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Re(I) derivatives functionalised with thioether crowns containing the 1,10-phenanthroline subunit as a new class of chemosensors†

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A series of luminescent *fac*-$[Re(CO)_3(L)(NN)]^+$ complexes, where L is a pyridine or an imidazole and NN is the 1,10-phenanthroline subunit of mixed donor pentadentate thioether crowns have been synthesised and their luminescence properties have been analysed. Then, heterometallic Re(I)/Au(I) complexes, with the Au(I) fragment bonded directly to the imidazole ligand, and heterometallic Re(I)/Ag(I) complexes, with the silver fragment coordinating the S-donor thioether linker of the rings have also been prepared. Analysis of their luminescence properties showed a considerable blue shift of the emission maxima for the Re(I)/Ag(I) derivatives, upon coordination of the silver centre to the S-donor atoms of the aliphatic chain of the macrocyclic units.

Introduction

Since the pioneering work of Pedersen, Lehn and Cram involving the synthesis of cation selective crown ethers, cryptands and spherands,[1] many studies have been devoted to the development of selective receptors for host–guest interactions and molecular recognition. Their wide application in the area of ion transport and chemosensing makes this research field very appealing. In this sense, transition d^6 metal complexes have lately attracted much interest due to their versatile photophysical and photochemical properties.[2] In general they showed metal-to-ligand charge transfer (MLCT) transitions, with relatively large Stokes shifts, long lifetimes and good quantum yields. In the particular case of luminescent rhenium(I) complexes, the archetypal system is $[Re(CO)_3(L)(NN)]^{0/+1}$ where (NN) represents a diimine derivative and L is a halogen atom or pyridine derivative. The specific phosphorescence process is, generally, a ^{3}MLCT transition originating from a $Re(d\pi) \rightarrow NN(\pi^*)$ excited state, where the rest of the ligands in the coordination sphere barely affect the luminescence properties.[3] Regardless of the great amount of work devoted to the development of rhenium(I) based transition metal complexes as selective sensors for either alkali and alkaline earth metals,[4] only a few examples have been reported as chemosensors of transition metals. The incorporation of soft donor atoms like sulfur or selenium into crown units is key for achieving such selectivity. Several examples reported by Yam and coworkers demonstrated that functionalised rhenium(I) derivatives with thia-, selena- and azacrown moieties can be used for selective and specific binding of soft metal ions such Ag^+, Hg^{2+} and/or Pb^{2+}.[5] This work aims to increase the scope of soft metal ion sensors by developing new rhenium(I) systems bearing thia and mixed thia/oxo aliphatic linkers anchored directly to the diimine unit. Functionalisation at the 2,9-positions of the diimine rather than the axial ligand bound to the rhenium(I) centre will be preferred in order to affect directly the electronic properties of the ligand portion implicated in the emission process.

Results and discussion

Synthetic procedure and characterization

The synthesis of the macrocyclic ligands **L1** and **L2** has been described somewhere else and it is summarised in Scheme 1.[6] Briefly, it entailed the oxidation of 2,9-dimethyl-1,10-phenanthroline to the corresponding dialdehyde, then its reduction to 2,9-bis(hydroxymethy1)-1,10-phenanthroline and thereafter a chlorination step followed by a cyclisation reaction with the correspondent dithiol to afford **L1** and **L2**.[7]

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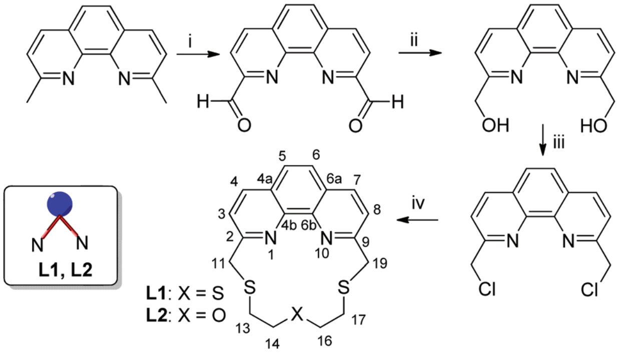
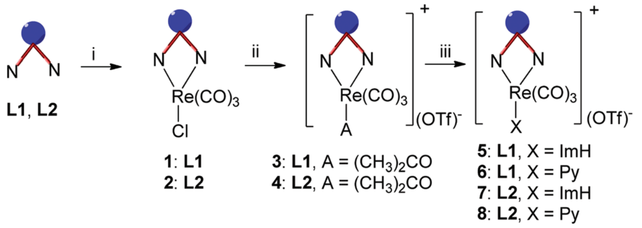
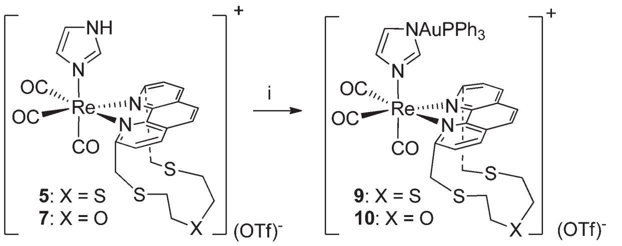
† Electronic supplementary information (ESI) available: Short contact interaction in complex **5** (Fig. S1); emission spectra of complexes **1**, **2**, **5–12** and **8** (Fig. S2). CCDC 1413449–1413455. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt02723c



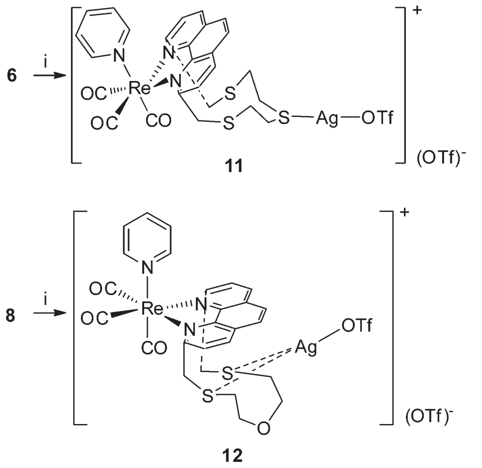
Scheme 1 Depiction of the synthesis of ligands **L1** and **L2** with the numbering scheme adopted for ^{1}H and ^{13}C NMR assignments. (i): SeO_2, dioxane, reflux; 4 h; (ii) $NaBH_4$, ethanol, reflux 2 h; (iii) $SOCl_2$, r.t., 8 h; (iv) $(HSCH_2CH_2)_2S$ (**L1**) or $(HSCH_2CH_2)_2O$ (**L2**), Cs_2CO_3, dimethylformamide (dmf), 55 °C.



Scheme 2 Depiction of the synthesis of species **1–8** (i): $[ReCl(CO)_5]$, toluene, reflux 1 h; (ii) $Ag(CF_3SO_3)$, acetone, r.t. 12 h; (iii) Py/ImH, THF/acetone, r.t., 1d/4d.



Scheme 3 Depiction of the synthesis of complexes **9–10** (i): Cs_2CO_3, $[Au(CF_3SO_3)(PPh_3)]$, dichloromethane, r.t., 1–2 h.



Scheme 4 Depiction of the synthesis of complexes **11** and **12** with the proposed structure in solution (i): $Ag(CF_3SO_3)$, acetone, r.t., 1–3d.

Complexes *fac*-[Re(Cl)(CO)$_3$(**L1**)] (**1**) and *fac*-[Re(Cl)(CO)$_3$(**L2**)] (**2**) were obtained by reaction of the commercially available [Re(Cl)(CO)$_5$] with the previously synthesised **L1** and **L2**, which involved the substitution of two carbonyl ligands for the nitrogen atoms of the phenanthroline subunit of **L1** and **L2**. The adopted bidentate coordination mode of **L1** and **L2** contrasted with that previously observed for Pb(II), Rh(III), Ni(II), and Ru(II) complexes.[6a,8] In those cases, **L1** and **L2** bound the metal centre through the nitrogen atoms as well as the heteroatoms of the mixed thioether crown, affording either octahedral or tetrahedral complexes. Therefore, the bidentate coordination mode observed for the complexes described herein might be the reason for the severe distortion present in the phenanthroline unit, which contrary to what was expected, was not lying in the equatorial plane defined by the two nitrogen atoms and the *trans* carbonyl ligands. This particular disposition will be discussed in detail in the sections below. Complexes *fac*-[Re((CH$_3$)$_2$CO)(CO)$_3$(**L1**)](CF$_3$SO$_3$) (**3**) and *fac*-[Re((CH$_3$)$_2$CO)(CO)$_3$(**L2**)](CF$_3$SO$_3$) (**4**), which can be considered as activated intermediate species, were obtained by abstraction of the chloride ligand with silver triflate in a coordinating solvent. Finally, the cationic complexes *fac*-[Re(CO)$_3$(L)(**L1**)](CF$_3$SO$_3$) and *fac*-[Re(CO)$_3$(L)(**L2**)](CF$_3$SO$_3$) [L = ImH (**5**, **7**), Py (**6**, **8**)] were synthesised by reaction of the activated rhenium(I) complexes **3** and **4** with either pyridine or imidazole, see Scheme 2.

