-1,10-phenanthroline core, have been synthesised utilising a one-pot methodology. The ligands include two points of structural variety, allowing multiply-substituted aryl groups (including hydroxy and methoxy moieties) to be attached to the ligand core. The ligands **L1**-**L8** are fluorescent (λ_{em} = 399–426 nm) and react with pentacarbonylbromorhenium to give coordination complexes of the form *fac*-[ReBr(CO)$_3$(N^N)] (where N^N = **L1**-**L8**). The complexes were characterised using a variety of spectroscopic and analytical techniques, including single crystal X-ray diffraction studies on two examples. The rhenium complexes were all found to be luminescent, revealing classical ^{3}MLCT emission at 579–587 nm in aerated solution with corresponding lifetimes in the range 149–166 ns.

1. Introduction

Lophine (2,4,5-triphenylimidazole [1]) based chromophores (Scheme 1) have been known for >50 years [2] and primarily investigated for their fluorescence and chemiluminescence properties [3]. Syntheses have been developed [4] and the emission characteristics can be tuned through the imidazole substituents [5]. These systems have shown great application in analytical disciplines [6]. The versatility and ease of functionalisation of the lophine core has allowed a huge variety of new systems to be developed including those that have application in coordination chemistry. The closely related fused unit imidazo[4,5-*f*]-1,10-phenanthroline (Scheme 1) has become a popular ligand motif in the last few years, and can be easily functionalised for a variety of potential applications. For example, metallomesogens based on imidazo[4,5-*f*]-1,10-phenanthroline have been described that incorporate metal ions such as Pt(II), Ln(III) and uranyl [7].

One of the most common metal ions to be used in conjunction with imidazo[4,5-*f*]-1,10-phenanthroline type ligands is Ru(II). Such complexes have been studied for their excited state properties [8] and biological application [9], particularly with respect to DNA binding, which is promoted by the planar imidazo[4,5-*f*]-1,10-phenanthroline ligand. Ru(II) complexes of 4-(1*H*-imidazo[4,5-*f*]-1,10-phenanthrolin-2-yl)benzene-1,2-diol (a ligand closely related to those in this paper) have also been reported showing pH dependent luminescence properties [10]. Imidazo[4,5-*f*]-1,10-phenanthroline derived ligands have also been combined with metal ions such as Ir(III), [11] Pt(II), [12] and Cu(I) [13] complexes, and have also been used in the development of a chemosensor for Co(II) ions [14]. Ir(III) complexes with a coumarin chromophore conjugated to the imidazo[4,5-*f*]-1,10-phenanthroline core have been developed for the efficient photogeneration of singlet oxygen [15]. This ligand class has also been utilised in the design of metal complexes for cell imaging studies. Examples of Ir(III), which show good two-photon excitation properties [16], and aggregation-induced phosphorescence [17,18] have been successfully explored in targeted imaging. Related Ru(II) complexes have demonstrated mitochondrial targeting behaviour through cell imaging studies and have been postulated as anticancer agents [19]. The potential

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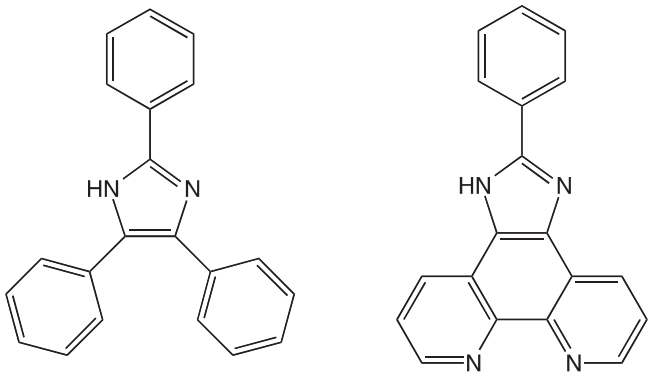


Scheme 1. Molecular structures of 2,4,5-triphenylimidazole (left) and 2-phenylimidazo[4,5-*f*]-1,10-phenanthroline (right).

multidenticity of these ligands has also been exploited in the development of coordination polymers (including for the *f*-block) [20] and also in the design of complex architectures with interesting magnetic properties [21].

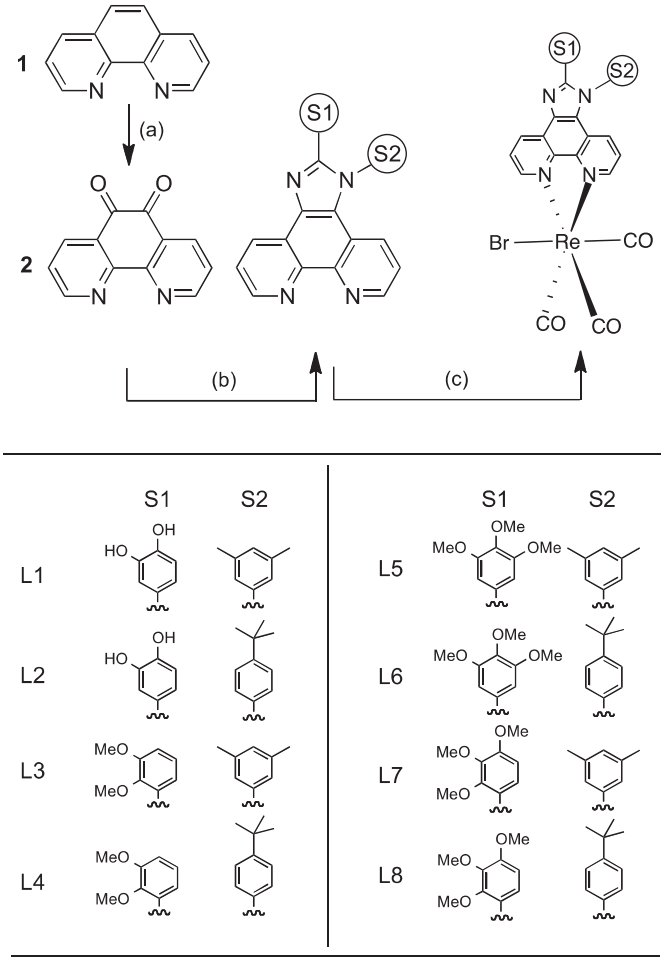
In the context of Re(I), only a handful of reports exist on the coordination chemistry of imidazo[4,5-*f*]-1,10-phenanthroline type ligands, including within heterobimetallic assemblies [22]. In our previous studies we have shown that the imidazo[4,5-*f*]-1,10-phenanthroline ligand is ideally suited to Re(I) allowing the formation of [ReBr(CO)$_3$(N^N)] type complexes; the substitution of different groups at the ligand core can allow subtle tuning of the ^{3}MLCT wavelengths when incorporated into Re(I) complexes [23]. Interest in luminescent d^6 Re(I) has flourished over the last few decades. In particular, [ReX(CO)$_3$(N^N)] complexes provide huge opportunity for the design of complexes for different optoelectronic applications since the luminescent properties of *fac*-[ReX(CO)$_3$(-diimine)] type complexes are often ascribed to metal-to-ligand charge transfer (MLCT) excited states [24,25]. Such complexes have found application in the design of chemosensors [26,27,28,29,30,31,32] and cell imaging agents [33].

In this paper we present the synthesis of a new series of chromophoric ligands based upon the fused imidazo[4,5-*f*]-1,10-phenanthroline core that are functionalised with different substituted aryl groups. We report the synthesis and spectroscopic characterisation of eight new *fac*-[Re(Br(CO)$_3$(N^N)] complexes, including the X-ray structures of two examples. The variation in ligand structure is discussed in the context of the photophysical properties of the complexes.

2. Results and discussion

2.1. Synthesis and characterisation

The ligands (**L1-L8**) were synthesised according to an adaption of previously reported approaches (Scheme 2), allowing a range of aryl amine (**S2-NH$_2$**) and aldehyde (**S1-CHO**) reagents to be utilised in the procedure. The functionalised imidazo[4,5-*f*]-1,10-phenanthroline ligands possessed good solubility in a range of organic solvents (imparted by the different substituted aryl groups, **S1** and **S2**) and were characterised using a range of standard spectroscopic and analytical techniques, confirming the proposed formulations in each case. The relevant details and data are presented in the experimental section. The coordination chemistry of the ligands (**L1-L8**) was explored with Re(I), wherein heating stoichiometric equivalents of ligand and ReBr(CO)$_5$ in toluene for 24 h produced the desired complexes as yellow coloured solids of the general formulation *fac*-[ReBr(CO)$_3$(N^N)] (where N^N = **L1-L8**).



