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Tricarbonyl Rhenium(I) and Technetium(I) Complexes with Hydrazones Derived from 4,5-Diazafluoren-9-one and 1,10-Phenanthroline-5,6-dione

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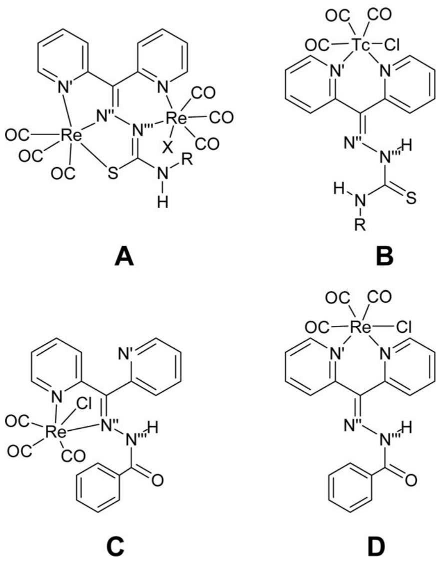
Tricarbonylrhenium(I) and -technetium(I) halide (halide = Cl and Br) complexes of ligands derived from 4,5-diazafluoren-9-one (df) and 1,10-phenanthroline-5,6-dione (phen) derivatives of benzoic and 2-hydroxybenzoic acid hydrazides have been prepared. The complexes have been characterized by elemental analysis, MS, IR, ^{1}H NMR and absorption and emission UV/Vis spectroscopic methods. The metal centres (Re^I and Tc^I) are coordinated through the nitrogen imine atoms and establish five-membered chelate rings, whereas the hydrazone groups stand uncoordinated. The ^{1}H NMR spectra suggest the same behaviour in solution on the basis of only marginal variations in the chemical shifts of the hydrazine protons.

Introduction

The high stability of $\{M(CO)_3\}^+$ complexes (M = Re, Tc) with aromatic N-heterocycles, for instance pyridine, has encouraged the use of this motive in ligand design for nuclear medical applications. Thus, metallic fragments with *N*,*N′*-chelating coordination, which make use of the chelate effect, may be anchored to (bio)molecules for therapeutic applications[1] or for labelling of targeting biomolecules.[2–6] In the latter case, a second functional group, for conjugation and/or interaction to a biomolecule, is required. In addition to applications that are based on the radioactivity of Re or Tc isotopes, the luminescent properties of rhenium(I) tricarbonyl *N*,*N′*-diimine may have potential use in biological imaging as fluorochromes in fluorescence microscopy.[7]

Several groups have used the di-2-pyridyl ketone moiety to design different ligands, mainly by coupling to hydrazones and thiosemicarbazones, and studied the potential use of the resulting complexes as chemical sensors[8] or radiopharmaceuticals.[9–11] However, the coordinated ligand is often hydrolyzed, and undesirable compounds are then formed.[10,12] Furthermore, we observed an unforeseen coordination behaviour of these types of ligands with tricarbonylrhenium(I) and -technetium(I) cores. For instance, the thiosemicarbazone ligands form dinuclear complexes with rhenium(I) in a way that the pyridine binding sites and the thiosemicarbazone nitrogen atom are used to bridge two rhenium(I) centres (mode μ-$\kappa N',N'',S:N,N'''$, Scheme 1A),[9] while the main product formed with technetium seems to be a mononuclear complex with a non-coordinating thiosemicarbazone binding site (mode $\kappa N,N'$, Scheme 1B).[11] Reactions of $\{Re(CO)_3\}^+$ precursors with benzoic acid hydrazone affords two linkage isomers, which result from the coordination of one ($\kappa N,N''$) or two pyridine groups ($\kappa N,N'$), but with relevant differences in their



Scheme 1. The reported coordination behaviour of di-2-pyridyl ketone thiosemicarbazone and hydrazone Re/Tc complexes.

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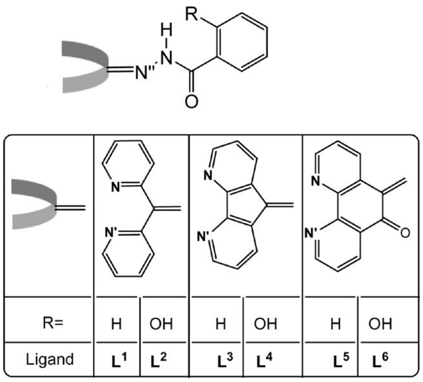
solubilities (Scheme 1C, D).[10] Both effects are not desirable in the design of radiopharmaceuticals based on ^{99m}Tc because the complex should preferably be obtained “in situ” in a single step and without considerable impurities. The formation of isomers results in a biodistribution of unpredictable characteristics.

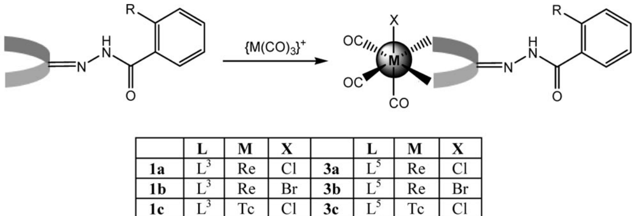
In the present study, we have chosen hydrazone ligands in which the diimine groups are included as phenanthroline or diazafluorene (Scheme 2). In this case, we expect ambidentate behaviour of the ligands because of the rigidity imposed by joining the imine rings with π delocalization in the hydrazone arm, although the number and nature of the donor atoms are maintained (Scheme 2). Consequently, the structural characterization of rhenium(I) and technetium(I) complexes in the solid state and in solution have also been performed to elucidate the coordination mode of the ligands.



Scheme 2. Relationships of the ligands included in this work (L^3–L^6) to those reported before (L^1 and L^2).

Results and Discussion

The ligands were synthesized by Schiff base condensation by using benzohydrazide or 2-hydroxybenzohydrazide and the corresponding ketones. Reactions of these ligands with *fac*-[ReX(CO)$_3$(CH$_3$CN)$_2$] (X = Cl, Br), [ReBr(CO)$_5$] and [NEt$_4$]$_2$ *fac*-[ReBr$_3$(CO)$_3$] were performed to study the potential effects of different precursors and the reaction media on the nature of the product complexes (Scheme 3). Therefore, different solvents such as chloroform, methanol, acetonitrile and toluene were also used. The complexes were isolated as air stable solids, which are moderately soluble in alcohols and other organic solvents. Generally, a lower solubility was observed for the phenanthroline derivatives. Similarly, reactions of [NEt$_4$]$_2$[TcCl$_3$(CO)$_3$] in methanol or acetonitrile with the ligands give the technetium complexes (with the exception of **1c**) in high yields. The technetium compounds show lower solubility than the rhenium(I) derivatives.