The synthesis of the heterometallic complexes *fac*-[Re(CO)$_3$(**L1**)(ImAu(PPh$_3$))](CF$_3$SO$_3$) (**9**) and *fac*-[Re(CO)$_3$(**L2**)(ImAu(PPh$_3$))](CF$_3$SO$_3$) (**10**) was performed successfully by assisting the deprotonation of the imidazole ligand in complexes **5** and **7** with Cs$_2$CO$_3$ in the presence of [Au(CF$_3$SO$_3$)(PPh$_3$)], see Scheme 3.[9] In addition, complexes **6** and **8** were treated with Ag(CF$_3$SO$_3$) in acetone affording the heterometallic complexes *fac*-[Re(CO)$_3$(**L1**)(Py)Ag](CF$_3$SO$_3$)$_2$ (**11**) and *fac*-[Re(CO)$_3$(**L2**)(Py)Ag](CF$_3$SO$_3$)$_2$ (**12**), see Scheme 4. Spectroscopic characterization was performed using IR, ^{1}H, ^{13}C-NMR, and UV-vis spectroscopy. Further analytical data for each complex was provided through mass spectrometry and, in specific cases, by elemental analysis thus, corroborating the accomplishment of the synthesis of the mono- and heterometallic species. Additionally, crystals of **2**, **5**, **6**, **7**, **8**, **11** and **12** suitable for X-ray analysis (SHELX programs) were obtained by slow diffusion of ether or hexane into a solution of the complex in dichloromethane or acetone.

^{1}H-NMR spectroscopy of complexes **1–12** was performed in either acetone-d$_6$ or dichloromethane-d$_2$. In all cases, the spectra are well defined and exhibit the characteristic downfield shift of the aromatic protons upon coordination to the rhenium metal centre when compared to the corresponding proton resonances of the free ligand. This phenomenon is generally rationalised in terms of the σ donation of the chelated ligand.[10,6a] It is important to point out the appearance of only four set of signals in the aromatic region belonging to the diimine ligand **L1** or **L2** for complexes **1–12**, which indicates its symmetry within the complex.[11] Moreover, a more complicated pattern is seen for the aliphatic protons as a consequence of their different environment upon coordination to the rhenium metal centre. Thus, these pairs of diastereotopic protons are either pointing in, towards the coordination sphere of the metal centre, or outwards, affording an AB subspectrum for methylenic protons CH_2(11 and 19) and ABXY systems for CH_2(13, 14, 16 and 17). The same features have been previously reported for similar complexes of Rh(III), Ru(II), Pt(II) and Pd(II).[6] ^{13}C-NMR spectra showed six and three peaks in the aromatic and aliphatic region respectively, belonging to either **L1** or **L2** in each complex. This indicates the existence of a plane of symmetry passing through the Re(I) atoms, S(15)/O(15) atoms and the ligands coordinated to the metal in the axial position and therefore, implying that the CO ligands adopt a facial disposition rather than meridional. In comparison with the uncoordinated ligands **L1** and **L2**, a drastic downfield shift, particularly for C(2) and C(9) from *ca.* 158 ppm to *ca.* 168 ppm, was observed after complexation. In contrast, the chemical shift of aliphatic carbons remained practically the same in complexes **1–10** indicating that none of the S or O atoms are implicated in the complexation of the Re(I) atom. Moreover, ^{31}P-NMR spectroscopy was performed for species **9** and **10** showing a single peak at 32 ppm, which is in the typical range of values for an N–Au–P environment.[12] In addition to that, protons of the imidazole fragment are shielded upon the complexation of the gold fragment and in consequence they are shifted upfield. In the case of the heterometallic complexes **11** and **12**, the ^{1}H-NMR spectroscopy showed that the aliphatic protons are lowfield shifted in comparison with their monometallic precursors. Specifically, in complex **11** CH_2(14) and CH_2(16) protons moved from 1.63 ppm and 2.24 ppm to 1.80 and 2.40 ppm respectively, suggesting that S(15) is coordinated to the silver(I) atom. The lack of shifts for both, CH_2(11) and CH_2(19) protons in comparison with those of its precursor complex **6**, together with the symmetry observed in the ^{1}H-NMR spectrum (AB system for CH_2(11, 19) and ABXY for CH_2(13–17)) proposes the S(15) atom as the only coordinative site in solution, Scheme 4 and Fig. 1.

The same ^{1}H-NMR pattern was observed for complex **12**, thus, indicating once again that symmetric species are present in solution. In this case, CH_2(11) and CH_2(19) protons are shifted from 4.99 ppm and 4.73 ppm to 5.19 ppm and 4.85 ppm, pointing towards S(12) and S(18) as the coordinative sites of the silver atom. A fluxional process, where the coordination of the silver atom is swapping from the sulfur atoms S(12) and S(18), is feasible in solution, granting in this way the symmetry observed by NMR spectroscopy.

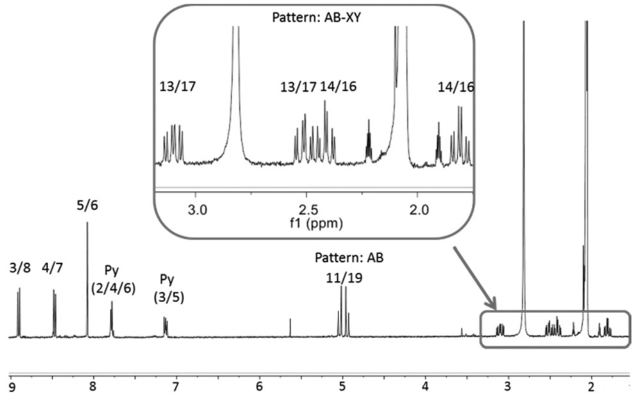


Fig. 1 ^{1}H-NMR spectrum of complex **11**.

Table 1 IR stretching frequencies and relevant ^{1}H-NMR and ^{13}C-NMR chemical shifts for complexes **1–12** and **L1** and **L2**

Compound	ν(C≡O)	δ(C2/9)	δ(H)(C3/8)	δ(H)(C11/19)
L1	—	159.5^a	8.21^a	4.11 (s)
L2	—	158.9^b	8.26^b	4.07 (s)
1	2012, 1884	165.7^a	8.49^a	4.92 (d), 4.39(d)
2	2017, 1910, 1882	166.0^a	8.48^a	4.77 (d), 4.41 (d)
3	2031, 1932$_{(sh)}$, 1904	—	9.04	
4	2033, 1932$_{(sh)}$, 1903	165.1^c	8.99^c	5.33 (d), 5.05 (d)
5	2024, 1909$_{(sh)}$, 1887	169.4^c	8.86^c	4.91 (s)
6	2029, 1932$_{(sh)}$, 1914	169.8^c	8.88^c	4.97 (d) 4.90 (d)
7	2033, 1937$_{(sh)}$, 1920	169.7^c	8.84^c	4.92 (d), 4.74 (d)
8	2028, 1936$_{(sh)}$, 1904	170.2^c	8.86^c	4.99 (d), 4.73 (d)
9	2023, 1932$_{(sh)}$, 1882	—	8.84^c	4.91 (q)
10	2024, 1931$_{(sh)}$, 1895	169.2^c	8.82^c	4.90 (d) 4.76 (d)
11	2031, 1932$_{(sh)}$, 1918	169.6^c	8.89^c	5.02 (d) 4.93 (d)
12	2034, 1937$_{(sh)}$, 1923	170.2^c	8.90^c	5.19 (d) 4.85 (d)

^{a} Dichloromethane-d$_2$. ^{b} $CDCl_3$. ^{c} (Acetone-d$_6$). $_{(sh)}$ shoulder.

Additional data on relevant ^{1}H-NMR, ^{13}C-NMR chemical shifts and stretching frequencies of CO are presented in Table 1. The IR spectra of complexes **1–12** showed the characteristic strong ν(CO) absorptions in the range between 1882 and 2037 cm^{-1}. Those values suggest an approximate C_{3v} symmetry around the rhenium centre, *i.e.* facial configuration, in line with ^{1}H and ^{13}C-NMR spectroscopic data.[6,13] Moreover the shift of the symmetric stretching mode from 2012 cm^{-1} and 2017 cm^{-1} in complexes **1** and **2** to *ca.* 2030 cm^{-1} in complexes **3–12** indicates the transition from the neutral rhenium species **1** and **2** to cationic species.[13a]

X-ray crystallography

Single crystals suitable for X-ray diffraction analysis of complexes **2**, **5**, **6**, **7** and *fac*-$[Re(CO)_3(Py)(\mathbf{L2})](PF_6)\cdot CH_2Cl_2$ (**8′**) were obtained by slow diffusion of diethyl ether or hexane into a solution of the complex in either dichloromethane or acetone, see Fig. 2. Compounds **2**, **5** and **7** crystallised in a monoclinic *P*2(1)/*c* space group, whereas complex **6** in a monoclinic *P*2(1)/*n* space group and complex **8′** in a triclinic $P\bar{1}$ space group. All of them showed a single molecule per asymmetric unit and the cationic species crystallised with their correspondent counterion. Moreover, compounds **7** and **8′** also presented a crystallisation solvent molecule, acetone and dichloromethane respectively in the asymmetric unit. The crystal structure of complex **8′**, analogous to **8**, but with PF_6^- as a counterion, has been obtained by a metathesis reaction of the initially prepared triflate salt **8** with KPF_6. Only in the case of complex **5** a short contact between one of the oxygens of the counter ion and one of the aromatic protons of the macrocyclic ligand has been observed, O(4)⋯H(9)–C(9): 2.550 Å, see Fig. S1.† As expected, the coordination sphere of each rhenium(I) metal is a distorted octahedron, where the three carbonyls are arranged in a facial disposition. For all the complexes the equatorial plane is defined by the chelated phenanthroline unit and two *trans* carbonyls. The third carbonyl is placed in the axial position, *trans* to the corresponding ligand: (a) a chloride atom (compound **2**), (b) an imidazole unit (compounds **5** and **7**) or (c) a pyridine unit (compounds **6** and **8′**). Deviation from the ideal octahedral disposition is mostly originating from the geometric restraints imposed by **L1** and **L2**. In each complex, the chelated angle N–Re–N is around 74° instead of the ideal 90°. Bond distances in the rhenium core are within the typical values, *i.e.* Re–CO distances are between 1.899(4) Å and 1.943(12) Å, Re–Cl is 2.4963(10) Å and Re–N(ImH/py) is between 2.1803(19) Å and 2.215(4) Å.[14] Contrary to the complexes already reported with **L1** and **L2**, where the metal centre was directly coordinated to the chelate ligand and the heteroatoms from the aliphatic chain within the macrocyclic cavity, the rhenium metal centre left the heteroatoms of the aliphatic chain free.[15] Therefore, the aliphatic chain adopted a folded conformation tilted towards the coordinated phenanthroline unit and away from the metal centre, leaving the correspondent axial ligand (either chloride, imidazole or pyridine) in the furthermost position in each case. Such a disposition promoted a severe distortion for the phenanthroline unit in the rhenium coordination sphere. In all cases, the phenanthroline plane is largely tilted from the rhenium coordination plane defined by the two phenanthroline nitrogen atoms and the correspondent *trans* carbon atoms

