Syntheses and structures of mononuclear {Re(CO)₃Cl(NN)} 'complex ligands' with a pendant imino–pyridine binding site, and preparation of some heterodinuclear Re(I)–lanthanide(III) complexes

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Abstract

A series of potentially dinucleating ligands, each with two bidentate imino–pyridine compartments, has been used to prepare the mononuclear complexes [Re(CO)₃Cl(L^n)] ($n = 1$–4) which each have a vacant binding site and so constitute 'complex ligands' for the stepwise synthesis of heterodinuclear complexes. Three of the complexes (with L^1, L^2 and L^4) have been structurally characterised. The mononuclear complex [Re(CO)₃Cl(L^5)], arising from decomposition of [Re(CO)₃Cl(L^3)] by hydrolysis of the non-coordinated imine unit, was also isolated and structurally characterised. Luminescence studies show that these compounds are only very weak emitters. The 'complex ligand' [Re(CO)₃Cl(L^1)] has been reacted with [Ln(hfac)₃]·2H₂O (Ln = Yb, Er) to prepare the heterodinuclear complexes [Re(CO)₃Cl(μ-L^1)Ln(hfac)₃] in which the {Ln(hfac)}₃ unit is attached to the second bidentate imino–pyridine site of [Re(CO)₃Cl(L^1)]. The crystal structures of these show that the bridging ligand has to twist to accommodate the two bulky metal fragments, and that the lanthanide units have an 8-coordinate square-antiprismatic geometry.
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1. Introduction

There has been extensive recent interest in the synthesis and photophysical characterisation of hetero-polynuclear complexes in which photoinduced energy-transfer occurs between the components [1,2]. Such studies are facilitated by the presence of two luminescent units in the complex since the extent of intramolecular energy transfer can be monitored either by luminescence quenching at the donor chromophore or/and by the amount of sensitised emission from the acceptor chromophore.

The syntheses of such heteropolynuclear complexes, involving metal complex fragments which are usually kinetically inert, is generally based on a 'complexes as ligands' approach in which a polytopic bridging ligand

has metal units added to its binding domains in a stepwise fashion [1,2]. This requires isolation of 'complex ligands' at the intermediate stages in which metal complexes are prepared which have residual vacant coordination sites for use as ligands in subsequent complexation steps. An extremely wide variety of bridging ligands has been used for this purpose, usually based on bidentate or terdentate polypyridyl (or similar) terminal binding sites to provide the required MLCT excited states of the metal fragments [1].

In this paper, we report the syntheses, characterisation, crystal structures and luminescence properties of a series of mononuclear Re(I) complexes based on the potentially bridging ligands L^1–L^4 (Chart 1), which all contain two pyridyl–imine binding sites; bidentate pyridyl–imine ligands have been examined by others as a synthetically convenient alternative to substituted bipyridines for the study of the photophysical properties of {Re(CO)₃Cl(NN)} chromophores [3]. To illustrate how the mononuclear 'complex ligands'

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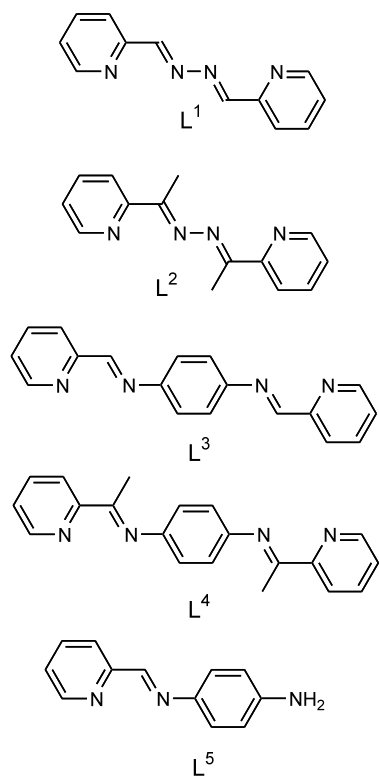*E-mail address:* mike.ward@bristol.ac.uk (M.D. Ward).