	L	**M**	**X**		**L**	**M**	**X**
1a	L^3	Re	Cl	**3a**	L^5	Re	Cl
1b	L^3	Re	Br	**3b**	L^5	Re	Br
1c	L^3	Tc	Cl	**3c**	L^5	Tc	Cl
2a	L^4	Re	Cl	**4a**	L^6	Re	Cl
2b	L^4	Re	Br	**4b**	L^6	Re	Br
2c	L^4	Tc	Cl	**4c**	L^6	Tc	Cl

Scheme 3. Preparation of the complexes.

Elemental analysis and mass spectrometry (FAB) strongly suggest a 1:1 stoichiometry. Deprotonation of the ligands was never observed in our experiments, which is in contrast to reactions with the di-2-pyridyl ketone thiosemicarbazone derivatives where deprotonation and formation of dinuclear complexes was observed.[9] All the mass spectra contain signals corresponding to the molecular ions. *Facial* geometry around the rhenium atom is strongly suggested by the three strong *ν*(CO) IR bands in the range between 2040 and 1883 cm^{-1}. The carbonyl bands of the hydrazone groups remain almost unaffected by complex formation, which suggests that the hydrazone oxygen atom is not involved in the coordination with the metal in the Re^{I}/Tc^{I} complexes.

X-ray Studies

The structures of the complexes **1a**–**c**, **2a**, **2c**, **3b** and **4a** were solved by X-ray diffraction studies. Table 1 lists selected structural parameters, and Table S1 lists the crystal and structure refinement data. Drawings of the molecular structure of these complexes are included in Figure 1.

All compounds crystallized as hydrates or solvates. The crystal structures of **1a**·1/2H$_2$O and **1c**·1/2H$_2$O may be defined as isostructural because the unit-cell similarity index (Π) is small, 0.0018.[13] The isostructural relation seems to be weaker in the crystals of **2a** and **2c** (Π = 0.0684) despite the fact that they are complexes of the same ligand, L^4. Seemingly, there is a better relation between **2a** and **4a** (Π = 0.0041). Although the solvent plays an important role in the molecular packing, this aspect will not be discussed here for brevity. A detailed description of these aspects and additional figures are provided in the Supporting Information.

The X-ray studies confirm the N(3),N(4)-coordination mode and the uncoordinated hydrazone group of the ligand, as was determined by IR and NMR spectroscopic techniques (vide infra). Possible effects of complex formation on the hydrazone group are difficult to evaluate because of the relatively high standard deviations associated with the bond lengths in the complexes. The hydrazone groups in the complexes maintain their configuration *Z* and *E* around the C(1)–N(1) and N(1)–N(2) bonds, as was observed in the free ligands L^3 and L^4.[14,15] On the other hand, with the exception of **1b**, the N(1)–N(2) bonds are longer in the complexes than those in the free ligands, while the C(1)–N(1) and C(8)–N(2) bonds are almost unaffected by the coordination. Therefore, the hydrazone groups seem to be only slightly perturbed by the coordination of the {MX(CO)$_3$} fragments.

The metal centres in the complexes adopt a distorted octahedral coordination geometry, and the carbonyl groups

Table 1. Selected bond lengths [Å] and angles [°] of the complexes under study.

	1a·1/2H_2O M = Re, X = Cl	**1b**·CH_3OH M = Re, X = Br	**1c**·1/2H_2O M = Tc, X = Cl	**2a**·2DMSO M = Re, X = Cl	**2c**·2DMSO M = Tc, X = Cl	**3b**·$CHCl_3$ M = Re, X = Br	**4a**·2DMSO M = Re, X = Cl
M(1)–N(4)	2.233(13)	2.202(15)	2.218(7)	2.221(8)	2.247(8)	2.144(9)	2.199(18)
M(1)–N(3)	2.242(16)	2.248(12)	2.226(7)	2.205(8)	2.221(9)	2.217(6)	2.210(16)
M(1)–X(1)	2.472(4)	2.569(3)[a]	2.4920(19)	2.465(3)	2.477(3)	2.6192(16)	2.485(7)
O(1)–C(1)	1.24(2)	1.239(19)	1.208(9)	1.199(11)	1.257(11)	1.20(2)	1.24(2)
N(1)–N(2)	1.345(17)	1.378(16)	1.358(10)	1.354(11)	1.345(10)	1.333(12)	1.318(19)
N(1)–C(1)	1.35(2)	1.346(19)	1.379(12)	1.356(10)	1.409(10)	1.44(2)	1.41(3)
N(2)–C(8)	1.26(2)	1.259(16)	1.299(11)	1.287(10)	1.267(9)	1.37(3)	1.31(2)
N(4)–M(1)–N(3)	78.3(5)	78.3(5)	79.0(3)	79.0(3)	80.4(3)	74.6(3)	73.2(7)
N(4)–M(1)–X(1)	84.8(3)	84.1(2)[a]	86.82(17)	81.6(2)	84.7(2)	82.4(3)	84.8(5)
N(3)–M(1)–X(1)	81.4(3)	84.7(2)[a]	82.65(15)	85.2(2)	85.8(3)	85.15(16)	82.8(5)
N(2)–N(1)–C(1)	119.1(14)	116.1(12)	119.5(8)	121.3(8)	119.1(7)	117.8(13)	118.3(17)
O(1)–C(1)–N(1)	120(2)	122.9(15)	119.9(11)	120.1(10)	119.4(8)	120.6(16)	119.5(18)
O(1)–C(1)–C(2)	120.9(18)	117.1(16)	122.1(11)	122.3(9)	122.8(8)	122.0(16)	122(2)
N(1)–C(1)–C(2)	118.6(15)	119.9(15)	117.9(8)	117.6(9)	117.6(8)	117.4(14)	118(2)
C(8)–N(2)–N(1)	118.3(14)	122.9(13)	119.0(7)	120.0(8)	116.4(7)	112.3(15)	120.2(18)
ϕ [°]	20.4(6)	4.9(5)	21.0(3)	8.9(4)	8.9(3)	6.9(6)	12.7(7)

[a] Mean values calculated following ref.[61]