Scheme 2. Route to the new ligands and complexes: (a) conc. H_2SO_4, conc. HNO_3, NaBr; (b) S1-CHO, S2-NH_2, AcOH; (c) $ReBr(CO)_5$, toluene, Δ.

Solid-state IR spectroscopic studies were conducted on the complexes to reveal either two or three bands, the two lower frequency absorption often overlapping, suggesting the local symmetry can be approximated to C_s or C_{3v} symmetry as expected for the facially capped coordination geometry. There is very little variation in the CO stretching frequencies suggesting that the donating ability of the diimine ligand is comparable across the series of complexes. High resolution electrospray mass spectrometry (positive mode) showed that the neutral complexes fragment in a predictable manner. The axial bromide ligand is substituted with MeCN, resulting in an overall cationic species [Re(CO)$_3$(MeCN)(N^N)]$^+$ with an isotopic distribution consistent for rhenium (and loss of Br). ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained for each complex and were consistent with the presence of the coordinated ligands in all cases. Typically, in the ^{1}H NMR the aromatic resonances of the phenanthroline fragment are shifted downfield upon coordination to rhenium suggesting a binding mode to the diimine domain rather than *via* the catechol-like terminating groups in **L1** and **L2**. For the ligands incorporating the methoxy substituents, the -OCH_3 resonances appear around 3.8 ppm and were relatively insensitive to coordination to Re(I).

2.2. X-ray structures of the complexes

Single crystal X-ray diffraction studies were undertaken on two complexes, *fac*-[ReBr(CO)$_3$(**L4**)] and *fac*-[ReBr(CO)$_3$(**L6**)]. Suitable

Table 1
Data collection parameters for the X-ray crystal structures.

Empirical formula	$C_{35}H_{30}BrN_4O_6Re$	$C_{34}H_{28}BrN_4O_5Re$
	fac-[ReBr(CO)$_3$(**L6**)]	*fac*-[ReBr(CO)$_3$(**L4**)]
Formula weight	868.74	838.71
Temperature	100(2) K	100(2) K
Wavelength	0.71075 Å	0.71075 Å
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
Unit cell dimensions	a = 11.686(5) Å, α = 90° b = 12.634(5) Å, β = 93.380(7)° c = 24.0993(10) Å, γ = 90°	a = 11.1587(8) Å, α = 111.784(8)° b = 13.0479(10) Å, β = 110.740(8)° c = 13.1431(10) Å, γ = 97.685°
Volume	3552(2) Å^3	1582.4(2) Å^3
Z	4	2
Density (calculated)	1.625 Mg/m^3	1.760 Mg/m^3
Absorption coefficient	4.594 mm^{-1}	5.150 mm^{-1}
$F(000)$	1704	820
Crystal	Block; yellow	Column; yellow
Crystal size	0.05 × 0.02 × 0.02 mm^3	0.27 × 0.06 × 0.06 mm^3
θ range for data collection	2.98–25.03°	2.58–27.55°
Index ranges	$-15 \le h \le 15$, $-16 \le k \le 16$, $-29 \le l \le 31$	$-14 \le h \le 13$, $-16 \le k \le 16$, $-13 \le l \le 17$
Reflections collected	61116	19957
Independent reflections	6269 [R_{int} = 0.1111]	7218 [R_{int} = 0.0468]
Completeness to θ_{max}	99.8%	98.9%
Absorption correction	Semi–empirical from equivalents	Semi–empirical from equivalents
Max. and min. transmission	0.914 and 0.803	0.747 and 0.337
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6269/53/461	7218/0/411
Goodness-of-fit on F^2	1.314	1.010
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.0742, $wR2$ = 0.1620	$R1$ = 0.0333, $wR2$ = 0.0797
R indices (all data)	$R1$ = 0.0825, $wR2$ = 0.1660	$R1$ = 0.0412, $wR2$ = 0.0828
Largest diff. peak and hole	1.419 and −0.813e Å^{-3}	2.087 and −2.051 e Å^{-3}

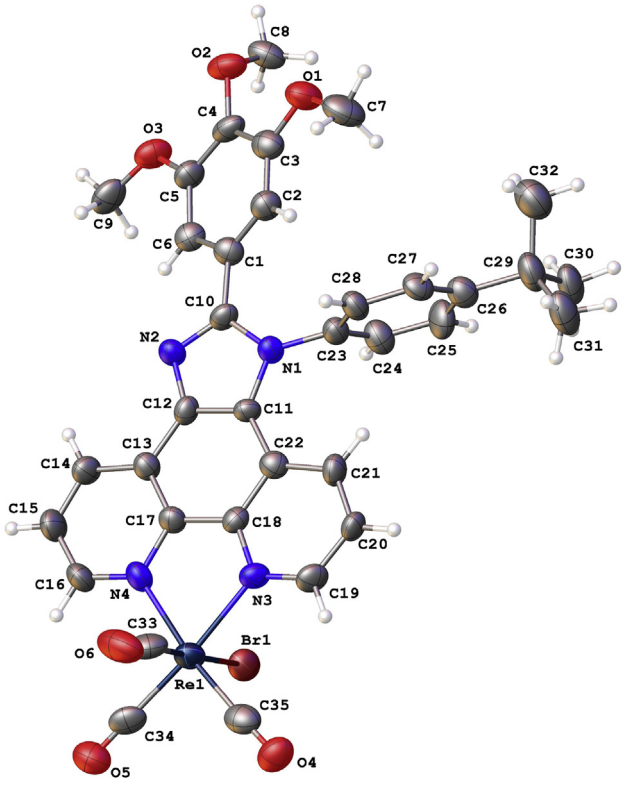


Fig. 1. Ortep3 plot of complex *fac*-[ReBr(CO)$_3$(**L6**)]. Ellipsoids are drawn at 50% probability. In the crystal structure *tert*-butyl goup is disordered and modelled over two positions with 53/47 ratio. For clarity only one component is shown. Selected data - bond lengths (Å): C33–Re1, 1.955(15); C34–Re1, 1.954(13); C35–Re1, 1.930(13); N3–Re1, 2.181(8); N4–Re1, 2.179(9); Br1–Re1, 2.6430(13). Bond angles(°): O6–C33–Re1, 173.8(10); O5–C34–Re1, 178.9(10); O4–C35–Re1, 176.0(11); C19–N3–Re1, 125.6(6); C18–N3–Re1, 115.9(6); C16–N4–Re1, 126.5(7); C17–N4–Re1, 115.8(6); C35–Re1–C33, 86.7(5); C35–Re1–C34, 90.1(4); C33–Re1–C34, 88.8(5); C35–Re1–N4, 173.3(4); C33–Re1–N4, 94.1(4); C34–Re1–N4, 96.6(4); C35–Re1–N3, 97.7(4); C33–Re1–N3, 96.9(4); C34–Re1–N3, 170.6(3); N4–Re1–N3, 75.6(3); C35–Re1–Br1, 95.3(4); C33–Re1–Br1, 178.0(3); C34–Re1–Br1, 91.3(3); N4–Re1–Br1, 83.9(2); N3–Re1–Br1, 82.8(2).

crystals were obtained by the slow diffusion of hexane into a toluene solution of the complex solution over a period of 72 h. The parameters associated with the data collection for both complexes are shown in Table 1, with selected bond length and angle data in the corresponding figure captions (Figs. 1 and 2).