Chart 1.

[Re(CO)$_3$Cl(L^n)] ($n = 1–4$) can be used as components for preparation of dinuclear complexes, the complexes [Re(CO)$_3$Cl(μ-L^1)Ln(hfac)$_3$] (Ln = Yb, Er; Hhfac = hexafluoroacetylacetone) have been prepared and structurally characterised, in which the d-block Re(I) chromophore [3,4] and the potentially near-IR luminescent f-block chromophore [5] are connected by the bis(pyridyl–imine) bridging ligand L^1. A mononuclear complex of L^5, arising from hydrolytic decomposition of [Re(CO)$_3$Cl(L^3)], is also described.

Of these ligands, L^1 and L^2, in which the two pyridyl–imine units are directly linked by means of a diazine bridge, have also been of interest because of their ability to form helicates with labile transition-metal ions, which depends on their capacity to twist about the flexible central N–N linkage [6]. A variety of related dinucleating ligands with two pyridyl–imine binding sites separated by aromatic spacers have recently been investigated by Hannon et al. for similar reasons [7].

2. Results and discussion

2.1. Mononuclear Re complexes

The ligands L^1 and L^2 were first prepared and studied by Stratton et al. [6b,6c,6d,6e]. Ligands L^3 and L^4 were simply prepared by condensation of 2-formylpyridine or 2-acetylpyridine, respectively with p-phenylenediamine;

L^3 was formed in much higher yield than L^4 and was noticeably more stable. The mononuclear complexes [Re(CO)$_3$Cl(L^n)] ($n = 1–4$) were prepared by reaction of the appropriate ligand with [Re(CO)$_5$Cl] in a non-polar solvent (typically hexane or toluene) under N$_2$, and usually precipitated in analytically pure form during the reaction. The choice of solvent for the synthesis of these complexes was based on the solubility of the ligands. Whenever possible hexane was used because the mononuclear complex precipitates pure from the reaction; reaction in toluene in contrast requires a large excess of ligands and careful control of temperature to prevent further reaction to the dinuclear complex. The complex [Re(CO)$_3$Cl(L^5)] resulted from an attempt to purify [Re(CO)$_3$Cl(L^3)] by column chromatography; clearly, the non-coordinated imine unit hydrolysed during this process. All five complexes were satisfactorily characterised by elemental analysis and fast atom bombardment mass spectrometry (FAB MS). All complexes are well soluble in THF and chlorinated solvents (although we note that CHCl$_3$ leads to slight decomposition), and insoluble in ether and hexane. The complexes with the methyl-substituted ligands are more readily soluble.