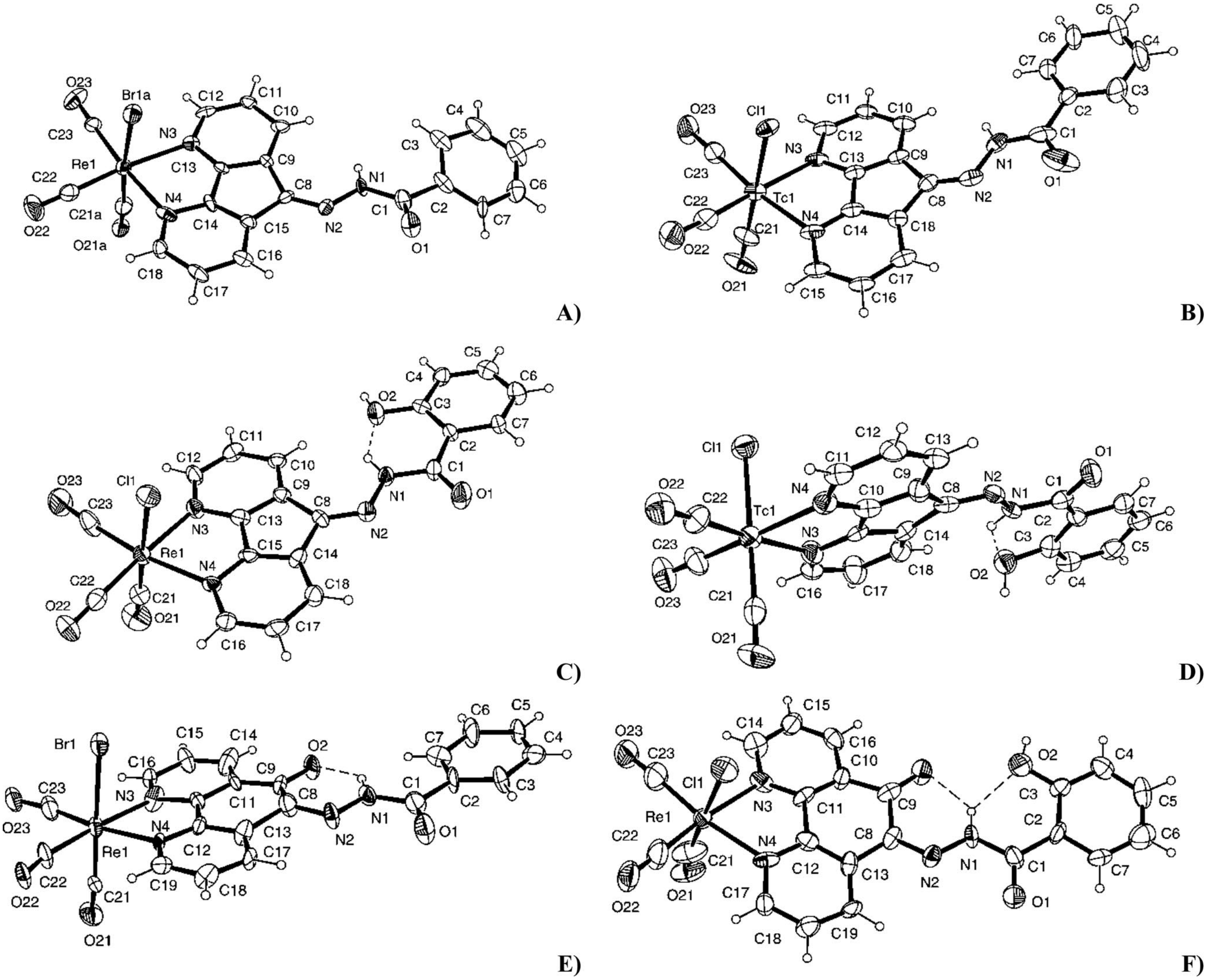
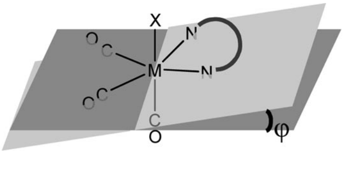


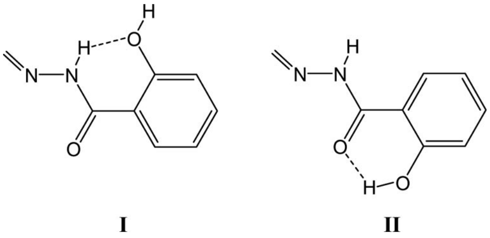
Figure 1. Molecular structures of (A) **1b**·MeOH, (B) **1c**·1/2H_2O, (C) **2a**·2DMSO, (D) **2c**·2DMSO, (E) **3b**·$CHCl_3$ and (F) **4a**·2DMSO.

are arranged in a facial orientation. The M–N distances and the N–M–N angles are very similar, regardless of the metal, the co-coordinated halide and the individual ligand. The values come close to those found in other ligands based on 4,5-diazafluorene (df)[16] and 1,10-phenanthroline (phen).[17–23,23–33] This fact is surprising because the N(3)–N(4) distances (bite distance) of the phen-based ligands are substantially longer (about 2.8 Å) than those in the df derivatives (about 2.6 Å).

An interesting aspect is the relative orientation of the phen or df planes with respect to those defined by the metal atoms and the two carbonyl groups in a *trans* orientation to the chelate ring. This orientation may be described by the angle ϕ, as defined in the diagram (for values for all the complexes under study, see Table 1). The values for **1a** and **1c** are the highest values observed in similar rhenium(I) complexes (see Table S2). This type of distortion has been attributed to a combination of crystal packing effects and disruption of the π–π stacking interactions between the ligands. Thus, phenanthroline ligands without or with a small aromatic substituent show weak distortions (see for instance $[ReCl(phen)(CO)_3]$[19] with ϕ = 4.48°). However, other factors such as the steric constraints imposed by substituents close to the coordination site also have to be considered and may have a considerable influence {as in the square-planar platinum(II) complex $[PtCl_2(MePhen)]$ (MePhen = 2,9-dimethyl-1,10-phenanthroline-5,6-dione, γ = 44.42°)}.[34]



The conformation of 2-hydroxybenzylhydrazone in the complexes of ligands L^4 and L^6 is also interesting. The hydroxy group may adopt two possible orientations (Scheme 4) depending on its role as acceptor (I) or donor (II) in the framework of intramolecular hydrogen bonds. Both conformations maintain highly stabilized six-membered rings by this interaction. Thus, the formation of the individually observed conformation seems also to depend on different factors such as intermolecular hydrogen bonding (which is easier in conformation I than in II).[35] A survey of the Cambridge Structural Database[36] reveals 92 structures of complexes containing the 2-hydroxybenzylhydrazone motif (and additionally 662 non-organometallic compounds). Conformation II is only present in 11 of them. Thus, the 2-hydroxybenzylhydrazone unit seems to behave differently to 2-hydroxybenzamide, for which conformer I is predominant.[37] As we observed in other structures,[35] the ability of the N(1)–H group to establish intermolecular interactions (for instance with donor solvents) is limited by the nature of the substituent at the N(2) atom. The structure of free L^4 (XAFSIG)[15] represents conformation I, and this conformation is also established in the rhenium and technetium complexes **2a** and **2c**. Similarly, this conformation is present in **4a**·2DMSO, although, in this case, the interaction of the N(1)–H group with the ketone oxygen atom of the phenanthroline is likely to be a stabilizing factor for this conformation.