Both structures reveal the expected coordination environment for the d^6 Re(I) in each case with **L4/L6** chelating *trans* to two carbonyl ligands, with the third CO ligand and bromide donors occupying axial positions. Bond lengths and angles are typical for a {ReBr(CO)$_3$} complex of a chelating diimine [34]. For *fac*-[ReBr(CO)$_3$(**L6**)] the imidazo[4,5-*f*]-1,10-phenanthroline core of the ligand framework is essentially co-planar with the 'Re(CO)$_2$' fragment of the complex, whilst the trimethoxy-phenyl group deviates from co-planarity with the heterocyclic core of the ligand with a torsion angle of 25.0°; the *p*-*tert*-butylphenyl group is almost orthogonal to the ligand core with a torsion angle of 81.8° (the *tert*-butyl group is also disordered). An increased torsion angle (away from planarity) is observed (65.8°) for the apical substituent "R" of *fac*-[ReBr(CO)$_3$(**L4**)] compared to *fac*-[ReBr(CO)$_3$(**L6**)]. This is most likely due to the ortho-positioning of the methoxy substituent on the apical phenyl in *fac*-[ReBr(CO)$_3$(**L4**)], which bears only a H atom for *fac*-[ReBr(CO)$_3$(**L6**)]. The added steric clashing that would be involved with the sidearm R′ group results in significant rotation of the apical group. An increased torsion angle away from planarity such as this reduces the effective conjugation of the ligand fragment.

2.3. UV-vis. Absorption and visible luminescence studies

The UV-vis and luminescence data were collected for **L1**-**L8**. In general, the absorption spectra (obtained on either aerated DMSO or chloroform solutions at room temperature) revealed a number of strong bands dominating the UV region below 350 nm, which are assigned to various $\pi \rightarrow \pi^*$ transitions. It is also possible that weaker $n \rightarrow \pi^*$ bands may contribute to a lower energy portion of the spectra (350–425 nm). The precise positioning of these bands was subtly dependent upon the nature of the aryl substitution in **S**1 and

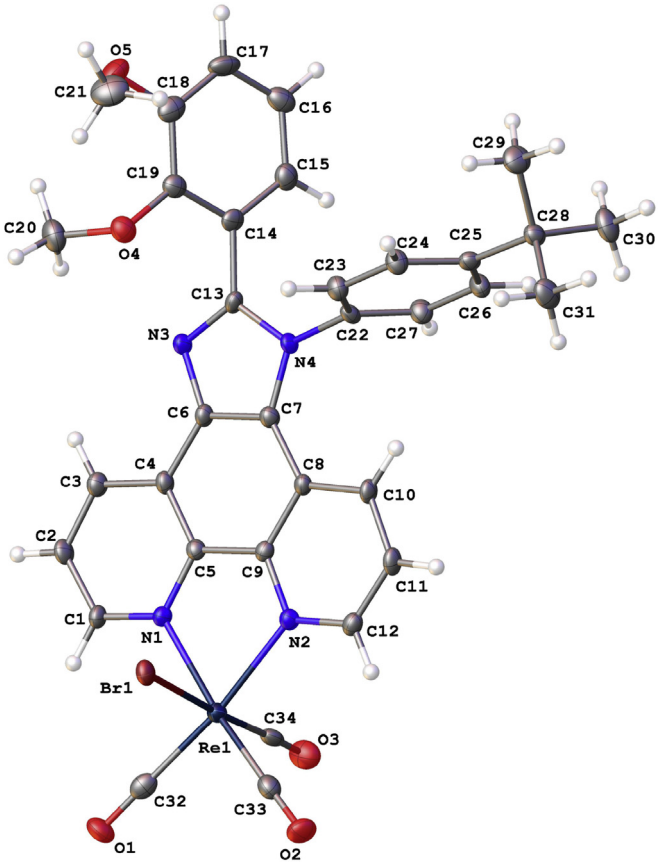


Fig. 2. Ortep3 plot of complex *fac*-[ReBr(CO)$_3$(**L4**)]. Ellipsoids are drawn at 80% probability and hydrogen atoms have been omitted for clarity. Selected data - bond lengths (Å): C32–Re1, 1.931(4); C34–Re1, 1.926(4); C33–Re1, 1.908(4); Br1–Re1, 2.6332(5); N1–Re1, 2.171(3); N2–Re1, 2.177(3). Bond angles(°): O1–C32–Re1, 178.7(3); O3–C34–Re1, 177.2(4); O2–C33–Re1, 177.7(4); C1–N1–Re1, 125.7(3); C5–N1–Re1, 115.8(2); C12–N2–Re1, 125.2(3); C9–N2–Re1, 116.0(2); C33–Re1–C34, 90.55(17); C33–Re1–C32, 89.01(17); C34–Re1–C32, 88.91(17); C33–Re1–N1, 171.05(13); C34–Re1–N1, 95.09(14); C32–Re1–N1, 98.01(15); C33–Re1–N2, 97.57(15); C34–Re1–N2, 93.49(14); C32–Re1–N2, 172.96(15); N1–Re1–N2, 75.20(12); C33–Re1–Br1, 90.24(12); C34–Re1–Br1, 177.25(11); C32–Re1–Br1, 93.74(12); N1–Re1–Br1, 83.81(8); N2–Re1–Br1, 83.79(8).

S2 (Scheme 2). Corresponding time resolved luminescence data showed that each of the ligands was fluorescent (lifetimes 3.3–4.3 ns) with emission wavelengths in the range 399–423 nm (Fig. 3).

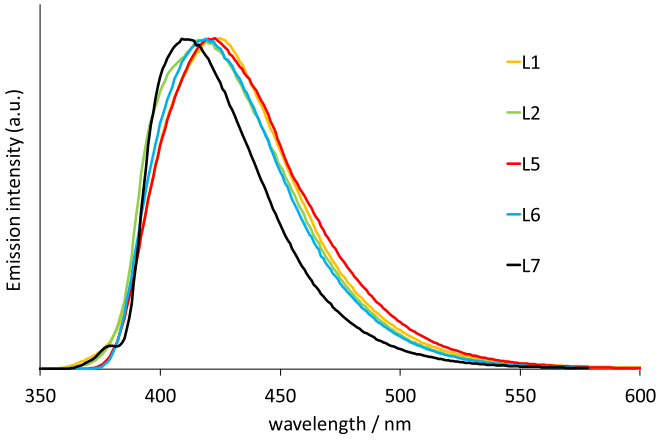


Fig. 3. Comparison of the normalised emission spectra of selected ligands (λ_{ex} = 265 nm; 10^{-5} M $CHCl_3$).

The slightly broadened and unstructured emission peaks suggest that the origin of the emission may be a mixture of $^1\pi$-π^* and n-π^* excited states. The very subtle variation in values can be attributed to the different substitution patterns of **S**1 and **S2**. The data suggests that the change in hydroxyl/methoxy substitution pattern at **S1** induces more pronounced changes in emission wavelength for the free ligands than the variations at **S2**. **L1** possessed the most bathochromically shifted fluorescence wavelength.

For the complexes, two main absorption characteristics were observed. Firstly, the high energy ligand-centred $\pi \rightarrow \pi^*$ transitions are expected for the extended π-framework at 260–330 nm, and secondly the presence of a weaker band that tails into the visible region ^{1}MLCT absorption (Re(d)$\rightarrow\pi^*$) with the longest wavelengths observed at >400 nm as broadened shoulders. This data is consistent with that obtained for related Re(I) complexes that incorporate the imidazo[4,5-*f*]-1,10-phenanthroline chromophore [23]. Across the series of complexes there was a subtle shift in the ^{1}MLCT absorption wavelengths (408–426 nm) for the isolated complexes with *ortho* methoxy-substitution of the **S1** group leading to slightly higher ^{1}MLCT energies. In comparison, the ^{1}MLCT absorption (Re(5d)$\rightarrow\pi^*$) for [ReCl(CO)$_3$(phen)] has been reported at 383 nm, which is a higher energy absorption compared to the value of the complexes described herein, reflecting the increased conjugation across the imidazole[4,5-*f*]-1,10-phenanthroline core.