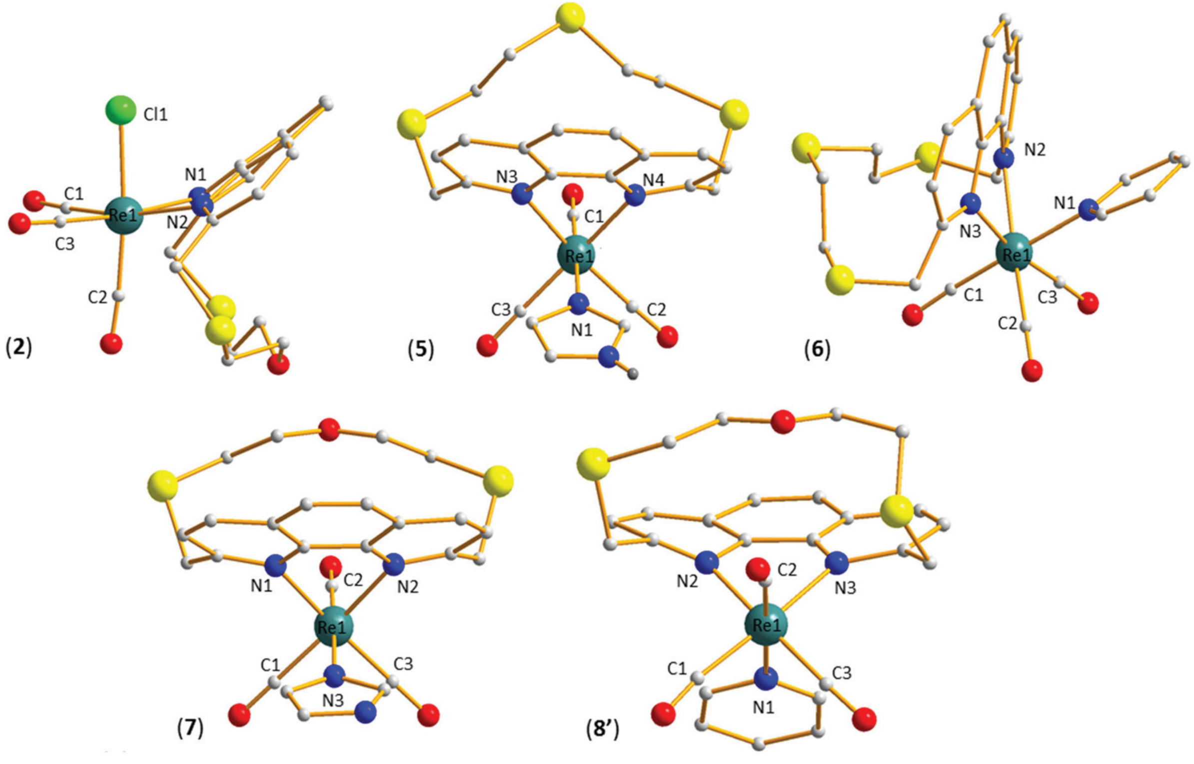


Fig. 2 Molecular structure of complex **2** and complex cations in **5**, **6**, **7** and **8′** respectively. The most relevant bond lengths (Å) and angles (°): complex **2**: Re(1)–C(1) = 1.903(3), Re(1)–C(2) = 1.903(3), Re(1)–C(3) = 1.912(3), Re(1)–N(1) = 2.206(3), Re(1)–N(2) = 2.237(3), Re(1)–Cl(1) = 2.4963(10); N(1)–Re(1)–N(2) = 74.01(10), Cl(1)–Re(1)–C(2) = 174.85(9); complex **5**: Re(1)–C(1) = 1.915(4), Re(1)–C(2) = 1.905(3), Re(1)–C(3) = 1.925(4), Re(1)–N(1) = 2.187(3), Re(1)–N(3) = 2.214(3), Re(1)–N(4) = 2.195(3); N(4)–Re(1)–N(3) = 74.35(10), C(1)–Re(1)–N(1) = 177.04(12); Complex **6**: Re(1)–C(1) = 1.935(13), Re(1)–C(2) = 1.943(12), Re(1)–C(3) = 1.924(13), Re(1)–N(1) = 2.209(10), Re(1)–N(2) = 2.219(9), Re(1)–N(3) = 2.206(9); N(3)–Re(1)–N(2) = 74.9(3), C(1)–Re(1)–N(1) = 177.6(4); complex **7**: Re(1)–C(1) = 1.924(4), Re(1)–C(2) = 1.920(2), Re(1)–C(3) = 1.913(4), Re(1)–N(1) = 2.204(3), Re(1)–N(2) = 2.199(3), Re(1)–N(3) = 2.1803(19); N(2)–Re(1)–N(1) = 74.62(10), C(2)–Re(1)–N(3) = 177.61(12); Complex **8′**: Re(1)–C(1) = 1.919(5), Re(1)–C(2) = 1.920(5), Re(1)–C(3) = 1.899(4), Re(1)–N(1) = 2.215(4), Re(1)–N(2) = 2.220(4), Re(1)–N(3) = 2.209(3); N(3)–Re(1)–N(2) = 74.58(13), C(2)–Re(1)–N(1) = 174.74(14).

of the carbonyl groups. The dihedral angle between the equatorial plane previously defined with that containing the phenanthroline unit varies from 33.8° to 35.1°. Such deviation from the ideal coplanar disposition is much larger than those found in the literature for analogous 2,9-dimethyl-1,10-phenanthroline rhenium(I) derivatives (from 7.3° to 25.9°) and it might be ascribed to the higher steric requirement of the thioether or mixed thio/oxo ether crown in comparison with the methyl derivative.[16]

X-ray diffraction for complexes **11** and **12** was also recorded, Fig. 3. Crystals were small and diffracted weakly. Furthermore, in both complexes there were some disorder problems. Compound **11** crystallised as a dimer but only half of the molecule is in the asymmetric unit, where there are one and two halves trifluoromethanesulfonate disordered molecules. Complex **12** crystallised as an infinite polymeric chain, where one of the S–C bonds in the macrocycle is disordered over two positions. Both of them present similar bond length and angle values in the rhenium(I) environment to those seen in compounds **2**, **5**, **6**, **7** and **8′**. Re–CO bond distances range between 1.874(10) Å and 1.940(11) Å, Re–N(py) bond distances are 2.212(10) Å and 2.225(8) Å and chelate angles of N(phen)–Re–N(phen) are 74.2(4)° and 75.4(3)°, respectively. Moreover they also display deviation of the phenanthroline unit from the Re(I) equatorial plane defined by the two phenanthroline nitrogen atoms and the corresponding *trans* carbon atoms of the carbonyl groups, affording dihedral angles of 32.5° (complex **11**) and 33.9° (complex **12**). These values are slightly smaller than the dihedral values observed for their precursors, *i.e.* 32.9 for complex **6** and 34.9° in the case of complex **8′**. The main difference between these two molecular structures relies on the coordination site preferred by the silver(I) atom of the macrocycle ligands, which ultimately promotes the formation of either a dimer or a polymeric chain respectively. In complex **11**, where the coordinated macrocyclic ligand **L1** contains three S-donor atoms in the aliphatic portion, the silver(I) atom is coordinated to the central S-donor of one macrocyclic unit and to the S-donor at the end of the aliphatic chain of a second macrocyclic unit from the symmetry related Re(I) complex units of **6** forming dimers (Fig. 2 and 3). Instead, in complex **12**, where the coordinated macrocyclic ligand **L2** contains two S-donor atoms and one O-donor in the aliphatic portion, the silver(I) atom binds to the S-atoms of two adjacent molecule units from the symmetry related Re(I) complex units of *fac*-$[\mathrm{Re(CO)_3(Py)(\mathbf{L2})}]^+$, originating polymeric chains (Fig. 3). In both cases, bond distances for Ag(I)–S range from 2.473(4) Å to 2.656(5) Å, which is in agreement with bond distance values for similar complexes found in the literature.[14b] In addition, complex **11** showed a molecule of triflate coordinated to the silver(I) atom, arranging the donor atoms in a trigonal disposition around the metal centre. In the case of complex **12**, the silver atom acting as a linker is also coordinated to a triflate molecule and an acetone molecule from the crystallisation solvent mixture, providing a distorted tetrahedral environment around the metal centre, S1–Ag1–S2#2 129.30(14)° instead of the ideal 109.4°.