Scheme 4. The observed conformations in the 2-hydroxybenzylhydrazone fragment.

Solution Studies

NMR Studies

^1H NMR spectroscopy is a very suitable tool to detect multiple coordination modes in samples of Re^I/Tc^I complexes that present single peaks in HPLC analysis.[38,39] All the complexes included in this work, irrespective of the conditions of synthesis, present signals in the ^1H NMR spectra attributable to a single species. The assignment of the signals has been performed on the basis of previously published data for L^3 and L^4[40–42] or in similar systems for L^5 and L^6.[25,32,34,43]

The ^1H NMR spectra can readily be used to ensure the coordination mode of the hydrazone ligands in the rhenium complexes under study. In complexes in which the N–H group is part of the chelate ring by N,O ligand coordination, we have observed strong low-field shifts of these proton signals (about 2 ppm)[35,44] with respect to those for the free ligand. However, when the acyl group is not involved in the coordination, the signal is almost unmodified, even when it may be slightly shielded.[45] This behaviour seems to be a general feature, and it has also been observed in thiosemicarbazone analogs.[46–50] The corresponding signals are only slightly deshielded (0.2–0.30 ppm) for the complexes of the ligands L^3 and L^4 or they are completely unaffected, as in the rhenium complexes of L^5 and L^6. These findings strongly support the conclusion that the observed solid-state structures with non-coordinated hydrazone groups are also present in solution. This means that *N*,*N′*-coordination is maintained even when strongly labilizing solvents such as DMSO are used.

The ^{99}Tc NMR spectra show signals close to –1000 ppm, at positions similar to those found for other tricarbonyltechnetium(I) complexes $[TcX(CO)_3(N)_2]$ where N is an aromatic amine or a monodentate ketonoxime.[51] Similar chemical shifts have been also observed for several thiosemicarbazone complexes in which the ligand is coordinated by *N*,*N′*-imine groups.[11]

Electronic Absorption Studies

The spectra of the complexes containing ligands L^3 and L^4 were recorded in two solvents, chloroform and methanol, while those of L^5 and L^6 were recorded in DMSO because of their lack of solubility in other solvents (Figure 2).

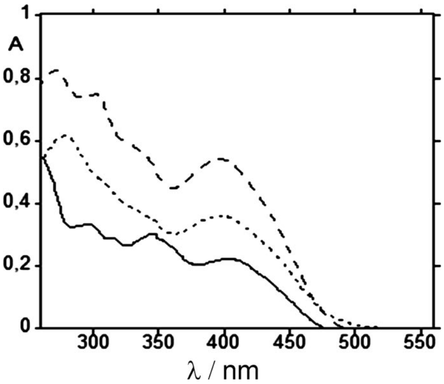


Figure 2. (a) Absorption spectra of L^6 (–), **4a** (---) and **4b** (···) in DMSO solution.

The absorption spectra of the 4,5-diazafluorene derivatives, L^3 and L^4, show intense bands below 350 nm, which are attributable to ligand-centred π–π* transitions, similar to the findings for the ruthenium(II) complex of the 3-hydroxy-2-naphthoylhydrazone derivative (L^7), [Ru(bpy)$_2$(L^7)]$^{2+}$.[52] With the exception of slight variations in the intensities, this area in the spectra is almost unaffected by the coordination. The bands at high wavelengths have tails up to around 400–450 nm, which are responsible for the orange colour of both complexes. These weak bands are tentatively attributed to a mixture of metal-to-ligand charge transfer states, dπ(Re)→π*(ligand).[53] The positions of these bands undergo a positive bathochromic shift with increasing polarity of the solvents.

Table 2. UV/Vis absorption data for the free ligands and their rhenium(I) complexes.

		λ(absorption)[a,b]		
	Solvent	π*←π	Mixed	MLCT
L^3	CHCl$_3$	314(19.9), 330(16.6)		
	MeOH	300(22.4), 314(24.6), 335(19.9)		
1a	CHCl$_3$	251(11.3), 322(12.6)		≈400
	MeOH	257(24.3), 321(27.5)		≈425
1b	CHCl$_3$	261(17.6), 323(16.3)		≈400
	MeOH	255(29.4), 322(27.5)		≈425
L^4	CHCl$_3$	299(32.5), 346(29.5)		
	MeOH	312(25.1), 343(21.9)		
2a	CHCl$_3$	272(25.8), 322(11.5), 347(9.5)		
	MeOH	263(12.5), 319(13.0), 348(10.2)		≈426
2b	CHCl$_3$	273(16.2), 323(5.8), 347(4.9)		
	MeOH	264(13.4), 321(8.3), 349(6.3)		≈428
L^5	DMSO	260(35.1), 298(20.3), 347(19.1), 402(10.8)		
3a	DMSO	265(29.6), 302(25.1), 331(21.5)	387(16.8)	
3b	DMSO	272(19.0), ≈318	389(9.8)	
L^6	DMSO	260(29.5), 297(18.0), 347(16.3), 404(12.1)		
4a	DMSO	271(22.2), 302(20.2)	397(14.6)	
4b	DMSO	278(33.3)	397(19.5)	

[a] λ in nm. [b] ε in L mol^{-1} cm^{-1} × 10^{-3}.

The absorption spectra of L^5 and L^6 display intense transitions at about 300 and 350 nm and weaker bands in the 420 nm region. On the basis of the similarity of the spectra to those of related ligands, these bands may be assigned to π–π* ligand centred (LC) transitions.

Coordination to tricarbonylrhenium(I) centres results in a redshift of these bands (Table 2). The ^{1}MLCT transitions are likely to be overlapped by the lowest LC transitions, as observed for the functionalized dipyrido[3,2-a:2′,3′-c]phenazine rhenium(I) complexes.[23]

Conclusions

The hydrazones derived from phen and df show a unique coordination mode when they react with different rhenium(I) and technetium(I) complexes in different media. In contrast to the products obtained from reactions with the di-2-pyridyl ketone ligands (L^1 and L^2 in Scheme 2), the *N,N′*-coordination mode is exclusively observed in the solid state and in solution, which include labilizing solvents such as DMSO.