In the luminescence studies, following irradiation of the ^{1}MLCT band ~410 nm, the Re(I) complexes all showed a broad unstructured emission peak *ca.* 580 nm in aerated chloroform (Table 2). This observed emission is therefore distinct from the fluorescence noted for the corresponding free ligands, and was associated with a relatively large Stokes' shift (~6500 cm^{-1}). Fig. 4 shows the excitation and emission spectra for *fac*-[ReBr(CO)$_3$(**L4**)] (together with other selected emission spectra) where it is clear from the emission profile that there is no residual fluorescence from the imidazole [4,5-*f*]-1,10-phenanthroline ligand. The excitation spectrum shows a weak feature around 500 nm, which may be due to a direct ^{3}MLCT excitation. Corresponding emission lifetimes for these complexes lie in the range 149–166 ns, which are characteristic of neutral Re(I) based lumophores of this type, and again suggest that fluorescence from the ligand is quenched [23]. Taken together, and in comparison to related examples in the literature, the emission properties from this series of complexes can therefore be characterised as ^{3}MLCT in nature. Despite the variation noted in the ^{1}MLCT absorptions, the emission data suggests that the ^{3}MLCT energy is relatively insensitive to the variation of the substituents attached to the imidazole[4,5-*f*]-1,10-phenanthroline ligand.

3. Conclusion

The one-pot synthesis described herein has allowed a variety of fluorescent imidazole[4,5-*f*]-1,10-phenanthroline based ligands to be isolated, incorporating a variety of hydroxy- and methoxy substituents. The ligands react conveniently with ReBr(CO)$_5$ to give complexes of the general formulation *fac*-[ReBr(CO)$_3$(N^N)] (where N^N = **L1-L8**). Two examples were characterised using X-ray crystallography and confirm the proposed formulations of the complexes. Each of the rhenium complexes possessed a ^{3}MLCT emitting state giving visible luminescence in fluid medium at room temperature, and it was shown that this could be subtly tuned via the electronic character of the substituents at the ligand. The functionality of the ligands, in particular the hydroxyl-substituted species lends themselves to further reactivity towards multimetallic supramolecular architectures (*i.e.* the complexes themselves can be used as synthons).

Table 2
IR, UV-vis. and luminescence spectroscopic data for the complexes.

Complex	υ(CO)/cm^{-1}[a]	^{1}MLCT, λ_{abs}/nm[b]	^{3}MLCT, λ_{em}/nm[c,d]	^{3}MLCT, τ/ns[d,e]
fac-[ReBr(CO)$_3$(**L1**)]	2023, 1912, 1884	418	580 (423)	166 (4.1)
fac-[ReBr(CO)$_3$(**L2**)]	2022, 1896 br	418	587 (417)	156 (4.0)
fac-[ReBr(CO)$_3$(**L3**)]	2020, 1892 br	414	578 (400)	168 (3.3)
fac-[ReBr(CO)$_3$(**L4**)]	2020, 1891 br	418	580 (399)	163 (3.3)
fac-[ReBr(CO)$_3$(**L5**)]	2020, 1869 br	425	579 (421)	163 (4.3)
fac-[ReBr(CO)$_3$(**L6**)]	2020, 1894 br	426	580 (419)	158 (4.2)
fac-[ReBr(CO)$_3$(**L7**)]	2020, 1891 br	417	580 (411)	149 (3.6)
fac-[ReBr(CO)$_3$(**L8**)]	2020, 1893 br	408	584 (416)	149 (3.6)

[a] Solid state.
[b] $CHCl_3$ solution 1×10^{-5} M.
[c] $\lambda_{ex} = 365$ nm or 410 nm, $CHCl_3$ solution 1×10^{-5} M.
[d] Values in parentheses are for the corresponding free ligand (**L1**-**L8**).
[e] $\lambda_{ex} = 372$ nm, $CHCl_3$ solution 1×10^{-5} M.

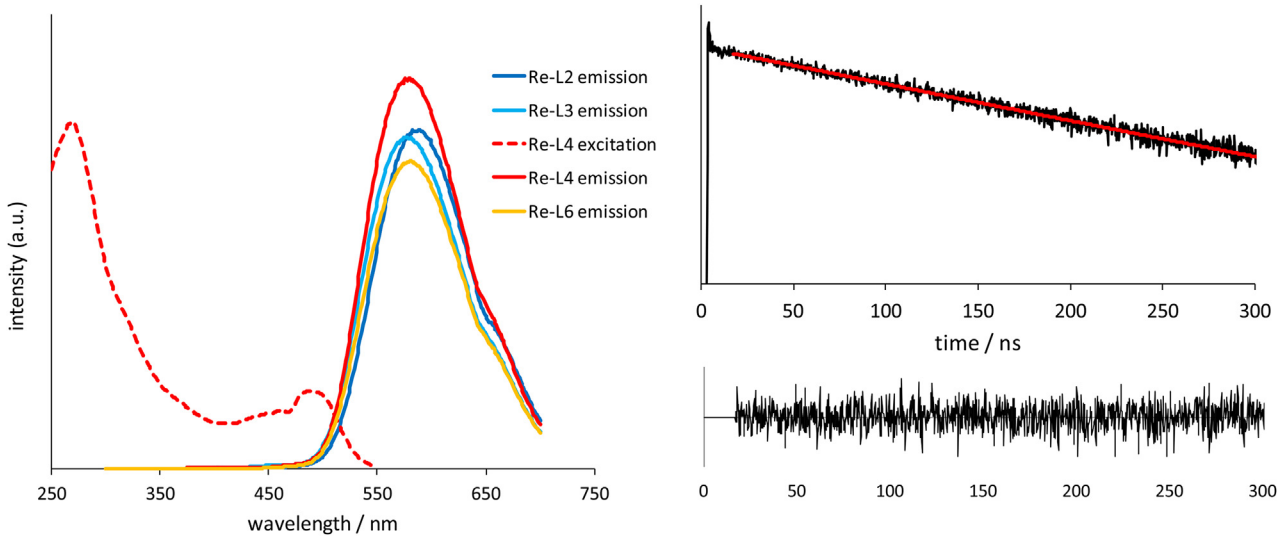


Fig. 4. Left: Example of excitation ($\lambda_{em} = 580$ nm) and emission ($\lambda_{ex} = 355$ nm) spectra for selected complexes (10^{-5} M $CHCl_3$). Right: example of a lifetime decay (with fit) for [ReBr(CO)$_3$(**L5**)].

4. Experimental

All reactions were performed with the use of vacuum line and Schlenk techniques. Reagents were commercial grade and were used without further purification. [ReBr(CO)$_5$] was prepared according to the literature procedure [35]. 1,10-phenanthroline-5,6-dione prepared as previously reported [36]. ^{1}H and ^{13}C-{^{1}H} NMR spectra were run on NMR-FT Bruker 400 or 250 spectrometers and recorded in $CDCl_3$. ^{1}H and ^{13}C-{^{1}H} NMR chemical shifts (δ) were determined relative to internal TMS and are given in ppm. Low-resolution mass spectra were obtained by the staff at Cardiff University. High-resolution mass spectra were carried out by at the EPSRC National Mass Spectrometry Service at Swansea University. UV-Vis studies were performed on a Jasco V-570 spectrophotometer as MeCN solutions (10^{-5} M). Photophysical data were obtained on a JobinYvon-Horiba Fluorolog spectrometer fitted with a JY TBX picosecond photodetection module as MeCN solutions. Emission spectra were uncorrected and excitation spectra were instrument corrected. The pulsed source was a Nano-LED configured for 372 nm output operating at 1 MHz. Luminescence lifetime profiles were obtained using the JobinYvon-Horiba FluoroHub single photon counting module and the data fits yielded the lifetime values using the provided DAS6 deconvolution software.

4.1. Data collection and processing

X-ray diffraction datasets were measured on a Rigaku AFC12 diffractometer equipped with enhanced sensitivity (HG) Saturn724 + CCD detector mounted at the window of an FR-E + *SuperBright* rotating anode generator (Mo Kα, $\lambda = 0.71075$ Å) with VHF *Varimax* optics (70 μm focus) [37] using Crystal Clear software [38] for data collection and reduction.

4.2. Structure analysis and refinement

The structures were solved by direct methods using SHELXS-97 [39] and refined on F_o^2 by full-matrix least-squares refinements using SHELXL [40] within the OLEX2 suite [41]. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were added at calculated positions and refined using a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter (U_{eq}) of the parent atom. In the crystal structure of *fac*-[ReBr(CO)$_3$(**L6**)] -*tert*butyl group is disordered and modelled over two positions with 53/47 ratio. Only one component is shown. SIMU, DELU and RIGU restraints were used to model appropriately atomic displacement parameters.