Photophysical studies

UV-visible absorption spectra, recorded in a degassed dichloromethane or acetone solution at 298 K, showed the typical pattern for diimine Re(I) derivatives (Fig. 4 and S2†). Ligand centred transitions, $\pi \rightarrow \pi^*$ transitions among **L1**, **L2**, imidazole and pyridine units, were observed at higher energies, and metal-to-ligand-charge-transfer transitions (^{1}MLCT), formally attributed to $\mathrm{Re(d\pi)} \rightarrow \mathrm{L(\pi^*)}$ transitions appeared at lower energies around 400 nm, with a tail extending in some cases up to

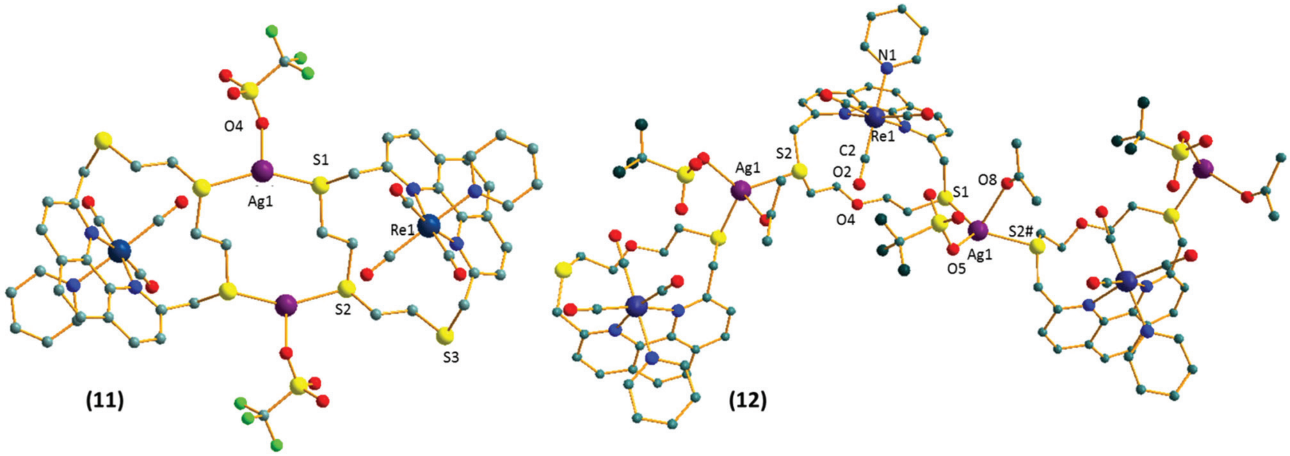


Fig. 3 Molecular structure of dimeric and polymeric assemblies in compounds **11** and **12**. The most relevant bond lengths (Å) and angles (°): complex **11**: Re(1)–C(1) = 1.921(15), Re(1)–C(2) = 1.906(13), Re(1)–C(3) = 1.918(17), Re(1)–N(1) = 2.214(12), Re(1)–N(2) = 2.215(10), Re(1)–N(3) = 2.214(13), Ag(1)–O(4) = 2.365(18), Ag(1)–S(2) = 2.470(4), Ag(1)–S(1) = 2.522(4); N(2)–Re(1)–N(3) = 74.2(4), C(1)–Re(1)–N(2) = 169.9(5), O(4)–Ag(1)–S(2) = 106.4(5), O(4)–Ag(1)–S(1) = 86.3(5), S(1)–Ag(1)–S(2) = 148.81(14); complex **12**: Re(1)–C(1) = 1.940(11), Re(1)–C(2) = 1.874(10), Re(1)–C(3) = 1.893(12), Re(1)–N(1) = 2.225(8), Re(1)–N(2) = 2.212(10), Re(1)–N(3) = 2.215(9), Ag(1)–S(2) = 2.656(5), Ag(1)–S(1) = 2.502(3); N(2)–Re(1)–N(3) = 75.4(3), C(2)–Re(1)–N(1) = 176.7(4), S(1)–Ag(1)–S(2)#2 = 129.30(14) (#2 = *x*, −*y*, *z* + 1/2).

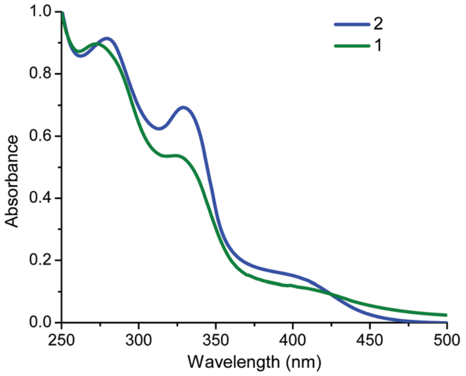


Fig. 4 UV-absorption spectra of complexes **1** and **2** recorded in degassed dichloromethane at 298 K.

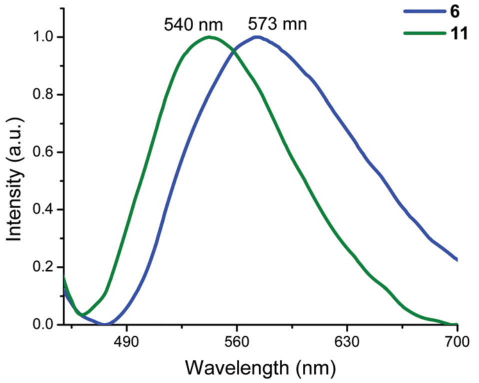


Fig. 5 Emission spectra of complexes **6** and **11** recorded in degassed dichloromethane at 298 K.

475 nm. The most significant absorption data together with the emission and excitation maxima values for all complexes are collected in Table 2.

Luminescence spectra of complexes **1**, **2**, **5–12** were recorded in degassed dichloromethane solution at 298 K (Fig. 5 and S3†). All of them showed a broad emission between 573–633 nm originated from the ^{3}MLCT Re(dπ) → phen(π*) excited state, which has been previously reported in many rhenium(I) diimine tricarbonyl complexes.[17]

The neutral complexes **1** and **2** showed their emission maxima at 608 nm and 633 nm, respectively. Comparison with the emission maxima seen for the analogous phenanthroline derivative, [ReCl(CO)$_3$(2,9-dimethyl-1,10-phenanthroline)], that appears at 578 nm in the dimethyl sulfoxide solution or 589 nm in dimethylformamide, revealed the high influence of the aliphatic chain of the coordinated macrocyclic ligands on the photophysical properties[18] The constriction observed for the phenanthroline unit, which is tilted towards itself and away from the metal centre, might be implicated in the observed red shift for the complexes described here. It would be reasonable to think that such a distortion could be favouring the destabilisation of the HOMO orbitals, mainly Re(dπ) orbitals, in comparison with the analogue phenanthroline species. In addition, it could also be suggested that the presence of thioether or mixed thio/oxoether crown systems grafted on the phenanthroline might exert, to some extent, an inductive effect as no conjugation in the system is present. Therefore, reduction of the energy gap between the HOMO and LUMO orbitals would take place. Furthermore, the mixed S/O-donor ligand **L2** seems to greatly affect the emissive properties as compared to **L1**, possibly because of the higher electronegativity of the oxygen atom. As expected, the emission maxima of cationic species in **5–8** experienced a shift of *ca.* 30 nm to lower energy in comparison with their neutral precursors, species **1** and **2**. Additionally, a slightly red shifted emission maximum was observed for the heterometallic complexes **9** and **10** when compared with their respective precursors, complexes **5** and **7**. Such behaviour contrasted with that of the heterometallic complexes **11** and **12** whose emission maxima shifted drastically from *ca.* 573 nm to 540 nm and from 595 nm to 560 nm, respectively, when compared to that of their monometallic analogues, complexes **6** and **8**. It might be reasonable to suggest that the coordination of the second metallic fragment to the heteroatoms of the crown system might influence the emissive properties to a higher degree than when the coordination is performed in the axial imidazole ligand (complexes **9** and **10**), which is in line with the idea that the molecular orbitals involved in the emissive process are mainly those centred in the phenanthroline unit.[3,17] The blue shifted emissions observed for complexes **11** and **12** could be partially explained in terms of either the stabilisation of HOMO orbitals and/or destabilisation of LUMO orbitals. The fact that the silver atom is coordinated with different positions of the crown system, *i.e.* to S(15) for complex **11** and to S(12) and S(18) for complex **12**, might indicate that the blue shift would be strongly related to changes in the metal based orbitals rather than in the ligand. Therefore, a possible explanation could be that, somehow, the coordination of the second metallic fragment led to less constricted species

Table 2 Absorption bands, excitation and emission maxima values (298 K)

	UV-vis (×10^4 3/dm^3 mol^{-1} cm^{-1})	λ_{exc} (nm)	λ_{em} (nm)
1^a	272 (13 900), 332 (8000), 416 (1600)	448	608
2^a	279(30 700), 329(23 200), 402(5000)	440	633
5^a	250(24 000), 331(14 400), 406 (2600)	410	586
6^a	257 (21 600), 330(11 700), 400(2600)	400	573
7^a	230(32 500), 235(32 000), 253(23 400), 275(19 000), 329(16 300), 403(3500)	430	608
8^a	236(28 000), 256(26 700), 283(19 000), 329(16 100), 394 (3700)	420	595
9^a	336(3900), 408 (1200)	444	600
10^a	290(8100), 331(8100), 414(1600)	456	612
11$^{a/b}$	326(3900), 401(2800)^b	400^a	540^a
12^a	259(25 400), 287(19 900), 334(9700), 403(2000)	339	560

^{a} Degassed dichloromethane. ^{b} Degassed acetone.

promoting the stabilisation of the HOMO orbitals, and consequently a blue shifted emission.