Both the rhenium and technetium complexes, with the exception of **1c**, are obtained in high yields. This indicates that such compounds may be used as building blocks for supramolecular arrangements, since the uncoordinated hydrazone arms are available for coordination with a second metal ion. Slight modifications of the ligands (e.g. bis- or tris-substitution at the aromatic backbone with hydrazone functionalities) allow the ready design of two-dimensional frameworks.

Experimental Section

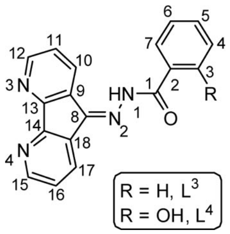
Materials and Methods: All solvents were dried with appropriate drying agents, degassed by using a vacuum line and distilled under an Ar atmosphere. [ReX(CO)$_5$],[54] [ReX(CO)$_3$(CH$_3$CN)$_2$][55] and [NEt$_4$]$_2$[TcCl$_3$(CO)$_3$][56] were obtained by literature methods. Elemental analyses were carried out on a Fisons EA-1108 instrument. Melting points (m.p.) were determined on a Gallenkamp MFB-595 and are uncorrected. Mass spectra were recorded on a VG Autospec Micromass spectrometer operating under FAB conditions (nitrobenzyl alcohol matrix). Infrared spectra were recorded from KBr pellets on a Bruker Vector 22FT spectrometer. UV/Vis spectra were obtained on a CARY 100 (Varian) spectrophotometer. ^{1}H NMR and ^{99}Tc-NMR spectra were obtained on Bruker AMX 400 and JEOL 400 MHz spectrometers, respectively, from [D$_6$]acetone and [D$_6$]DMSO solutions.

X-ray Data Collection, Structure Determination and Refinement: Crystallographic data collection and refinement parameters are listed in Table S1. All crystallographic measurements were performed on a Bruker Smart CCD apparatus at CACTI (University of Vigo) at room temperature [293(2) K] by using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The data were corrected for absorption effects with the program SADABS.[57] Structure analyses were carried out by direct methods.[58] Least-squares full-matrix refinements on F^2 were performed by using the program SHELXL97. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for Crystallography.[59] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined as riders. Graphics were obtained with MERCURY.[60] CCDC-776594, -776595, -776596, -776597, -776598, -776599, -776600 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/datarequest/cif.

Synthesis of the Ligands: 4,5-Diazafluoren-9-one Derivatives: The ligands derived from 4,5-diazafluoren-9-one were prepared as reported before for related compounds:[41] the ketone (182 mg, 1.0 mmol) was added to solutions of benzohydrazide (136 mg, 1.0 mmol) or 2-hydroxybenzohydrazide (152 mg, 1.0 mmol) in ethanol (25 mL). After the addition of *p*-toluenesulfonic acid (catalytic equiv.), the solution was heated at reflux for 6 h. The ethanol was partly removed on a vacuum line, and the remainder kept in a refrigerator overnight. The colourless solids formed were filtered, washed with ethanol and vacuum dried with $CaCl_2$/KOH. Single crystals of L^3 were obtained from the mother liquor when allowed to stand at room temperature for several days.

L^3 (4,5-Diazafluorene-9-one Benzoylhydrazone): Yield: 216 mg (72.1%). M.p. 122–127 °C. $C_{18}H_{12}N_4O$ (300.32): calcd. C 71.99, H 4.03, N 18.66; found C 71.03, H 4.03, N 18.54. MS: *m*/*z* (%) = 601.23 (6.06) $[2M]^+$, 301.13(100.00) $[M + H]^+$, 300.12 (5.12) $[M]^+$. IR (KBr pellets): $\tilde{\nu}$ = 3444 (m br.), 3283 [w sh., ν(NH)], 1667 [s, ν(C=O)], 1590 (w), 1566 (m), 1518 (m), 1487 [w, ν(C=N)+ ν(C=C)] cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 314 nm; UV/Vis (MeOH): λ_{max} = 314, 335 nm. ^1H NMR ([D$_6$]DMSO): δ = 12.10 (s, 1 H,N–H); 8.80 (dd, 2 H, C12–H/C15–H); 8.60 (d, 1 H), 8.20 (d, 1 H) (C10–H/C17–H); 8.00 (d, 2 H, C11–H/C16–H); 7.80 [m, 5 H, C(Ph)–H] ppm; (Scheme 5).

L^4 (4,5-Diazafluorene-9-one Salicyloylhydrazone): Yield: 308 mg (97.4%). M.p. >250 °C. $C_{18}H_{12}N_4O_2$ (316.32): calcd. C 68.35, H 3.82, N 17.71; found C 67.77, H 3.83, N 17.23. MS: *m*/*z* (%) = 317.04 (66.41) $[M + H]^+$. IR (KBr pellets): $\tilde{\nu}$ = 3437 (m br.), 3320 [m sh., ν(OH)/ν(NH)], 1685 [s, ν(C=O)], 1640 (w), 1602 (w), 1565 (w), 1518 (m), 1487 [w, ν(C=N) + ν(C=C)] cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 299, 346 nm; UV/Vis (MeOH): λ_{max} = 312, 343 nm. ^1H NMR ([D$_6$]DMSO): δ = 12.30 (s, 1 H, O–H); 12.10 (s, 1 H, N–H); 8.80 (dd, 2 H, C12–H/C15–H); 8.60 (d, 1 H, C7–H); 8.20–8.00 (dd, 2 H, C10–H/C17–H); 7.60 (t, 1 H, C5–H); 7.50 (m, 2 H, C11–H/C16–H); 7.10 (d, 1 H, C4–H); 7.05 (t, 1 H, C6–H) ppm; (Scheme 5).

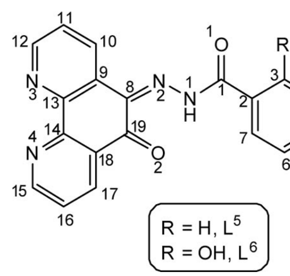


Scheme 5. Numbering scheme used for ligands L^3 (R = H) and L^4 (R = OH) and their complexes.

Synthesis of the Ligands: 1,10-Phenanthroline-5,6-Dione Derivatives: The ligands were prepared in a similar manner to the ligands of the previous section: 1,10-phenanthroline-5,6-dione (210 mg, 1.0 mmol) was added to solutions of benzoylhydrazide (136 mg, 1.0 mmol) or 2-hydroxybenzohydrazide (152 mg, 1.0 mmol) in ethanol. After the addition of *p*-toluenesulfonic acid (catalytic equiv.), the solution was heated at reflux for 6 h. The yellow–orange products formed after cooling were filtered, washed with ethanol and dried with $CaCl_2$/KOH.