4.3. Data collection and processing

Diffraction data for *fac*-[ReBr(CO)$_3$(**L4**)] and *fac*-[ReBr(CO)$_3$(**L6**)] were collected on a Nonius KappaCCD using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 150 K. Software package Apex 2 (v2.1) was used for the data integration, scaling and absorption correction.

4.4. Structure analysis and refinement

The structure was solved by direct methods using SHELXS-97 and was completed by iterative cycles of ΔF-syntheses and full-matrix least squares refinement. All non-H atoms were refined anisotropically and difference Fourier syntheses were employed in positioning idealised hydrogen atoms and were allowed to ride on their parent C-atoms. All refinements were against F^2 and used SHELX-97.

4.5. Synthesis

4.5.1. Synthesis of L1

This material was prepared by combining 3,4-dihydroxy benzaldehyde (0.198 g, 1.43 mmol), 1,10-phenanthroline-5,6-dione (0.300 g, 1.43 mmol), 3,5-dimethylaniline (0.18 ml, 1.43 mmol) and ammonium acetate (1.10 g, 14.3 mmol) in acetic acid (10 ml). The reaction mixture was stirrer vigorously under reflux for 4 h, subsequently allowed to cool to room temperature and poured over crushed ice (200 g). The mixture was neutralised with aqueous ammonia. Bleach (several drops, sodium hypochlorite solution) was added to remove strongly coloured impurities and the resulting solution was extracted with dichloromethane (4 × 50 ml). After drying over $MgSO_4$ the solvent was removed and the crude product was recrystallised from a small volume of warm chloroform with the subsequent addition of hexane to yield product (**L1**) as a pale brown powder (0.346 g, 0.80 mmol, 56%). ^{1}H NMR (400 MHz, d6-DMSO): δ 9.06 (1H, d, J = 3.0 Hz), 8.97 (1H, d, J = 7.7 Hz), 8.92 (1H, d, J = 3.1 Hz), 7.85 (1H, dd, J = 7.8, 4.3 Hz), 7.48 (1H, dd, J = 8.4, 4.2 Hz), 7.37 (1H, s), 7.32 (3H, m), 7.22 (1H, d, J = 1.9 Hz), 6.81 (1H, dd, J = 8.3, 1.9 Hz), 6.66 (1H, d, J = 8.3 Hz), 2.38 (6H, s) ppm. ^{13}C{^{1}H} NMR (101 MHz, d6-DMSO): δ 152.1, 148.4, 147.3, 146.9, 145.0, 143.7, 143.6, 143.5, 140.1, 137.8, 134.9, 134.8, 131.8, 127.3, 126.2, 123.7, 123.4, 122.6, 120.9, 120.5, 119.5, 116.8, 115.3, 20.8 ppm. HRMS (ES)(%): found m/z = 433.1658 [M + H]$^+$; $\{C_{27}H_{20}N_4O_2\}^+$ requires 433.1659. IR (KBr plates): 3155 (bs), 1610 (m), 1601 (m), 1567 (m), 1510 (m), 1484 (s), 1425 (m), 1392 (w), 1343 (m), 1287 (s), 1240 (s), 1115 (w), 1081 (w), 1023 (w), 888 (m), 830 (m), 808 (m), 740 (s) cm^{-1}. UV-vis λ_{max} (ε/M^{-1} cm^{-1}) (DMSO): 262 (sh) (54 200), 280 (58 500), 304 (sh) (46 300) nm.

4.5.2. Synthesis of L2

This material was prepared by a similar method to **L1** using 3,4-dihydroxy benzaldehyde (0.198 g, 1.43 mmol), 1,10-phenanthroline-5,6-dione (0.300 g, 1.43 mmol), 4- terbutylaniline (0.23 ml, 1.43 mmol) and ammonium acetate (1.10 g, 14.3 mmol). The crude product was recrystallised using chloroform and hexane to give product (**L2**) as a brown/green powder (0.270 g, 0.80 mmol). ^{1}H NMR (400 MHz, MeOD): δ 9.01 (2H, m), 8.92–8.84 (1H, m), 7.84–7.67 (3H, m), 7.55–7.30 (4H, m), 7.07 (1H, d, J = 2.1 Hz), 6.82 (1H, dd, J = 8.2, 2.1 Hz), 6.69 (1H, d, J = 8.2 Hz), 1.45 (9H, s) ppm. ^{13}C{^{1}H} NMR (101 MHz, MeOD): δ 155.12, 154.60, 149.25, 148.42, 148.30, 146.37, 144.68, 144.38, 136.15, 135.75, 131.51, 129.55, 129.24, 128.45, 127.40, 126.51, 124.81, 123.56, 122.75, 121.66, 120.96, 120.78, 117.93, 115.92, 35.94, 31.74 ppm. HRMS (ES)(%): found m/z = 461.1976 [M + H]$^+$; $\{C_{29}H_{25}N_4O_2\}^+$ requires 461.1972. IR (KBr plates): 3058 (bw), 2961 (m), 1598 (m), 1576 (w), 1563 (w), 1511 (s), 1464 (w), 1438 (m), 1392 (w), 1364 (w), 1267 (s), 1110(w), 1033 (w), 993 (w), 910 (w), 808 (m), 740 (s) cm^{-1}. UV-vis λ_{max} (ε/M^{-1} cm^{-1}) ($CHCl_3$): 276 (31 800), 316(sh) (15 500), 423 (3100) nm.

4.5.3. Synthesis of L3

This material was prepared by a similar method to **L1** using 2,3-dimethoxy benzaldehyde (0.237 g, 1.43 mmol), 1,10-phenanthroline-5,6-dione (0.300 g, 1.43 mmol), 3,5-dimethylaniline (0.18 ml, 1.43 mmol) and ammonium acetate (1.10 g, 14.3 mmol). The crude product was recrystallised using chloroform and hexane to give product (**L3**) as an off-white powder (0.390 g, 0.85 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.17 (1H, dd, J = 4.4, 1.8 Hz), 9.10 (1H, dd, J = 8.1, 1.8 Hz), 9.05 (1H, dd, J = 4.3, 1.6 Hz), 7.72 (1H, dd, J = 8.1, 4.4 Hz), 7.51 (1H, dd, J = 8.4, 1.6 Hz), 7.32 (1H, dd, J = 8.4, 4.3 Hz), 7.10 (1H, s), 7.07–6.90 (5H, m), 3.85 (3H, s), 3.80 (3H, s), 2.32 (6H, s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 153.0, 149.2, 148.7, 148.3, 140.0, 137.3, 136.1, 131.9, 130.9, 128.8, 126.7, 126.1, 125.6, 124.5, 124.1, 124.0, 123.9, 122.6, 120.3, 118.0, 114.6, 62.0, 56.4, 21.7 ppm. HRMS (ES)(%): found m/z = 461.1968 [M + H]$^+$; $\{C_{29}H_{25}N_4O_2\}^+$ requires 461.1972. IR (KBr plates): 2937 (s), 1594 (m), 1562 (m), 1521 (w), 1502 (m), 1475 (s), 1420 (w), 1393 (w), 1377 (w), 1341 (w), 1263 (s), 1233 (w), 1168 (w), 1083 (s), 1045 (m), 999 (m), 856 (w), 824 (m), 809 (m), 742 (s) cm^{-1}. UV-vis λ_{max} (ε/M^{-1} cm^{-1}) ($CHCl_3$): 256 (55 600), 276 (sh) (42 500), 312 (14 000) nm.