Conclusions

In summary, we have synthesised and characterized a new family of luminescent *fac*-$[Re(CO)_3(\mathbf{L})(NN)]^+$ complexes, where **L** is a pyridine (py) or an imidazole (ImH) ligand, and NN are macrocyclic ligands featuring a 1,10-phenanthroline subunit functionalised at the 2,9-positions with either a thioether (**L1**) or a mixed thio-oxoether linker (**L2**). Moreover, we have prepared the corresponding heterometallic species Re(I)/Au(I) and Re(I)/Ag(I), specifically *fac*-$[Re(CO)_3(\mathbf{L1})(ImAu(PPh_3))](CF_3SO_3)$ (**9**), *fac*-$[Re(CO)_3(\mathbf{L2})(ImAu(PPh_3))](CF_3SO_3)$ (**10**), *fac*-$[Re(CO)_3(\mathbf{L1})(Py)Ag](CF_3SO_3)_2$ (**11**) and *fac*-$[Re(CO)_3(\mathbf{L2})(Py)Ag](CF_3SO_3)_2$ (**12**). Structural characterization by X-ray diffraction studies showed the expected octahedral disposition around the Re(I) metal centre with the aliphatic chains of the macrocyclic ligands adopting a folded conformation tilted towards the phenanthroline unit and away from the metal centre, leaving the corresponding axial ligand in the furthermost position. Complexes **11** and **12** displayed coordination of the silver(I) centre to the sulfur atoms of the coordinated macrocyclic ligands, giving two different structural motifs, a dinuclear compound (**11**) with two *fac*-$[Re(CO)_3(Py)(\mathbf{L1})]^+$ metalloligands bridged by two Ag(I) centres and a polynuclear chain (**12**) with the silver(I) atom bonded to one sulfur of the adjacent *fac*-$[Re(CO)_3(Py)(\mathbf{L2})]^+$ metalloligands. Photophysical analysis showed the typical behavior for Re(I) complexes, *i.e.* emission from a ^{3}MLCT transition at around 600 nm, being those of the heterometallic complexes **11** and **12** blue shifted in comparison with their monometallic analogues. These results, contrary to previous reports published on similar crown phenanthroline Re(I) derivatives,[5] emphasize the importance of the phenanthroline-based ligand design in order to obtain the specific emission properties of the resulting systems.

Experimental section

General measurements and analysis instrumentation

Mass spectra were recorded on a BRUKER ESQUIRE 3000 PLUS, with the electrospray (ESI) technique and on a BRUKER (MALDI-TOF). ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR, including 2D experiments, were recorded at room temperature on a BRUKER AVANCE 400 spectrometer (^{1}H, 400 MHz, ^{13}C, 100.6 MHz, ^{31}P, 162 MHz) with chemical shifts (δ, ppm) reported relative to the solvent peaks of the deuterated solvent. Infrared spectra were recorded in the range 4000–250 cm^{-1} on a Perkin-Elmer Spectrum 100 FTIR spectrometer. Room temperature steady-state emission and excitation spectra were recorded with a Jobin–Yvon–Horiba fluorolog FL3-11 spectrometer fitted with a JY TBX picosecond detection module. UV/vis spectra were recorded with a 1 cm quartz cells on an Evolution 600 spectrophotometer.

Crystal structure determinations

Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of an Xcalibur Oxford Diffraction diffractometer equipped with a low-temperature attachment. Data were collected using monochromated MoKα radiation (λ = 0.71073 Å). Scan type ω. Absorption corrections based on multiple scans were applied using spherical harmonics implemented in the SCALE3 ABSPACK scaling algorithm. The structures were solved by direct methods and refined on F^2 using the program SHELXL-97.[19] All non-hydrogen atoms were refined anisotropically, with the exception of complex **7**. Further details on the crystal refinements are shown in Table 3. Special constraints to all the bond distances and angles to the disordered triflate molecules in complexes **11** and **12** have been applied.

Materials and procedures

The starting material $[AuCl(PPh_3)]$ was prepared according to literature procedures.[20] $[Au(CF_3SO_3)(PPh_3)]$ was prepared *in situ* by reaction of $[AuCl(PPh_3)]$ with $Ag(CF_3SO_3)$ in dichloromethane.[20] All other starting materials and solvents were purchased from commercial suppliers and used as received unless otherwise stated.

Synthesis of *fac*-[Re(Cl)(CO)$_3$(L1)] (1). $[ReCl(CO)_5]$ (111 mg, 0.30 mmol) and **L1** (112 mg, 0.31 mmol) were heated at reflux in dry toluene (10 ml) under a nitrogen atmosphere for 1 h. The solvent was removed to dryness and the yellow solid was washed with hexane and ether. Finally, the product was purified by chromatography (silica, dichloromethane/acetone (9.5/0.5)) (147 mg, 72% yield). ^{1}H NMR (dichloromethane-d$_6$, 400 MHz): δH 8.49 (d, *J* = 8.4 Hz, 2H, C*H*(3, 8)), 7.97 (d, *J* = 8.4 Hz, 2H, C*H*(4, 7)), 7,95 (s, 2H, C*H*(5, 6)), 4.92 (d, *J* = 14.0 Hz, 2H, C*H*$_2$(11a, 19a or 11b, 19b)), 4.39 (d, *J* = 14.0 Hz, 2H, C*H*$_2$(11a, 19a or 11b, 19b)), 3.08–2.91 (m, 2H, C*H*$_2$(13a, 17a or 13b, 17b)), 2.28–2.15 (m, 4H, C*H*$_2$ (13a, 17a or 13b, 17b and 14a, 16a or 14b, 16b)), 1.84–1.57 (m, 2H, C*H*$_2$(14a, 16a or 14b, 16b)). ^{13}C NMR (dichloromethane-d$_6$, 101 MHz): δC 195.7 (*C*O), 165.7 (*C*(2, 9)), 148.4 (*C*(4b, 6b)), 139.6 (*C*(3, 8)), 129.4 (*C*(4a, 6a)), 126.6 (*C*(5, 6)), 125.7 (*C*(4, 7)), 34.8 (*C*(11, 19)), 33.3 (*C*(14, 16)), 30.2 (*C*(13, 17)). MS (MALDI$^+$): *m*/*z* 629.1 ([M − Cl]$^+$ 100%) calculated: 629.0; IR (solid, cm^{-1}, (CO)): 2012, 1884; Anal. calc. for $ReC_{21}H_{18}ClN_2O_3S_3$: C, 37.97; H, 2.73; N, 4.22. Found: C, 38.04; H, 2.75; N, 4.15.

Synthesis of *fac*-[Re(Cl)(CO)$_3$(L2)] (2). This compound was prepared similarly to *fac*-$[ReCl(CO)_3(\mathbf{L1})]$ using **L2** instead of **L1** and purification by chromatography was not needed. The product obtained was a yellow solid (240 mg, 98%). ^{1}H NMR (400 MHz, (dichloromethane-d$_6$)) δ 8.48 (d, *J* = 8.4 Hz, 2H, C*H*(3, 8)), 7.94 (s, 2H, C*H*(5, 6)), 7.87 (d, *J* = 8.4 Hz, 2H, C*H*(4, 7)), 4.77 (d, *J* = 14.0 Hz, 2H, C*H*$_2$(11a, 19a or 11b, 19b)), 4.41 (d, *J* = 14.1 Hz, 2H, C*H*$_2$(11a, 19a or 11b, 19b)), 3.16–3.01 (m, 4H, C*H*$_2$(14, 16)), 2.41–2.27 (m, 4H, C*H*$_2$(13, 17)). ^{13}C NMR (101 MHz, CD_2Cl_2), δC 197.5 (*C*O), 195.4 (*C*O), 166.0 (C(2, 9)), 148.7 (C(4b, 6b)), 139.6 (C(3, 8)), 129.3 (C(4a, 6a)), 126.7 (C(5, 6)), 125.5 (C(4, 7)), 71.6 (C(14, 16)), 43.8 (C(11, 19)), 31.9 (C(13,

Table 3 X-ray crystallographic data of compounds **2**, **5**, **6**, **7**, **8′**, **11** and **12**