L^5, [5-Oxo-1,10-phenantrolin-6(5*H*)-ylidene]benzohydrazide: Yield: 272.0 mg (82.8%). M.p. 246 °C. $C_{19}H_{12}N_4O_2$ (328.33): calcd. C 69.51, H 3.68, N 17.06; found C 69.21, H 3.69, N 17.05. MS: *m*/*z* (%) = 329.06 (100.00) $[M + H]^+$, 210.10 (7.69) $[C_{12}H_6N_2O_2]^+$. IR (KBr pellets): $\tilde{\nu}$ = 3445 [s br., ν(NH)], 1716 [s, ν(C=O)], 1618 (m), 1584 (s), 1509 (m), 1451 [w, ν(C=N) + ν(C=C)] cm^{-1}. UV/Vis (DMSO): λ_{max} = 260, 298, 347, 402 nm. ^1H NMR ([D$_6$]DMSO): δ = 15.30 (s, 1 H, N–H); 9.10–8.90 (dd, 2 H, C12–H/C15–H); 8.60 (dd, 2 H, C10–H/C17–H); 8.00 (m, 2 H, C11–H/C16–H); 7.60 [m, 5 H, C(Ph)–H] ppm; (Scheme 6).

L^6, {2-Hydroxy-*N*′-[5-oxo-1,10-phenantrolin-6(5*H*)-ylidene]benzohydrazide}: Yield: 321.0 mg (93.2%). M.p. >250 °C. $C_{19}H_{12}N_4O_3$ (344.33): calcd. C 66.28, H 3.51, N 16.27; found C 66.14, H 3.54, N 16.34. MS: *m*/*z* (%) = 345.03 (19.05) $[M]^+$. IR (KBr pellets): $\tilde{\nu}$ = 3447 (w br.), 3091 [m, ν(OH)/ν(NH)], 1692 [s, ν(C=O)], 1636 (m), 1604 (m), 1496 (s), 1463 [s, ν(C=N) + ν(C=C)] cm^{-1}. UV/Vis (DMSO): λ_{max} = 260, 297, 347, 404 nm. ^1H NMR ([D$_6$]DMSO): δ = 15.60 (s, 1 H, N–H); 12.00 (s, 1 H, O–H); 9.10–8.90 (dd, 2 H, C12–H/C15–H); 8.65–8.55 (dd, 2 H, C10–H/C17–H); 8.00 (d, 1 H, C7–H); 7.70 (m, 2 H, C11–H/C16–H); 7.50 (t, 1 H, C5–H); 7.10 (d, 1 H, C4–H); 7.05 (t, 1 H, C6–H) ppm; (Scheme 6).



Scheme 6. Numbering scheme used for ligands L^5 (R = H) and L^6 (R = OH) and their complexes.

Synthesis of Rhenium(I) Complexes

$[ReX(L^{3,4})(CO)_3]$ (X = Cl, Br): A mixture of $[ReX(CO)_3(CH_3CN)_2]$ (50 mg, 0.12 mmol, X = Cl; 0.13 mmol, X = Br) and a stoichiometric amount of L^3 or L^4 in dry chloroform (10 mL) was heated under reflux for 2 h. The yellow solids formed were filtered and vacuum dried with $CaCl_2$. Single crystals of $[ReCl(L^3)(CO)_3]$, $[ReBr(L^3)(CO)_3]$ and $[ReCl(L^4)(CO)_3]$ were obtained from the mother liquor, methanol and dimethyl sulfoxide solutions, respectively, when allowed to stand at room temperature for several days.

$[ReCl(L^3)(CO)_3]$ (1a): Yield: 69.0 mg (87.6%). Mp: >250 °C. $C_{21}H_{12}ClN_4O_4Re$ (606.01): calcd. C 41.62, H 2.00, N 9.25; found C 41.37, H 1.81, N 9.23. MS: *m*/*z* (%) = 605.97 (11.41) $[M]^+$, 571.00 (18.64) $[M - Cl]^+$. IR (KBr pellets): $\tilde{\nu}$ = 3445 [m br., ν(N–H)] 2030 (s), 1922 (s), 1889 [vs, $\nu(CO_{fac})$], 1679 [m, ν(C=O)], 1646 (w), 1620 (w), 1517 (w), 1481 [w, ν(C=N) + ν(C=C)] cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 251, 322 nm; UV/Vis (MeOH): λ_{max} = 257, 321 nm. ^1H NMR ([D$_6$]DMSO): δ = 12.40 (s, 1 H, (N–H); 8.95 (dd, 2 H, C12–H/C15–H); 8.90 (d, 1 H), 8.50 (d, 1 H) (C10–H/C17–H); 8.05 (d, 2 H, C3–H/C7–H); 7.85 (dd, 1 H), 7.80 (dd, 1 H) (C11–H/C16–H); 7.70 (m, 1 H, C5–H); 7.60 (m, 2 H, C4–H/C6–H) ppm.

$[ReBr(L^3)(CO)_3]$ (1b): Yield: 63.0 mg (80.7%). M.p. >250 °C. $C_{21}H_{12}BrN_4O_4Re$ (650.46): calcd. C 38.78, H 1.86, N 8.61; found C 38.24, H 2.05, N 8.63. MS: *m*/*z* (%) = 649.94 (9.93) $[M]^+$, 571.02 (15.62) $[M - Br]^+$. IR (KBr pellets): $\tilde{\nu}$ = 3447 [m br., ν(NH)], 2032 (s), 1925 (s), 1890 [vs, $\nu(CO_{fac})$], 1677 [m, ν(C=O)], 1620 (w), 1596 (w), 1516 (w), 1481 [w, ν(C=N) + ν(C=C)] cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 261, 323 nm; UV/Vis (MeOH): λ_{max} = 255, 322 nm. ^1H

NMR ([D$_6$]DMSO): δ = 12.30 (s, 1 H, N–H); 8.95 (dd, 2 H, C12–H/C15–H); 8.85 (d, 1 H), 8.50 (d, 1 H) (C10–H/C17–H); 8.05 (d, 2 H, C3–H/C7–H); 7.85 (dd, 1 H), 7.80 (dd, 1 H) (C11–H/C16–H); 7.70 (t, 1 H, C5–H); 7.60 (m, 2 H, C4–H/C6–H) ppm.