4.5.4. Synthesis of L4

This material was prepared by a similar method to **L1** using 2,3-dimethoxy benzaldehyde (0.237 g, 1.43 mmol), 1,10-phenanthroline-5,6-dione (0.300 g, 1.43 mmol), 4-tertbutylaniline (0.23 ml, 1.43 mmol) and ammonium acetate (1.10 g, 14.3 mmol). The crude product was recrystallised using chloroform and hexane to give product (**L4**) as an off-white powder (0.350 g, 0.72 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.24–9.20 (1H, m), 9.16 (1H, d, J = 6.8 Hz), 9.08 (1H, dd, J = 4.3, 1.5 Hz), 7.77 (1H, dd, J = 8.1, 4.4 Hz), 7.51–7.42 (3H, m), 7.39–7.29 (3H, m), 6.99 (3H, m), 3.83 (3H, s), 3.77 (3H, s), 1.35 (9H, s) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 153.1, 152.6, 150.8, 148.8, 148.3, 148.0, 144.8, 144.3, 135.9, 134.4, 130.6, 128.3, 127.7, 126.7, 126.5, 125.4, 124.2, 123.9, 123.7, 123.5, 122.2, 120.0, 114.3, 61.6, 56.0, 35.0, 31.4 ppm. HRMS (ES)(%): found m/z = 489.2280 [M + H]$^+$; $\{C_{31}H_{29}N_4O_2\}^+$ requires 489.2285. IR (KBr plates): 2958 (m), 1599 (m), 1578 (m), 1560 (m), 1511 (s), 1465 (s), 1389 (w), 1339 (w), 1304 (w), 1263 (s), 1238 (w), 1131 (w), 1083 (s), 1071 (s), 1052 (s), 1004 (s), 989 (s), 872 (w), 847 (w), 818 (m), 806 (m), 797 (m), 785 (m) cm^{-1}. UV-vis λ_{max} (ε/M^{-1} cm^{-1}) ($CHCl_3$): 270 (97 600), 352 (sh) 2500 nm.

4.5.5. Synthesis of L5

This material was prepared by a similar method to **L1** using 3,4,5-trimethoxy benzaldehyde (0.281 g, 1.43 mmol), 1,10-phenanthroline-5,6-dione (0.300 g, 1.43 mmol), 3,5-dimethylaniline (0.18 ml, 1.43 mmol) and ammonium actetate (1.10 g, 14.3 mmol). The crude product was recrystallised using chloroform and hexane to give product (**L5**) as a brown powder (0.600 g, 1.22 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.19 (1H, dd, J = 4.4, 1.8 Hz), 9.15 (1H, dd, J = 8.1, 1.8 Hz), 9.06 (1H, dd, J = 4.3, 1.6 Hz), 7.76 (1H, dd, J = 8.1, 4.4 Hz), 7.51 (1H, dd, J = 8.4, 1.6 Hz), 7.36–7.30 (2H, m), 7.20 (2H, s), 6.93 (2H, s), 3.86 (3H, s), 3.72 (6H, s), 2.43 (6H, s) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 152.97, 151.60, 148.90, 147.97, 144.65, 144.13, 140.92, 139.01, 138.27, 135.76, 131.98, 130.92, 128.37, 127.10, 126.33, 125.03, 124.01, 123.64, 122.43, 120.02, 106.50, 61.05, 55.95, 21.41 ppm. HRMS (ES)(%): found m/z = 491.2076 [M+H]$^+$; $\{C_{30}H_{27}N_4O_3\}^+$ requires 491.2078. IR (KBr plates): 2935 (w), 1661 (w), 1588 (m), 1561 (w), 1523 (w), 1480 (m), 1418 (m), 1346 (w), 1247 (w), 1236 (w), 1126 (s), 1025 (w), 1000 (w), 804 (w), 738 (s) cm^{-1}. UV-vis λ_{max} (ε/M^{-1} cm^{-1}) ($CHCl_3$): 278

(54 900), 325(sh) (11 600), 368 (sh) (1600) nm.

4.5.6. Synthesis of L6

This material was prepared by a similar method to **L1** using 3,4,5-trimethoxy benzaldehyde (0.281 g, 1.43 mmol), 1,10-phenanthroline-5,6-dione (0.300 g, 1.43 mmol), 4-tertbutylaniline (0.23 ml, 1.43 mmol) and ammonium acetate (1.10 g, 14.3 mmol). The crude product was recrystallised using chloroform and hexane to give product (**L6**) as a brown powder (0.400 g, 0.77 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.16 (2H, m), 9.04 (1H, dd, $J = 4.3$, 1.6 Hz), 7.75 (1H, dd, $J = 8.1$, 4.4 Hz), 7.70–7.65 (2H, m), 7.54–7.46 (3H, m), 7.34–7.28 (2H, m), 6.84 (2H, s), 3.84 (3H, s), 3.67 (6H, s), 1.44 (9H, s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 153.9, 152.9, 151.6, 148.9, 147.9, 144.7, 144.2, 138.9, 135.8, 135.6, 130.7, 128.3, 128.1, 127.6, 126.9, 125.0, 123.9, 123.5, 122.3, 119.9, 106.4, 61.0, 55.9, 35.2, 31.4 ppm. HRMS (ES)(%): found m/z = 519.2386 $[M + H]^+$; $\{C_{32}H_{31}N_4O_3\}^+$ requires 519.2391. IR (KBr plates): 2965 (w), 1584 (m), 1559 (m), 1511 (s), 1473 (s), 1404 (m), 1344 (w), 1294 (w), 1247 (m), 1234 (m), 1187 (w), 1128 (s), 1069 (w), 1003 (m), 853 (m), 805 (m), 741 (s) cm^{-1}. UV-vis λ_{max} (ε/M^{-1} cm $^{-1}$) ($CHCl_3$): 281 (46 100), 314 (sh) (25 300), 361 (sh) (1600) nm.

4.5.7. Synthesis of L7

This material was prepared by a similar method to **L1** using, 2,3,4-trimethoxy benzaldehyde (0.280 g, 1.43 mmol), 1,10-phenanthroline-5,6-dione (0.300 g, 1.43 mmol), 3,5-dimethylaniline (0.18 ml, 1.43 mmol) and ammonium acetate (1.10 g, 14.3 mmol). The crude product was recrystallised using chloroform and hexane to give product (**L7**) as a brown powder (0.290 g, 0.59 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.18 (1H, dd, $J = 4.4$, 1.7 Hz), 9.11 (1H, dd, $J = 8.1$, 1.7 Hz), 9.07 (1H, dd, $J = 4.3$, 1.6 Hz), 7.74 (1H, dd, $J = 8.1$, 4.4 Hz), 7.56 (1H, dd, $J = 8.4$, 1.6 Hz), 7.34 (1H, dd, $J = 8.4$, 4.3 Hz), 7.09 (4H, m), 6.64 (1H, d, $J = 8.6$ Hz), 3.86 (3H, s), 3.77 (6H, d, $J = 1.5$ Hz), 2.33 (6H, s) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 186.6, 175.4, 155.3, 152.7, 151.0, 148.8, 147.9, 144.3, 143.8, 141.9, 139.5, 137.0, 135.5, 131.4, 131.0, 128.6, 126.6, 126.2, 125.8, 124.1, 123.6, 122.4, 120.0, 117.0, 106.8, 61.4, 60.9, 56.1, 21.3 ppm. HRMS (ES)(%): found m/z = 491.2069 $[M + H]^+$; $\{C_{30}H_{27}N_4O_3\}^+$ requires 491.2078. IR (KBr plates): 2935 (w), 2556 (w), 1750 (w), 1714 (s), 1612 (s), 1599 (s), 1563 (m), 1531 (w), 1510 (m), 1472 (s), 1429 (w), 1383 (w), 1341 (w), 1293 (s), 1233 (s), 1099 (s), 1061 (m), 1037 (s), 921 (m), 890 (m), 827 (s), 804 (s), 738 (s) cm^{-1}. UV-vis λ_{max} (ε/M^{-1} cm $^{-1}$) ($CHCl_3$): 258 (53 900), 275(sh) (45 900), 314(sh) (9900), 362 (1600) nm.