Compound	**2**	**5**	**6**	**7**	**8′**	**11**	**12**
Formula	$C_{21}H_{18}ClN_2O_4ReS_2$	$C_{25}H_{22}F_3N_4O_6ReS_4$	$C_{27}H_{23}F_3N_3O_6ReS_4\cdot 1.5Me_2CO$	$C_{25}H_{22}F_3N_4O_7ReS_3\cdot Me_2CO$	$C_{26}H_{23}F_6N_3O_4PReS_2\cdot CH_2Cl_2$	$C_{28}H_{23}AgF_6N_3O_9ReS_5$	$C_{28}H_{23}AgF_6N_3O_{10}ReS_4\cdot 2Me_2CO$
M_r	648.14	845.91	944.04	887.92	921.69	1113.86	1272.04
Crystal size (mm)	0.10 × 0.10 × 0.08	0.20 × 0.18 × 0.14	0.21 × 0.06 × 0.05	0.50 × 0.40 × 0.24	0.23 × 0.07 × 0.06	0.12 × 0.06 × 0.04	0.24 × 0.04 × 0.03
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$	$P2(1)/n$	$P2(1)$	$P\bar{1}$	$P\bar{1}$	Pc
Cell constants							
a (Å)	10.086(2)	18.6722(13)	8.3797(17)	7.8582(16)	8.1847(16)	8.0661(16)	8.1899(16)
b (Å)	13.533(3)	9.9873(7)	17.271(4)	21.123(4)	10.773(2)	14.506(3)	13.885(3)
c (Å)	16.015(3)	17.2914(12)	24.802(5)	9.834(2)	18.113(4)	16.119(3)	20.188(4)
α (°)	90	90	90	90	81.82(3)	95.31(3)	90
β (°)	103.95(3)	114.753(1)	90.20(3)	102.49(3)	85.44(3)	93.94(3)	97.00(3)
γ (°)	90	90	90	90	89.33(3)	101.67(3)	90
V (Å^3)	2121.6(7)	2928.3(4)	3568.5(13)	1593.6(6)	1575.8(5)	1831.8(6)	2278.6(8)
Z	4	4	4	2	2	2	2
D_x (Mg m^{-3})	2.029	1.919	1.757	1.850	1.942	2.019	1.854
μ (mm^{-1})	6.083	4.502	3.707	4.082	4.284	4.205	3.356
$F(000)$	1256	1656	1872	876	900	1080	1256
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
$2\theta_{max}$	51	51	51	51	51	51	51
No. of refl.							
Measured	16 262	29 550	28 191	16 561	24 933	27 491	22 812
Independent	3959	5450	6584	5874	5822	6796	8348
Transmissions	0.6418–0.5814	0.5714–0.4663	0.8364–0.5099	0.4408–0.2347	0.7831–0.4391	0.8498–0.6323	0.9060–0.4998
R_{int}	0.0275	0.0409	0.0925	0.0179	0.0597	0.0915	0.0824
Parameters	280	411	448	431	415	550	607
Restraints	0	0	89	1	0	400	170
Goodness of fit on F^2	1.044	1.043	1.244	1.078	1.079	1.039	1.048
wR(F^2, all Refl.)	0.0412	0.0690	0.1953	0.0346	0.0693	0.2084	0.1018
$R(I > 2\sigma(I))$	0.0193	0.0257	0.0853	0.0138	0.0323	0.0793	0.0547
max. $\Delta\rho$ (e Å^{-3})	0.877	2.510	4.562	0.921	1.333	4.497	1.699

17)), MS (ESI) *m*/*z* 612.8 [M − Cl] calculated 612.4; IR (solid, cm^{-1}, (CO)): 2017, 1910, 1882; Anal. calc. for $ReC_{21}H_{18}ClN_2O_4S_2$: C, 38.91; H, 2.80; N, 4.32. Found: C, 38.78; H, 2.75; N, 4.17.

Synthesis of *fac*-[Re((CH_3)$_2$CO)(CO)$_3$(L1)](CF_3SO_3) (3). *fac*-*fac*-[Re(Cl)(CO)$_3$(**L1**)] (17 mg, 0.02 mmol) and silver triflate (6.5 mg, 0.02 mmol) were stirred in 5 ml of acetone for 12 h, then the mixture was filtered through Celite to eliminate the silver chloride formed during the reaction. Finally, the solvent was removed under vacuum affording a yellow solid (20 mg, 83% yield). ^{1}H NMR (400 MHz, acetone-d$_6$) *δ* 9.04 (d, *J* = 8.4 Hz, 2H, C*H*(3, 8)), 8.47–8.37 (m, 4H, C*H*(4, 7)), 4.96 (dd, *J* = 34.6, 14.6 Hz, 4H, C*H*$_2$(11, 19)), 3.35–3.28 (m, 2H), 3.18–3.10 (m, 2H), 2.97–2.87 (m, 4H), 2.09 (s, 6H, C*H*$_3$). MS (MALDI$^+$): *m*/*z* 629.1 ([M − ((CH_3)$_2$CO)]$^+$ 100%) calculated: 629.0; IR (solid, cm^{-1}, (CO)): 2031, 1932, 1904.

Synthesis of *fac*-[Re((CH_3)$_2$CO)(CO)$_3$(L2)](CF_3SO_3) (4). This compound was prepared similarly to *fac*-[Re((CH_3)$_2$CO)(CO)$_3$(**L1**)](CF_3SO_3) using *fac*-[ReCl(CO)$_3$(**L2**)] instead of *fac*-[ReCl(CO)$_3$(**L1**)]. The product obtained was a yellow solid (80%). ^{1}H NMR (400 MHz, acetone-d$_6$) *δ* 8.99 (d, *J* = 8.4 Hz, 2H, C*H*(3, 8)), 8.42 (d, *J* = 8.4 Hz, 2H C*H*(4, 7)), 8.32 (s, 2H, C*H*(5, 6)), 5.33 (d, *J* = 16.0 Hz, 2H, C*H*$_2$(11a, 19a or 11b, 19b)), 5.09 (d, *J* = 16.0 Hz, 2H, C*H*$_2$(11a, 19a or 11b, 19b)), 3.95–3.87 (m, 2H, C*H*$_2$(14a, 16a or 14b, 16b)), 3.49 (ddd, *J* = 10.8, 5.5, 2.3 Hz, 2H, C*H*$_2$(14a, 16a or 14b, 16b)), 3.10 (dd, *J* = 13.9, 4.4 Hz, 2H, C*H*$_2$(13a, 17a or 13b, 17b)), 2.41–2.30 (m, 2H, C*H*$_2$(13a, 17a or 13b, 17b)), 2.09 (s, 6H, C*H*$_3$).^{13}C NMR (101 MHz, acetone-d$_6$) *δ* 165.1 (*C*(2, 9)), 148.8 (*C*(4b, 6b)), 141.1 (*C*(3, 8)), 130.3 (*C*(4a, 6a)), 127.9 (*C*(5, 6)), 125.9 (*C*(4, 7)), 72.5 (C(14, 16), 49.3 (C(11, 19)), 34.3 (C(13, 17)), 30.6 (2CH_3); IR (solid, cm^{-1}, (CO)): 2033, 1932, 1903.

Synthesis of *fac*-[Re(CO)$_3$(ImH)(L1)](CF_3SO_3) (5). A solution of *fac*-[Re((CH_3)$_2$CO)(CO)$_3$(**L1**)](CF_3SO_3) (31 mg, 0.04 mmol) and imidazole (27 mg, 0.4 mmol) in dry THF (3 ml) were stirred for 24 h at room temperature under an argon atmosphere. Then, the solvent was removed under vacuum and the residue was triturated with ether and hexane affording complex **5** as yellow solid (21 mg, 72%). ^{1}H NMR (400 MHz, acetone-d$_6$) *δ* 8.86 (d, *J* = 8.5 Hz, 2H, C*H*(3, 8), **L1**), 8.36 (d, *J* = 8.5 Hz, 2H, C*H*(4, 7), **L1**), 8.10 (s, 2H, C*H*(5, 6), **L1**), 7.33 (t, *J* = 1.2 Hz, 1H, C*H*(2) ImH), 6.85–6.80 (m, 1H, C*H*(4) ImH), 6.12 (t, *J* = 1.4 Hz, 1H, C*H*(5) ImH), 4.91 (s, 4H, CH(11, 19)), 3.03 (ddd, *J* = 14.3, 13.2, 4.9 Hz, 2H, C*H*$_2$(13a, 17a or 13b, 17b)), 2.43–2.30 (m, 2H, C*H*$_2$(13a, 17a or 13b, 17b)), 2.22 (td, *J* = 13.3, 4.1 Hz, 2H, C*H*$_2$(14a, 16a or 14b, 16b)), 1.61 (td, *J* = 13.5, 4.9 Hz, 2H, C*H*$_2$(14a, 16a or 14b, 16b)). ^{13}C NMR (101 MHz, acetone-d$_6$): *δ*C 197.0 (*C*O), 195.4 (*C*O), 169.4 (C(2, 9), **L1**), 147.5 (C(4b, 6b), **L1**), 142.2 (C(3, 8), **L1**), 140.7 (C(2), ImH), 131.1 (C(4a, 6a), **L1**), 130.1(C(5), ImH), 128.9 (C(5, 6), **L1**), 128.8 (C(4, 7), **L1**), 120.3 (C(4), ImH), 44.9 (C(11, 19), **L1**), 36.1 (C(14, 16, **L1**), 34.6 (C(13, 17, **L1**); MS (MALDI$^+$): *m*/*z* 629.1 ([M − ImH]$^+$ 34.6%) calculated: 629.0, *m*/*z* 697.1 ([M]$^+$ 3.81%) calculated: 696.0; IR (solid, cm^{-1}, (CO)): 2024, 1909, 1887; Anal. calc. for $ReC_{25}H_{22}F_3N_4O_6S_4$: C, 35.50; H, 2.62; N, 6.62. Found: C, 35.86; H, 2.73; N, 6.45.