In addition, crystal structures have been obtained for the complexes with L^1, L^2, L^3 and L^5 (see Figs. 1–4, respectively, and Tables 1 and 2). In all four mononuclear complexes, the Re(I) centres have the usual pseudo-octahedral fac-(CO)$_3$N$_2$Cl coordination geometry with unremarkable metal–ligand distances (Table 2). In [Re(CO)$_3$Cl(L^1)], the ligand is slightly twisted, such that the mean planes of the coordinated and pendant pyridyl rings have an angle of 25.5° between them. In [Re(CO)$_3$Cl(L^2)], the steric effect of the methyl groups results in a much larger distortion from planarity, with 65.5° between the mean planes of the free and coordinated pyridyl rings, and a torsion angle of 89.1° about the N(21)–N(22) bond which makes the two methyl groups essentially perpendicular to one another. In [Re(CO)$_3$Cl(L^4)], the ligand is also twisted, with the mean plane of the central phenyl ring being at an angle of 79.7° to that of the coordinated pyridyl ring and 40.6°
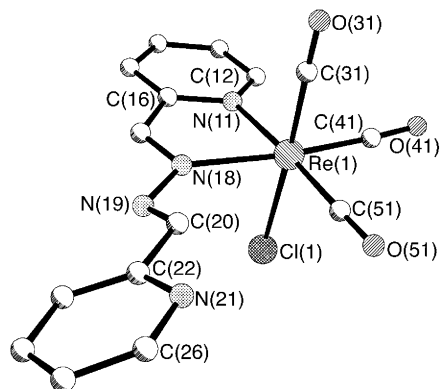
Fig. 1. Molecular structure of [Re(CO)$_3$Cl(L^1)].
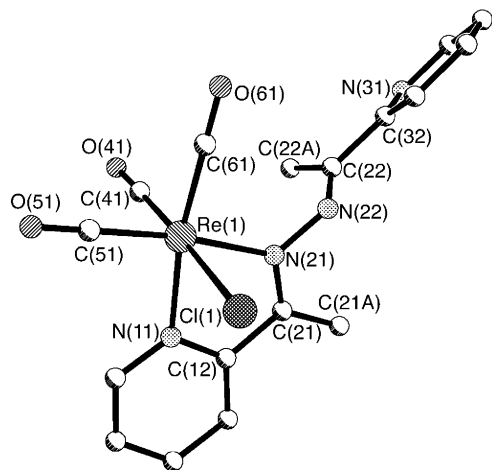
Fig. 2. Molecular structure of [Re(CO)₃Cl(L²)].
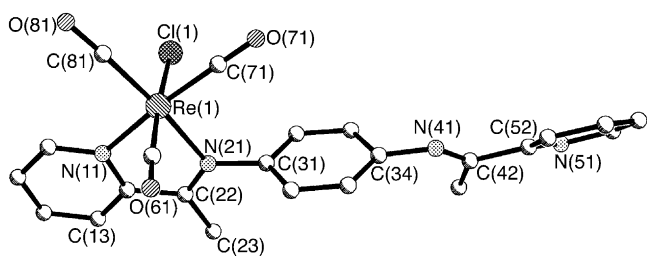
Fig. 3. Molecular structure of [Re(CO)₃Cl(L⁴)].
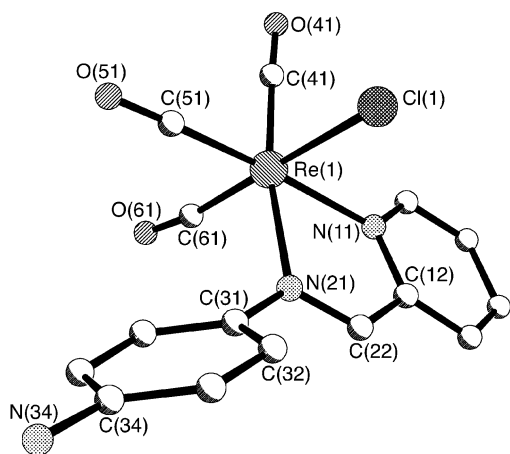
Fig. 4. Molecular structure of [Re(CO)₃Cl(L⁵)].

to that of the pendant pyridyl ring. In [Re(CO)$_3$Cl(L^5)], the mean plane of the pendant phenyl ring is at an angle of 53.9° with respect to the coordinated pyridyl ring. In all of [Re(CO)$_3$Cl(L^n)] ($n = 1, 2, 4$) the arrangement of pyridyl and imino N-donors at the pendant coordination site is approximately *transoid* to prevent unfavourable electronic interactions between the two lone pairs.

The electronic spectra of [Re(CO)$_3$Cl(L^n)] ($n = 1–4$) all show a transition in the 400–450 nm range which may be assigned as a Re → imino–pyridine MLCT