4.5.8. Synthesis of L8

This material was prepared by a similar method to **L1** using 2,3,4-trimethoxy benzaldehyde (0.280 g, 1.43 mmol), 1,10-phenanthroline-5,6-dione (0.300 g, 1.43 mmol), 4-tertbutylaniline (0.23 ml, 1.43 mmol) and ammonium acetate (1.10 g, 14.3 mmol). The crude product was recrystallised using chloroform and hexane to give product (**L8**) as a light brown powder (0.250 g, 0.48 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.17 (1H, dd, $J = 4.4$, 1.8 Hz), 9.11 (1H, dd, $J = 8.1$, 1.8 Hz), 9.05 (1H, dd, $J = 4.3$, 1.6 Hz), 7.73 (1H, dd, $J = 8.1$, 4.4 Hz), 7.58 (1H, dd, $J = 8.4$, 1.6 Hz), 7.49–7.45 (2H, m), 7.35–7.29 (3H, m), 7.17 (1H, d, $J = 8.5$ Hz), 6.67 (1H, d, $J = 8.6$ Hz), 3.87 (3H, s), 3.68 (6H, d, $J = 5.5$ Hz), 1.36 (9H, s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.3, 153.0, 152.5, 151.3, 148.9, 148.0, 144.8, 144.3, 141.8, 135.9, 134.6, 130.7, 128.5, 127.9, 126.8, 126.4, 126.4, 124.2, 123.6, 122.2, 120.0, 117.4, 107.0, 61.4, 61.0, 56.2, 35.0, 31.4 ppm. HRMS (EI)(%): found m/z = 519.2380; $\{C_{32}H_{31}N_4O_3\}$ requires 519.2380. IR (KBr plates): 2960 (s), 2017 (w), 1915 (w), 1601 (m), 1561 (w), 1512 (m), 1464 (s), 1410 (m), 1340 (w), 1293 (s), 1222 (w), 1095 (s), 1070 (m), 1037 (m), 1013 (m), 985 (w), 807 (w), 748 (s), cm^{-1}. UV-vis λ_{max} (ε/M^{-1} cm $^{-1}$) ($CHCl_3$): 270 (77 900), 427 (sh) (2000) nm.

4.5.9. Synthesis of fac-[ReBr(CO)$_3$(L1)]

Into a round bottom flask was L1 (0.053 g, 0.123 mmol), pentacarbonylbromorhenium (0.05 g, 0.123 mmol) and toluene (30 ml) and the reactants were left at reflux for 3 h under a nitrogen atmosphere. The solvent was removed in vacuo to yield orange oil. The residue was dissolved in $CHCl_3$ (2 ml) to which was added hexane to yield a precipitate that upon filtration afforded [ReBr(CO)$_3$(**L1**)] as a yellow/green powder (0.065 g). ^{1}H NMR (400 MHz, d6-DMSO): δ 9.52 (1H, bs), 9.43 (1H, d, $J = 5.1$ Hz), 9.34 (1H, d, $J = 8.2$ Hz), 9.29 (2H, m), 8.18 (1H, dd, $J = 8.2$, 5.2 Hz), 7.84 (1H, dd, $J = 8.6$, 5.1 Hz), 7.56 (1H, d, $J = 8.6$ Hz), 7.43 (2H, s), 7.36 (1H, s), 7.26 (1H, d, $J = 1.9$ Hz), 6.87 (1H, dd, $J = 8.3$, 1.8 Hz), 6.69 (1H, d, $J = 8.3$ Hz), 2.40 (6H, d, $J = 2.7$ Hz). ^{13}C{^{1}H} NMR (101 MHz, d6-DMSO): δ 154.0, 152.1, 151.1, 147.5, 145.2, 143.9, 143.9, 140.5, 140.4, 136.9, 135.5, 132.9, 132.3, 130.2, 127.0, 126.1, 126.0, 125.9, 125.3, 121.6, 120.8, 120.1, 117.9, 116.8, 115.4, 20.9 ppm. HRMS (ES)(%): found m/z = 803.0035 $[M + Na]^+$; $\{C_{30}H_{20}BrN_4NaO_5^{185}Re\}^+$ requires 803.0039. IR (KBr plates): 2921 (w), 2023 (s), 1913 (s), 1884 (s), 1616 (w), 1593 (w), 1516 (w), 1447 (w), 1273 (w), 819 (w) cm^{-1}. UV-vis λ_{max} (ε/M^{-1} cm $^{-1}$) ($CHCl_3$): 275 (45 800), 308(sh) (30 000), 359(sh) (10 000), 418 (5700) nm.

4.5.10. Synthesis of fac-[ReBr(CO)$_3$(L2)]

The title compound was prepared in a similar manner to [ReBr(CO)$_3$(**L1**)] but using **L2** (0.057 g, 0.123 mmol) and pentacarbonylbromorhenium (0.05 g, 0.123 mmol) to give the product [ReBr(CO)$_3$(**L2**)] as a yellow/green solid (0.080 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.34 (1H, s), 9.28–9.10 (2H, m), 7.81 (2H, m), 7.64 (2H, d, $J = 8.7$ Hz), 7.49 (3H, m), 7.13 (1H, bs), 6.50 (1H, bs), 6.21 (1H, bs), 1.48 (6H, s) ppm. HRMS (ES)(%): found m/z = 807.0366 $[M + H]^+$; $\{C_{32}H_{23}BrN_4O_5^{185}Re\}$ requires 807.0387. IR (KBr plates): 2022 (s), 1896 (bs), 1599 (m), 1511 (m), 1450 (m), 1399 (w), 1362 (w), 1269 (w), 1108 (w), 808 (m), 724 (m) cm^{-1}. UV-vis λ_{max} (ε/M^{-1} cm $^{-1}$) ($CHCl_3$): 276 (38 600), 357(sh) (8500), 418 (6200) nm.

4.5.11. Synthesis of fac-[ReBr(CO)$_3$(L3)]

The title compound was prepared in a similar manner to [ReBr(CO)$_3$(**L1**)] but using **L3** (0.057 g, 0.123 mmol) and pentacarbonylbromorhenium (0.05 g, 0.123 mmol) to give the product [ReBr(CO)$_3$(**L3**)] as a green solid (0.085 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.38 (1H, d, $J = 4.0$ Hz), 9.34 (1H, d, $J = 8.2$ Hz), 9.29 (1H, d, $J = 5.0$ Hz), 7.92 (1H, dd, $J = 8.2$, 5.2 Hz), 7.67 (1H, d, $J = 8.5$ Hz), 7.54 (1H, m), 7.19 (1H, s), 7.09–6.90 (5H, m), 3.85 (3H, s), 3.81 (3H, s), 2.35 (6H, s) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 197.3, 197.3, 189.3, 153.1, 153.0, 152.0, 151.3, 148.6, 145.8, 145.4, 140.8, 140.7, 136.1, 133.3, 132.8, 130.8, 127.1, 126.5, 125.8, 125.6, 125.3, 124.4, 123.4, 122.4, 115.3, 62.0, 56.4, 21.7. HRMS (ES)(%): found m/z = 809.0546 $[M + H]^+$; $\{C_{32}H_{25}O_5N_4Br^{185}Re\}$ requires 809.5032. IR (KBr plates): 2020 (s), 1892 (bs), 1709 (w), 1594 (w), 1478 (m), 1399 (w), 1345 (w), 1267 (m), 1234 (w), 1078 (w), 1059 (w), 999 (w), 808 (w), 725 (w) cm^{-1}. UV-vis λ_{max} (ε/M^{-1} cm $^{-1}$) ($CHCl_3$): 261 (77 700), 287 (sh) (46,800), 414 (6500) nm.

4.5.12. Synthesis of fac-[ReBr(CO)$_3$(L4)]

The title compound was prepared in a similar manner to [ReBr(CO)$_3$(**L1**)] but using **L4** (0.060 g, 0.123 mmol) and pentacarbonylbromorhenium (0.05 g, 0.123 mmol) to give the product [ReBr(CO)$_3$(**L4**)] as a yellow solid (0.085 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.39 (1H, dd, $J = 5.1$, 1.2 Hz), 9.32 (1H, dd, $J = 8.3$, 1.1 Hz), 9.27 (1H, dd, $J = 5.1$, 0.9 Hz), 7.93 (1H, dd, $J = 8.2$, 5.2 Hz), 7.65 (1H, dd, $J = 8.6$, 0.9 Hz), 7.55–7.48 (3H, m), 7.36 (2H, m), 7.11–7.03 (1H, m), 7.03–6.93 (2H, m), 3.85 (3H, s), 3.76 (3H, s), 1.37 (9H, s) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 197.6, 197.6, 189.7, 154.6, 153.7, 153.3, 152.1, 151.3, 148.7, 146.0, 145.5, 137.1, 134.0, 133.4, 130.9, 128.2, 127.9, 127.8, 127.7, 127.5, 127.1, 126.6, 125.5, 125.0, 124.8, 123.7, 122.8, 115.3,

62.2, 56.6, 35.7, 31.9 ppm. HRMS (ES)(%): found m/z = 837.0848 $[M + H]^+$; $\{C_{34}H_{29}BrN_4O_5^{185}Re\}^+$ requires 837.0845. IR (KBr plates): 2020 (s), 1891 (bs), 1709 (w), 1600 (w), 1512 (w), 1478 (m), 1459 (m), 1266 (m), 1085 (w), 1061 (w), 993 (w), 808 (w), 725 (w) cm^{-1}. UV-vis λ_{max} (ε/M^{-1} cm^{-1}) ($CHCl_3$): 262 (115 800), 418 (1800) sh nm.