Synthesis of *fac*-[Re(CO)$_3$(L1)(Py)](CF_3SO_3) (6). A solution of *fac*-[Re((CH_3)$_2$CO)(CO)$_3$(**L1**)](CF_3SO_3) (31 mg, 0.03 mmol) and pyridine (23 μl, 0.3 mmol) in acetone (5 ml) were stirred for 4 days at room temperature under an argon atmosphere. Then, hexane was added affording the precipitation of a yellow solid which was further washed with ether and hexane (26 mg, 80%). ^{1}H NMR (400 MHz, acetone-d$_6$) *δ* 8.88 (d, *J* = 8.5 Hz, 2H, C*H*(3, 8), **L1**), 8.44 (d, *J* = 8.5 Hz, 2H, C*H*(4, 7), **L1**), 8.07 (s, 2H, C*H*(5, 6), **L1**), 7.82–7.73 (m, 3H, C*H*(2, 4, 6), Py), 7.16–7.09 (m, 2H, CH(3, 5), Py), 4.97 (d, *J* = 13.9 Hz, 2H, CH$_2$(11a, 19a or 11b, 19b)), 4.90 (d, *J* = 13.9 Hz, 2H, CH$_2$(11a, 19a or 11b, 19b)), 3.03 (ddd, *J* = 14.3, 13.2, 4.9 Hz, 2H, CH2(13a, 17a or 13b, 17b)), 2.47–2.34 (m, 2H, CH$_2$(13a, 17a or 13b, 17b)), 2.32–2.18 (m, 2H, C*H*$_2$(14a, 16a or 14b, 16b)), 1.63 (td, *J* = 13.5, 5.0 Hz, 2H, C*H*$_2$(14a, 16a or 14b, 16b)). ^{13}C NMR (101 MHz, acetone-d$_6$): *δ*C 169.8 (C(2, 9), **L1**), 153.6 (C(2, 6), Py), 147.1 (C(4b, 6b), **L1**), 142.5 (C(3, 8), **L1**), 142.2 (C(4), Py), 131.3 (C(4a, 6a), **L1**), 129.6 (C(5, 6), L1), 128.9 (C(4, 7), **L1**), 128.3 (C(3, 5), Py), 45.1 (C(11, 19), **L1**), 36.1 (C(14, 16, **L1**), 34.7 (C(13, 17), **L1**); MS (MALDI$^+$): *m*/*z* 629.1 ([M − Py]$^+$ 76.21%) calculated: 629.0, *m*/*z* 708.1 ([M]$^+$ 19.56%) calculated 707.3; IR (solid, cm^{-1}, (CO)): 2029, 1932, 1914; Anal. calc. for $ReC_{27}H_{23}F_3N_3O_6S_4$: C, 37.84; H, 2.71; N, 4.90. Found: C, 37.98; H, 2.73; N, 4.82.

Synthesis of *fac*-[Re(CO)$_3$(ImH)(L2)](CF_3SO_3) (7). This compound was prepared similarly to *fac*-[Re(CO)$_3$ImH(**L1**)](CF_3SO_3) using *fac*-[Re((CH_3)$_2$CO)(CO)$_3$(**L2**)](CF_3SO_3) instead of *fac*-[Re((CH_3)$_2$CO)(CO)$_3$(**L1**)](CF_3SO_3). The product obtained was a yellow solid (31 mg, 62%). ^{1}H NMR (400 MHz, acetone-d$_6$) *δ* 11.87 (s, NH), 8.84 (d, *J* = 8.5 Hz, 2H, C*H*(3, 8); **L2**), 8.28 (d, *J* = 8.5 Hz, 2H, C*H*(4, 7); **L2**), 8.08 (s, 2H, C*H*(5, 6), **L2**), 7.28 (s, 1H, C*H*(2), IMH), 6.80 (s, 1H, C*H*(4), ImH), 6.09 (s, 1H, C*H*(5), ImH), 4.92 (d, *J* = 14.0 Hz, 2H, C*H*$_2$(11a, 19a or 11b, 19b)), 4.74 (d, *J* = 14.0 Hz, 2H, C*H*$_2$(11a, 19a or 11b, 19b)), 3.49–2.47 (m, 4H, C*H*$_2$(14, 16)), 2.52–2.44 (m, 2H, C*H*$_2$(13a, 17a or 13b, 17b)), 2.31–2.25 (m, 2H, C*H*$_2$(13a, 17a or 13b, 17b)); ^{13}C NMR (101 MHz, acetone-d$_6$), *δ*C 196.9 (*C*O), 195.5 (*C*O), 169.7 (C(2, 9) **L2**), 147.8 (C(4b, 6b), **L2**), 142.1 (C(3, 8), **L2**), 139.9 (C(2), ImH), 131.0 (C(4a, 6a), **L2**), 130.1 (C(5), ImH), 128.7 (C(5, 6), **L2**), 128.5 (C(4, 7), **L2**), 127.1 (C(4), ImH), 72.7 (C(14, 16), **L2**), 45.3 (C(11, 19), **L2**), 33.3 (C(13, 17), **L2**); MS (MALDI$^+$): *m*/*z* 613.0 ([M − ImH]$^+$ 100%) calculated: 613.1, *m*/*z* 681.1 ([M]$^+$ 7.82%) calculated 681.1; IR (solid, cm^{-1}, (CO)): 2033, 1937, 1920; Anal. calc. for $ReC_{25}H_{22}F_3N_4O_7S_3$: C, 36.18; H, 2.67; N, 6.75. Found: C, 35.87; H, 2.78; N, 6.58.

Synthesis of *fac*-[Re(CO)$_3$(L2)(Py)](CF_3SO_3) (8). This compound was prepared similarly to *fac*-[Re(CO)$_3$ImH(**L2**)](CF_3SO_3) using pyridine instead of imidazole. The product obtained was a yellow solid (81 mg, 74%). ^{1}H NMR (400 MHz, acetone-d$_6$) *δ* 8.86 (d, *J* = 8.5 Hz, 2H, C*H*(3, 8), **L2**)), 8.36 (d, *J* = 8.5 Hz, 2H, C*H*(4, 7), **L2**), 8.05 (s, 2H, C*H*(5, 6), **L2**), 7.82–7.69 (m, 3H, C*H*(2, 4, 6), Py), 7.11 (ddd, *J* = 7.2, 4.6, 1.7 Hz, 2H, C*H*(3, 5), Py), 4.99 (d, *J* = 14.1 Hz, 2H, C*H*$_2$(11a, 19a or 11b, 19b)), 4.73 (d, *J* = 14.1 Hz, 2H, C*H*$_2$(11a, 19a or 11b, 19b)), 3.19–3.03 (m, 4H, C*H*$_2$(14, 16)), 2.56–2.49 (m, 2H, C*H*$_2$(13a, 17a or 13b, 17b)), 2.29–2.23 (m, 2H, C*H*$_2$(13a, 17a or 13b, 17b)); ^{13}C (101 MHz, acetone-d$_6$), *δ*C 196.3 (*C*O), 195.2 (*C*O), 170.2 (C(2, 9) **L2**), 153.7

(C(2, 6) Py), 147.3 (C(4b, 6b) **L2**), 142.4 (C(8, 3) **L2**), 142.0 (C(4) Py), 131.2 (C(4a, 6a) **L2**), 129.5 (C(5, 6) **L2**), 128.7 (C(4, 7) **L2**), 128.2(C(3, 5) Py), 72.6 (C(14, 16) **L2**), 45.3 (C(11, 19) **L2**), 33.4 (C(13, 17) **L2**). MS (MALDI+): *m*/*z* 613.1 ([M − Py]$^+$ 100%) calculated: 613.1, *m*/*z* 692.2 ([M]$^+$ 2.38%) calculated 692.1; IR (solid, cm^{-1}, (CO)): 2028, 1936, 1904; Anal. calc. for $ReC_{27}H_{23}F_3N_3O_7S_3$: C, 38.57; H, 2.76; N, 5.00. Found: C, 38.91; H, 2.63; N, 5.15.

Synthesis of *fac*-[Re(CO)$_3$(ImAu(PPh$_3$))(L1)](CF$_3$SO$_3$) (9). To a mixture of *fac*-[Re(CO)$_3$ImH(**L1**)](CF$_3$SO$_3$) (12.5 mg, 0.018 mmol) and [Au(CF$_3$SO$_3$)(PPh$_3$)][17] (22 mg, 0.035 mmol) in dry dichloromethane (5 ml) was added Cs$_2$(CO)$_3$ (17.6 mg, 0.05 mmol). The suspension was stirred at room temperature under an argon atmosphere for 2 hours. Then, the mixture was filtered through Celite and the solvent was removed under vacuum affording a beige solid which was further washed with ether and hexane. (10 mg, 54% yield). ^{1}H NMR (400 MHz, acetone-d$_6$) δ 8.84 (d, *J* = 8.5 Hz, 2H, C*H*(3, 8); **L1**), 8.35 (d, *J* = 8.5 Hz, 2H, C*H*(4, 7), **L1**), 8.07 (s, 2H, C*H*(5, 6), **L1**), 7.78–7.46 (m, 15H, Ph), 6.86 (s, 1H C*H*(2), Im), 6.59 (s, 1H, C*H*(4), Im), 5.97 (d, *J* = 1.2 Hz, 1H, C*H*(5), Im), 4.91 (q, *J* = 13.9 Hz, 4H, C*H*$_2$(11, 19)), 3.08–2.98 (m, 2H, C*H*$_2$(14a, 16a or 14b, 16b)), 2.39–2.30 (m, 4H, C*H*$_2$(13a, 17a or 13b, 17b and 14a, 16a or 14b, 16b)), 1.61 (td, *J* = 13.5, 5.0 Hz, 2H, C*H*$_2$(14a, 16a or 14b, 16b)); ^{31}P NMR (162 MHz, acetone-d$_6$): δP 31.7. MS (MALDI$^+$): *m*/*z* 1155.2 ([M]$^+$, 100%) calculated: 1155.1, *m*/*z* 629.0 ([M − Im − Au(PPh)$_3$]$^+$, 61%) calculated 629.0; IR (solid, cm^{-1}, (CO)): 2023, 1932, 1882; Anal. calc. for $ReAuC_{43}H_{36}F_3N_4O_6PS_4$: C, 39.60; H, 2.78; N, 4.30. Found: C, 39.37; H, 2.83; N, 4.45.