process, characteristic of the {Re(CO)$_3$Cl(diimine)} chromophore (Fig. 5) [3,4]. For the complexes with L^1 and L^2, these are clearly defined maxima, with the transition in [Re(CO)$_3$Cl(L^1)] being at considerably lower energy than the analogous transition in [Re(CO)$_3$Cl(L^2)]; we ascribe this to the fact that L^1 has a more nearly planar geometry (see crystal structures above), so the acceptor π^* orbital is more extensively delocalised and hence lower in energy than that for L^2. For the complexes with L^3 and L^4, the MLCT transition is less clearly defined due to an adjacent and more intense ligand-centred transition, but the same pattern is evident with the more substituted (and hence twisted) ligand L^4 resulting in a higher-energy MLCT transition. Examination of the luminescence properties in CH$_2$Cl$_2$ at room temperature showed that in all cases the emission is very weak ($\phi < 10^{-4}$). For [Re(CO)$_3$Cl(L^2)] the emission maximum is at approximately 650 nm, with $\tau < 6$ ns; for [Re(CO)$_3$Cl(L^3)] the emission maximum is at approximately 730 nm with $\tau < 10$ ns. For the other two complexes (with L^1 and L^4), the luminescence is so weak that no quantification of the parameters is possible.

2.2. Dinuclear Re–Ln complexes

To exemplify the use of these mononuclear 'complex ligands' for the syntheses of dinuclear complexes, the heterodinuclear complexes [Re(CO)$_3$Cl(μ-L^1)Ln(hfac)$_3$] (Ln = Er, Yb) were prepared by reaction of [Re(CO)$_3$Cl(μ-L^1)] with the appropriate [Ln(hfac)$_3$]· 2H$_2$O in a mixture of benzene and heptane. Simply mixing the two components in a 1:1 ratio, followed by slow evaporation over a period of several days, give high yields of the heterodinuclear Re–Ln adducts. This preparation exploits the fact that neutral 6-coordinate complexes of the type [Ln(dik)$_3$] (where 'dik' is a chelating 1,3-diketonate monoanion) form 8-coordinate adducts [Ln(dik)$_3$(NN)] with bidentate N-donor diimine ligands [8]. Coordination of the electropositive lanthanide fragment to the second coordination site results in a red-shift of the Re-based MLCT transition from 437 nm
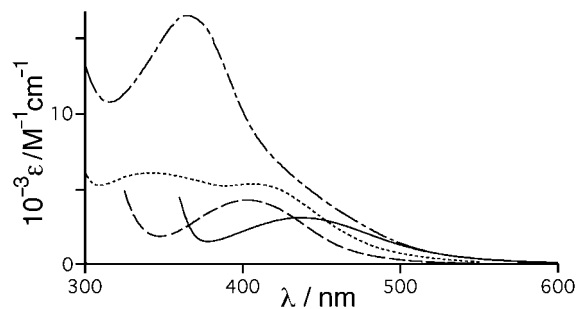

Fig. 5. Electronic spectra of mononuclear complexes [Re(CO)$_3$Cl(L^n)] ($n = 1$, ——; $n = 2$, – – – –; $n = 3$, –●–●–●–; $n = 4$, ●●●●●).

Table 1
Crystallographic data [a]

Compound	[Re(CO)₃Cl(L¹)]	[Re(CO)₃Cl(L²)]	[Re(CO)₃Cl(L⁴)]	[Re(CO)₃Cl(L⁵)]	[Re(CO)₃Cl(L¹)Yb(hfac)₃]	[Re(CO)₃Cl(L¹)Er(hfac)₃]
Empirical formula	$C_{15}H_{10}ClN_4O_3Re$	$C_{17}H_{14}ClN_4O_3Re$	$C_{23}H_{18}ClN_4O_3Re$	$C_{15}H_{11}ClN_3O_3Re$	$C_{30}H_{13}ClF_{18}N_4O_9ReYb$	$C_{30}H_{13}ClErF_{18}N_4O_9Re$
Formula weight	515.9	543.97	620.06	502.92	1310.13	1304.35
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$	$P2(1)/c$	$P2(1)/n$	$P2(1)/n$	$P2(1)/n$
Unit cell dimensions						
a (Å)	6.9851(12)	34.369(5)	11.9811(12)	12.8895(13)	11.6833(13)	11.684(2)
b (Å)	9.0303(19)	6.4829(12)	15.035(2)	8.9099(11)	29.425(5)	29.423(6)
c (Å)	13.1710(15)	17.195(3)	13.6591(17)	13.907(3)	12.0644(14)	12.034(3)
α (°)	81.313(19)	90	90	90	90	90
β (°)	84.537(15)	111.191(9)	114.990(9)	99.593(12)	104.981(10)	104.86(2)
γ (°)	72.379(13)	90	90	90	90	90
V (Å³)	781.6(2)	3572.3(10)	2230.2(5)	1574.8(4)	4006.5(9)	3998.6(15)
Z	2	8	4	4	4	4
D_{calc} (Mg m⁻³)	2.192	2.023	1.847	2.121	2.172	2.167
Data/restraints/parameters	3566/0/217	4098/0/237	5100/34/286	3627/0/208	9136/0/577	9161/0/577
μ (mm⁻¹)	7.966	6.978	5.601	7.903	5.544	5.315
$R_1 [I > 2\sigma(I)]$, wR_2 [a]	0.0315, 0.0717	0.0261, 0.0574	0.0309, 0.0695	0.0258, 0.0563	0.0349, 0.0813	0.0331, 0.0688