[ReCl(L^4)(CO)$_3$] (2a): Yield: 60.0 mg (74.2%). M.p. >250 °C. $C_{21}H_{12}ClN_4O_5Re$ (622.01): calcd. C 40.55, H 1.94, N 9.01; found C 40.00, H 2.32, N 8.98. MS: *m/z* (%) = 621.96 (4.51) [M]$^+$, 586.98 (6.55) [M – Cl]$^+$. IR (KBr pellets): $\tilde{\nu}$ = 3442 (m br.), 3299 [w sh., ν(O–H)/ν(N–H)], 2037 (s), 1919 [vs, ν(CO$_{fac}$)], 1688 [m, ν(C=O)], 1604 (w), 1529 (m), 1484 (m), 1459 [w, ν(C=N) + ν(C=C)] cm^{-1}. UV/Vis (CHCl$_3$): λ_{max} = 272, 347 nm; UV/Vis (MeOH): λ_{max} = 263, 319 nm. ^{1}H ([D$_6$]DMSO): δ = 12.50 (s, 1 H, O–H); 12.20 (s, 1 H, N–H); 8.95 (dd, 2 H, C12–H/C15–H); 8.80 (d, 1 H), 8.55 (d, 1 H) (C10–H/C17–H); 8.05 (d, 1 H, C7–H); 7.90 (dd, 1 H), 7.80 (dd, 1 H) (C11–H/C16–H); 7.50 (t, 1 H, C5–H); 7.10 (d, 1 H, C4–H); 7.05 (t, 1 H, C6–H) ppm.

[ReBr(L^4)(CO)$_3$] (2b): Yield: 65.0 mg (81.3%). M.p. >250 °C. $C_{21}H_{12}BrN_4O_5Re$ (666.46): calcd. C 37.85, H 1.81, N 8.41; found C 37.32, H 1.72, N 8.77. MS: *m/z* (%) = 665.79 (5.21) [M]$^+$, 586.92 (6.75) [M – Br]$^+$. IR (KBr pellets): $\tilde{\nu}$ = 3421 (m br.), 3301 [m sh., ν(OH)/ν(NH)], 2037 (s), 1920 [vs, ν(CO$_{fac}$)], 1681 [m, ν(C=O)], 1605 (w), 1529 (m), 1484 (w), 1459 [w, ν(C=N) + ν(C=C)] cm^{-1}. UV/Vis (CHCl$_3$): λ_{max} = 273, 347 nm; UV/Vis (MeOH): λ_{max} = 264, 321 nm. ^{1}H NMR ([D$_6$]DMSO): δ = 12.50 (s, 1 H, O–H); 12.20 (s, 1 H, N–H); 9.00 (dd, 2 H, C12–H/C15–H); 8.80 (d, 1 H), 8.55 (d, 1 H) (C10–H/C17–H); 8.00 (d, 1 H, C7–H); 7.85 (dd, 1 H), 7.75 (dd, 1 H) (C11–H/C16–H); 7.50 (t, 1 H, C5–H); 7.10 (d, 1 H, C4–H); 7.05 (t, 1 H, C6–H) ppm.

Synthesis of [ReX(L^{5,6})(CO)$_3$] (X = Cl, Br): A mixture of [ReX(CO)$_3$(CH$_3$CN)$_2$] (X: Cl, Br) (50 mg) and a stoichiometric amount of L^5 or L^6 in dry chloroform (10 mL) was heated under reflux for 2.5 h. The orange solids formed were filtered and vacuum dried with CaCl$_2$. Single crystals of [ReBr(L^5)(CO)$_3$] and [ReCl(L^6)(CO)$_3$] were obtained from chloroform and dimethyl sulfoxide solutions, respectively, when allowed to stand at room temperature for several days.

[ReCl(L^5)(CO)$_3$] (3a): Yield: 71.0 mg (86.1%). Mp: >250 °C. $C_{22}H_{12}ClN_4O_5Re$ (634.02): calcd. C 41.68, H 1.91, N 8.84; found C 41.69, H 1.87, N 8.88. MS: *m/z* (%) = 633.92 (1.27) [M]$^+$, 598.96 (2.36) [M – Cl]$^+$. IR (KBr pellets): $\tilde{\nu}$ = 3445 [m br., ν(NH)], 2034 (s), 1932 (s), 1888 [vs, ν(CO$_{fac}$)], 1705 [m, ν(C=O)], 1647 (w), 1512 (m), 1453 [m, ν(C=N) + ν(C=C)] cm^{-1}. UV/Vis (DMSO): λ_{max} = 265, 302, 387 nm. ^{1}H NMR ([D$_6$]DMSO): δ = 15.20 (s, 1 H, N–H); 9.35 (dd, 1 H), 9.20 (dd, 1 H) (C12–H/C15–H); 8.90 (dd, 2 H, C10–H/C17–H); 8.05 (m, 2 H, C11–H/C16–H); 7.95 (m, 2 H, C3–H/C7–H); 7.80 (m, 1 H, C5–H); 7.70 (m, 2 H, C4–H/C6–H) ppm.

[ReBr(L^5)(CO)$_3$] (3b): Yield: 54.0 mg (66.3%). M.p. >250 °C. $C_{22}H_{12}BrN_4O_5Re$ (678.47): calcd. C 38.95, H 1.78, N 8.26; found C 38.72, H 1.75, N 8.21. MS *m/z* (%) = 677.96 (9.29) [M]$^+$, 599.03 (13.23) [M – Br]$^+$. IR (KBr pellets): $\tilde{\nu}$ = 3441 [m br., ν(NH)], 2032 (s), 1933 (s), 1893 [vs, ν(CO$_{fac}$)], 1706 [m, ν(C=O)], 1648 (w), 1510 (m), 1452 [m, ν(C=N) + ν(C=C)] cm^{-1}. UV/Vis (DMSO): λ_{max} = 272, 389 nm. ^{1}H NMR ([D$_6$]DMSO): δ = 15.20 (s, 1 H, N–H); 9.40 (dd, 1 H), 9.20 (dd, 1 H) (C12–H/C15–H); 8.90 (dd, 2 H, C10–H/C17–H); 8.05 (m, 2 H, C11–H/C16–H); 7.95 (m, 2 H, C3–H/C7–H); 7.80 (m, 1 H, C5–H); 7.70 (m, 2 H, C4–H/C6–H) ppm.