Synthesis of *fac*-[Re(CO)$_3$(ImAu(PPh$_3$))(L2)](CF$_3$SO$_3$) (10). *fac*-[Re(CO)$_3$ImH(**L2**)](CF$_3$SO$_3$) (20 mg, 0.024 mmol) Cs$_2$(CO)$_3$ (29 mg, 0.089 mmol) and [Au(CF$_3$SO$_3$)(PPh$_3$)][17] (59 mg, 0.97 mmol) in dry dichloromethane (5 ml) were stirred for 1 h at room temperature. Then, the mixture was filtered through Celite and ether was added affording the precipitation of the desired product as a light brown solid which was further washed with ether (9 mg, 27% yield). ^{1}H NMR (400 MHz, acetone-d$_6$) δ 8.82 (d, *J* = 8.5 Hz, 2H, C*H*(3, 8), **L2**)), 8.27 (d, *J* = 8.5 Hz, 2H, C*H*(4, 7), **L2**), 8.06 (s, 2H, C*H*(5, 6) **L2**), 7.73–7.46 (m, 15H, Ph), 6.84 (s, 1H, C*H*(2), Im), 6.58 (s, 1H(4), Im), 5.95 (d, *J* = 1.2 Hz, 1H, 1H(5), Im), 4.90 (d, *J* = 14.0 Hz, 2H, C*H*$_2$(11a, 19a or 11b, 19b)), 4.76 (d, *J* = 14.0 Hz, 2H, C*H*$_2$(11a, 19a or 11b, 19b)), 3.30–2.92 (m, 4H, C*H*$_2$(14, 16)), 2.59–2.38 (m, 2H, C*H*$_2$(13a, 17a or 13b, 17b)), 2.38–2.16 (m, 2H, C*H*$_2$(13a, 17a or 13b, 17b)). ^{31}P (162 MHz, acetone-d^6): δP 31.7; ^{13}C NMR (101 MHz acetone-d$_6$), δC 197.4 (CO), 196.1 (CO), 169.2 (C(2, 9) **L2**), 148.1 (C(4b, 6b) **L2**), 146.3 (C(2), Im), 141.9 (C(8, 3) **L2**), 135.0 (d, *J* = 13.6 Hz, *ortho*-Ph), 133.3 (d, *J* = 2.6 Hz, *para*-Ph), 130.5 (d, *J* = 11.9 Hz, *meta*-Ph), 129.3 (C(4a, 6a) **L2**), 128.9 (d, *J* = 63.5 Hz, *ipso*-Ph), 127.9 (C(5), Im), 127.51 (C(5, 6) **L2**), 127.52 (C(4, 7) **L2**), 127.2 (C(4), Im), 72.7 (C(14, 16) **L2**), 45.1 (C(1, 19) **L2**), 33.3 (C(13, 17) **L2**). MS (MALDI$^+$): *m*/*z* 985.1 ([M − 2Ph]$^+$ 94.4%) calculated: 985.04, *m*/*z* 909.0 ([M − 3Ph]$^+$ 4.8%) calculated: 908.0, *m*/*z* 612.8 ([M − Im − Au(PPh)$_3$]$^+$, 51.2%) calculated 613.03; IR (solid, cm^{-1}, (CO)): 2024, 1931, 1895; Anal. calc. for $ReAuC_{43}H_{36}F_3N_4O_7PS_3$: C, 40.09; H, 2.82; N, 4.35. Found: C, 39.88; H, 2.87; N, 4.23.

Synthesis of *fac*-[Re(CO)$_3$(L1)(Py)Ag](CF$_3$SO$_3$)$_2$ (11). To a solution of *fac*-[Re(CO)$_3$(**L1**)Py](CF$_3$SO$_3$) (17 mg, 0.02 mmol in acetone (5 ml) was added dropwise an acetone solution of AgCF$_3$SO$_3$ (5.1 mg, 0.02 mmol) and it was kept stirring at room temperature under an argon atmosphere for 3 days. Then, hexane was added and the desired product precipitated as a yellow solid. (17 mg, 79% yield). ^{1}H NMR (400 MHz, acetone-d$_6$) δ 8.89 (d, *J* = 8.5 Hz, 2H, C*H*(3, 8), **L1**), 8.46 (d, *J* = 8.5 Hz, 2H, C*H*(4, 7), **L1**), 8.06 (s, 2H, C*H*(5, 6), **L1**), 7.76 (td, *J* = 6.2, 2.1 Hz, 3H, C*H*(2, 4, 6), Py), 7.16–7.08 (m, 2H, C*H*(3, 5), Py), 5.02 (d, *J* = 14.0 Hz, 2H, C*H*$_2$(11a, 19a or 11b, 19b)), 4.93 (d, *J* = 14.1 Hz, 2H, C*H*$_2$(11a, 19a or 11b, 19b)), 3.15–3.02 (m, 2H, C*H*$_2$(13a, 17a or 13b, 17b)), 2.55–2.45 (m, 2H, C*H*$_2$(13a, 17a or 13b, 17b)) 2.40 (td, *J* = 13.4, 4.1 Hz, 2H, C*H*$_2$(14a, 16a or 14b, 16b)), 1.80 (td, *J* = 13.4, 5.0 Hz, 2H, C*H*$_2$(14a, 16a or 14b, 16b)).^{13}C-NMR (101 MHz, acetone-d$_6$): δC 169.6 (C(2, 9), **L1**), 153.6 (C(2, 6), Py), 147.2 (C(4b, 6b), **L1**), 142.6 (C(3, 8), **L1**), 142.2 (C(4), Py), 131.4 (C(4a, 6a), **L1**), 129.6 (C(5, 6), **L1**), 128.9 (C(4, 7), **L1**), 128.3 (C(3, 5), Py), 45.1 (C(11, 19), **L1**), 36.5, 34.7 (S*C*H$_2$*C*H$_2$S). MS (MALDI$^+$): *m*/*z* 847.3 ([M − CF$_3$SO$_3$ + CH$_3$OH]$^+$, 0.13%) calculated 847.0, *m*/*z* 708.3 ([M − AgCF$_3$SO$_3$]$^+$, 0.15%) calculated 708.0, *m*/*z* 629.3 ([M − Py − AgCF$_3$SO$_3$]$^+$, 47.7%) calculated 629.0; IR (solid, cm^{-1}, (CO)): 2031, 1932, 1918.

Synthesis of *fac*-[Re(CO)$_3$(L2)(Py)Ag](CF$_3$SO$_3$)$_2$ (12). To a solution of *fac*-[Re(CO)$_3$Py(**L2**)](CF$_3$SO$_3$) (25 mg, 0.029 mmol) in acetone (5 ml) was added dropwise an acetone solution of AgCF$_3$SO$_3$ (8 mg, 0.031 mmol) and it was kept stirring at room temperature under an argon atmosphere for 24 h. Then, hexane was added and the desired product precipitated as a yellow solid. (20 mg, 61% yield). ^{1}H NMR (400 MHz, acetone-d$_6$) δ 8.90 (d, *J* = 8.5 Hz, 2H, C*H*(3, 8), **L2**)), 8.44 (d, *J* = 8.5 Hz, 2H, C*H*(4, 7), **L2**), 8.07 (s, 2H, C*H*(5, 6), **L2**), 7.83–7.71 (m, 3H, C*H*(2, 4, 6), Py), 7.10 (dd, 2H, *J* = 7.5, 6.7 Hz, C*H*(3, 5), Py), 5.19 (d, *J* = 14.1 Hz, 2H, C*H*$_2$(11a, 19a or 11b, 19b)), 4.85 (d, *J* = 14.1 Hz, 2H, C*H*$_2$(11a, 19a or 11b, 19b)), 3.33–3.25 (m, 2H, C*H*$_2$(13a, 17a or 13b, 17b)), 3.13 (td, *J* = 10.2, 5.6 Hz, 2H, C*H*$_2$(14a, 16a or 14b, 16b)), 2.72–2.64 (m, 2H, C*H*$_2$(13a, 17a or 13b, 17b)), 2.28 (td, *J* = 10.4, 4.6 Hz, 2H, C*H*$_2$(14a, 16a or 14b, 16b)). ^{13}C (101 MHz, acetone-d$_6$), δC 194.2 (*C*O), 170.2 (C(2, 9) **L2**), 152.8 (C(2, 6) Py), 146.6 (C(4b, 6b) **L2**), 141.9 (C(8, 3) **L2**), 141.1 (C(4) Py), 130.5 (C(4a, 6a) **L2**), 128.6 (C(4, 7) **L2**), 127.9 (C(5,6) **L2**), 127.2 (C(3, 5) Py), 71.3 (C(14, 16) **L2**), 45.0 (C(11, 19) **L2**), 33.2 (C(13, 17) **L2**). MS (MALDI$^+$), *m*/*z* 863.4 ([M − OCF$_3$ + H], 8.80%) calculated 863.4, 692.2, ([M − AgCF$_3$SO$_3$]$^+$, 4.27%) calculated 692.07, 613.2 ([M − Py − AgCF$_3$SO$_3$]$^+$, 96.5%) calculated 613.03; IR (solid, cm^{-1}, (CO)): 2034, 1937, 1923.

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