4.5.13. Synthesis of fac-[ReBr(CO)$_3$(L5)]

The title compound was prepared in a similar manner to [ReBr(CO)$_3$**(L1)**] but using **L5** (0.060 g, 0.123 mmol) and pentacarbonylbromorhenium (0.05 g, 0.123 mmol) to give product [ReBr(CO)$_3$(**L5**)] as a green powder (0.080 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.41–9.33 (2H, m), 9.27 (1H, dd, J = 5.1, 1.2 Hz), 7.95 (1H, dd, J = 8.2, 5.2 Hz), 7.66 (1H, dd, J = 8.6, 1.2 Hz), 7.53 (1H dd, J = 8.6, 5.1 Hz), 7.38 (1H, s), 7.20 (1H, bs), 6.96 (2H, s), 3.88 (3H, s), 3.73 (6H, s), 2.47 (3H, s), 2.45 (3H, s) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.6, 153.2, 153.2, 151.7, 150.8, 145.4, 145.1, 141.8, 141.5, 139.70, 137.4, 136.5, 133.1, 132.7, 130.4, 127.5, 126.3, 126.1, 125.8, 125.1, 124.1, 122.2, 106.6, 63.66, 61.1, 56.0, 21.5, ppm. HRMS (ES)(%): found m/z = 863.0467 $[M + Na]^+$; $\{C_{33}H_{26}BrN_4O_6^{187}ReNa\}^+$ requires 863.0469. IR (KBr plates): 2020 (s), 1869 (bs), 1589 (m), 1479 (m), 1235 (w), 1126 (m), 999 (w), 808 (w), 725 (w) cm^{-1}. UV-vis λ_{max} (ε/M^{-1} cm^{-1}) ($CHCl_3$): 278 (30 200), 347(sh) (8600), 425 (3700) sh nm.

4.5.14. Synthesis of fac-[ReBr(CO)$_3$(L6)]

The title compound was prepared in a similar manner to [ReBr(CO)$_3$**(L1)**] but using **L6** (0.063 g, 0.123 mmol) and pentacarbonylbromorhenium (0.05 g, 0.123 mmol) to give product [ReBr(CO)$_3$(**L6**)] as a yellow powder (0.086 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.41–9.34 (2H, m), 9.26 (1H, dd, J = 5.1, 1.2 Hz), 7.95 (1H, dd, J = 8.2, 5.2 Hz), 7.76 (2H, d, J = 8.6 Hz), 7.69 (1H, dd, J = 8.6, 1.2 Hz), 7.54–7.48 (3H, m), 6.86 (2H, s), 3.87 (3H, s), 3.68 (6H, s), 1.47 (9H, s) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 197.2, 197.1, 189.2, 155.3, 153.9, 153.4, 152.0, 151.0, 145.7, 145.3, 140.0, 134.8, 133.2, 130.3, 128.5, 128.4, 128.2, 127.6, 126.3, 126.3, 125.2, 123.9, 122.3, 106.9, 61.3, 56.3, 35.6, 31.7 ppm. HRMS (ES)(%): found m/z = 869.0962 $[M + H]^+$; $\{C_{35}H_{31}BrN_4O_6^{187}Re\}^+$ requires 869.0963. IR (KBr plates): 2960 (m), 2020 (s), 1894 (s), 1585 (w), 1512 (w), 1477 (m), 1414 (m), 1383 (w), 1345 (w), 1301 (w), 1235 (m), 1127 (s), 1056 (w), 846 (w), 807 (w), 725 (m) cm^{-1}. UV-vis λ_{max} (ε/M^{-1} cm^{-1}) ($CHCl_3$): 278 (46 700), 341 (sh) (14 700), 426 (6000) sh nm.

4.5.15. Synthesis of [ReBr(CO)$_3$(L7)]

The title compound was prepared in a similar manner to [ReBr(CO)$_3$**(L1)**] using L7 (0.060 g, 0.123 mmol) and pentacarbonylbromorhenium (0.05 g, 0.123 mmol) to give product [ReBr(CO)$_3$(**L7**)] as a yellow solid (0.075 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.38 (1H, s), 9.34–9.25 (2H, m), 7.97–7.89 (1H, m), 7.72 (1H, d, J = 7.9 Hz), 7.57–7.50 (1H, m), 7.18 (1H, s), 7.11–7.02 (3H, m), 6.67 (1H, d, J = 8.4 Hz), 3.88 (3H, s), 3.78 (6H, s), 2.35 (6H, s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.8, 153.3, 152.6, 151.5, 150.8, 145.4, 145.0, 141.9, 140.3, 140.1, 136.5, 136.3, 132.9, 132.1, 130.5, 126.8, 126.6, 126.4, 126.1, 125.7, 125.3, 124.9, 122.2, 116.5, 107.1, 61.6, 61.0, 56.2, 21.4, 21.4 ppm. HRMS (EI)(%): found m/z = 841.0642; $\{C_{33}H_{27}BrN_4O_6Re\}$ requires 841.0653. IR (KBr plates): 2935 (w), 2020 (s), 1891 (s), 1599 (m), 1508 (w), 1474 (m), 1427(w), 1412 (w), 1293 (m), 1233 (w), 1215 (w), 1096 (m), 1055 (w), 1011 (w), 807 (w), 725 (w) cm^{-1}. UV-vis λ_{max} (ε/M^{-1} cm^{-1}) ($CHCl_3$): 239 (55 800), 261 (85 700), 295 (sh) (38 400), 417 (6300) sh nm.

4.5.16. Synthesis of [ReBr(CO)$_3$(L8)]

The title compound was prepared in a similar manner to [ReBr(CO)$_3$**(L1)**] but using **L8** (0.064 g, 0.123 mmol) and pentacarbonylbromorhenium (0.05 g, 0.123 mmol) to give product [ReBr(CO)$_3$(**L8**)] as a yellow solid (0.065 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.33–9.30 (1H, m), 9.25 (1H, dd, J = 8.2, 1.2 Hz), 9.21 (1H, d, J = 4.1 Hz), 7.86 (1H, dd, J = 8.2, 5.1 Hz), 7.73–7.69 (1H, m), 7.49–7.42 (3H, m), 7.30–7.22 (2H, m), 7.09 (1H, d, J = 8.6 Hz), 6.63 (1H, d, J = 8.6 Hz), 3.81 (3H, s), 3.64–3.60 (6H, m), 1.31 (9H, s) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 153.9, 153.6, 152.3, 151.6, 150.8, 145.4, 145.0, 141.9, 136.6, 133.6, 132.9, 130.4, 127.8, 127.6, 127.0, 126.8, 126.6, 126.5, 126.1, 124.9, 122.2, 116.5, 107.2, 61.4, 61.0, 56.2, 35.2, 31.4 ppm. LRMS (ES+): found m/z 830.12; $\{C_{37}H_{33}N_5O_6Re\}^+$ requires 830.20. IR (KBr plates): 2962 (w), 2020 (s), 1893 (bs), 1709 (m), 1600 (m), 1512 (m), 1463 (m), 1412 (w), 1342 (w), 1292 (m), 1221 (m), 1096 (m), 1081 (m), 808 (m) cm^{-1}. UV-vis λ_{max} (ε/M^{-1} cm^{-1}) ($CHCl_3$): 274 (260 000), 408 (3800) sh nm.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2017.04.021.

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