[ReCl(L^6)(CO)$_3$] (4a): Yield: 80.0 mg (94.7%). M.p. >250 °C. $C_{22}H_{12}ClN_4O_6Re$ (650.02): calcd. C 40.65, H 1.86, N 8.62; found C 39.76, H 1.79, N 8.50. MS: *m/z* (%) = 649.94 (0.62) [M]$^+$. IR (KBr pellets): $\tilde{\nu}$ = 3442 [m br., ν(OH)/ν(NH)], 2030 (s), 1929 (s), 1883 [s, ν(CO$_{fac}$)], 1694 [w, ν(C=O)], 1645 (m), 1611 (w), 1578 (w), 1510 (m), 1455 [w, ν(C=N) + ν(C=C)] cm^{-1}. UV/Vis (DMSO): λ_{max} = 271, 302, 397 nm. ^{1}H NMR ([D$_6$]DMSO): δ = 15.60 (s, 1 H, N–H); 12.10 (s, 1 H, O–H); 9.35 (dd, 1 H), 9.15 (dd, 1 H) (C12–H/C15–H); 8.90 (dd, 1 H), 8.80 (dd, 1 H) (C10–H/C17–H); 8.05 (d, 1 H, C7–H); 8.00 (m, 2 H, C11–H/C16–H); 7.55 (m, 1 H, C5–H); 7.10 (d, 1 H, C4–H); 7.05 (t, 1 H, C6–H) ppm.

[ReBr(L^6)(CO)$_3$] (4b): Yield: 74.0 mg (88.8%). M.p. >250 °C. $C_{22}H_{12}BrN_4O_6Re$ (694.47): calcd. C 38.05, H 1.74, N 8.07; found C 37.70, H 1.70, N 8.03. MS: *m/z* (%) = 693.90 (0.47) [M]$^+$. IR (KBr pellets): $\tilde{\nu}$ = 3440 [s, ν(OH)/ν(NH)], 2033 (s), 1913 [vs, ν(CO$_{fac}$)], 1705 [m, ν(C=O)], 1642 (m), 1494 (m), 1453 [m, ν(C=N) + ν(C=C)] cm^{-1}. UV/Vis (DMSO): λ_{max} = 278, 397 nm. ^{1}H NMR ([D$_6$]DMSO): δ = 15.60 (s, 1 H, N–H); 12.10 (s, 1 H, O–H); 9.35 (dd, 1 H), 9.20 (dd, 1 H) (C12–H/C15–H); 8.90 (dd, 1 H), 8.80 (dd, 1 H) (C10–H/C17–H); 8.05 (m, 1 H, C7–H); 8.00 (m, 2 H, C11–H/C16–H); 7.55 (m, 1 H, C5–H); 7.10 (d, 1 H, C4–H); 7.05 (t, 1 H, C6–H) ppm.

Synthesis of Technetium(I) Complexes: ^{99}Tc is a weak β-emitter; manipulations of ^{99}Tc compounds were performed in a laboratory approved for the handling of such materials.

Synthesis of [TcCl(L^{3,4})(CO)$_3$]: A mixture of (Et$_4$N)$_2$[TcCl$_3$(CO)$_3$] (50 mg, 0.1 mmol) and a stoichiometric amount of the corresponding ligand in methanol (15 mL) were heated under reflux for 2 h. The yellow solids formed were filtered and vacuum dried. Yellow single crystals of [TcCl(L^3)(CO)$_3$] and [TcCl(L^4)(CO)$_3$] were obtained from an acetone solution and the mother liquor, respectively, when allowed to stand at room temperature for several days.

[TcCl(L^3)(CO)$_3$] (1c): Yield: 30.0 mg (57.9%). IR (KBr pellets): $\tilde{\nu}$ = 3421 (s), 2947 [w, ν(NH)], 2037 (s), 1898 [vs, ν(CO$_{fac}$)], 1682 [m, ν(C=O)], 1628 (m), 1582 (m), 1516 (m), 1470 [w, ν(C=N) + ν(C=C)] cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 12.35 (s, 1 H, N–H); 8.90 (m, 2 H, C12–H/C15–H); 8.80 (d, 1 H), 8.50 (d, 1 H) (C10–H/C17–H); 8.05 (d, 1 H, C3–H/C7–H); 7.80 (m, 1 H, C11–H/C16–H); 7.70 (m, 1 H, C5–H); 7.60 (m, 2 H, C4–H/C6–H) ppm. ^{99}Tc NMR ([D$_6$]DMSO): δ = –987.50 ppm.

[TcCl(L^4)(CO)$_3$] (2c): Yield: 52 mg (97.4%). IR (KBr pellets): $\tilde{\nu}$ = 3425 (w br.), 3298 [w sh., ν(OH)/ν(NH)], 2044 (s), 1932 [vs, ν(CO$_{fac}$)] 1686 [m, ν(C=O)], 1601 (w), 1527 (m), 1481 (m), 1458 [w ν(C=N) + ν(C=C)] cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 12.50 (s, 1 H, O–H); 12.20 (s, 1 H, N–H); 8.90 (dd, 2 H, C12–H/C15–H); 8.70 (d, 1 H), 8.50 (d, 1 H) (C10–H/C17–H); 8.00 (d, 1 H, C7–H); 7.80 (m, 2 H, C11–H/C16–H); 7.50 (t, 1 H, C5–H); 7.10 (d, 1 H, C4–H); 7.05 (t, 1 H, C6–H) ppm. ^{99}Tc NMR ([D$_6$]DMSO): δ = –985.74 ppm.

Synthesis of [TcCl(L^{5,6})(CO)$_3$]: A mixture of (Et$_4$N)$_2$[TcCl$_3$(CO)$_3$] (50 mg, 0.1 mmol) and an equimolar amount of the corresponding ligand in acetonitrile (15 mL) were heated under reflux for 3 h. The orange solids formed were filtered and vacuum dried. Because of the lack of complete solubility of these compounds in any solvent, it was not possible to record NMR spectra.

[TcCl(L^5)(CO)$_3$] (3c): Yield: 48.0 mg (87.9%). IR (KBr pellets): $\tilde{\nu}$ = 3429 (w br.), 3070 [w sh., ν(NH)], 2040 (s), 1948 (vs), 1898 [vs, ν(CO$_{fac}$)], 1705 [m, ν(C=O)], 1647 (w), 1601 (w), 1570 (w), 1512 (m), 1454 [m, ν(C=N) + ν(C=C)] cm^{-1}.

[TcCl(L^6)(CO)$_3$] (4c): Yield: 53.0 mg (94.3%). IR (KBr pellets): $\tilde{\nu}$ = 3433 (w br.), 3090 [w sh., ν(OH)/ν(NH)], 2040 (s), 1925 [vs, ν(CO$_{fac}$)], 1693 [m, ν(C=O)], 1647 (w), 1605 (w), 1570 (w), 1596 (m), 1454 [m, ν(C=N) + ν(C=C)] cm^{-1}.

Supporting Information (see footnote on the first page of this article): Description of the intermolecular interactions in the crystal structures, experimental crystal data and structure refinement and values of the ϕ angle in other rhenium(I) compounds.

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