[a] The value of R_1 is based on selected data with $I > 2\sigma(I)$; the value of wR_2 is based on all data.

in mononuclear [Re(CO)₃Cl(L¹)] to 457 nm in dinuclear [Re(CO)₃Cl(μ-L¹)Ln(hfac)₃].

The crystal structures of the complexes with Ln = Yb and Er (which are isostructural and isomorphous) are shown in Figs. 6 and 7, respectively (see also Table 3). In both cases, binding of the lanthanide fragment to the second bidentate site of L¹ has resulted in two significant changes in the conformation of the bridging ligand L¹. Firstly, the pyridyl and the imine N atoms at the second coordination site are now necessarily mutually *cisoid* so that they can coordinate. Secondly, there is a greater twist about the central N–N bond, such that the angle between the mean planes of the two pyridyl rings
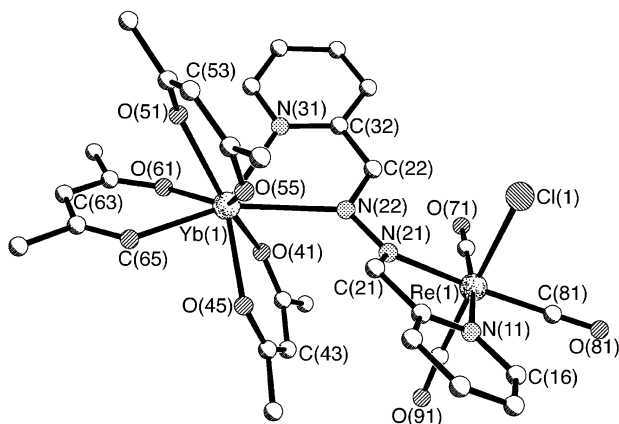

Fig. 6. Molecular structure of [Re(CO)₃Cl(μ-L¹)Yb(hfac)₃] with F atoms omitted for clarity.

is increased to 38.3° (M = Yb) or 38.5° (M = Er). The lanthanide ion in each case is 8-coordinate with an approximately square-antiprismatic coordination geometry; for M = Yb the two (approximate) square planes are formed from O(51)/O(55)/N(31)/N(22) and O(41)/O(45)/O(61)/O(65); for M = Er the two planes are formed from O(51)/O(55)/O(61)/O(65) and N(22)/N(31)/O(41)/O(45).

Heterodinuclear complexes in which potentially luminescent d- and f-block chromophores are connected are rare [9], but are desirable targets because of the possibility of studying photoinduced energy- and electron-transfer between components in the way that is very well known for complexes based solely on d-block luminophores [1,2]. Although the mononuclear Re complexes of L¹–L⁴ are only weakly luminescent at room temperature, the possibility of sensitised emission from suitable lanthanide components by excitation of the Re-based MLCT absorption still exists, especially at lower temperatures. Such photophysical studies are in progress and will be reported in due course.

3. Experimental

3.1. General details

The ligands L¹ and L² were prepared according to the literature methods [6b,6e]. [Yb(hfac)₃]·2H₂O and
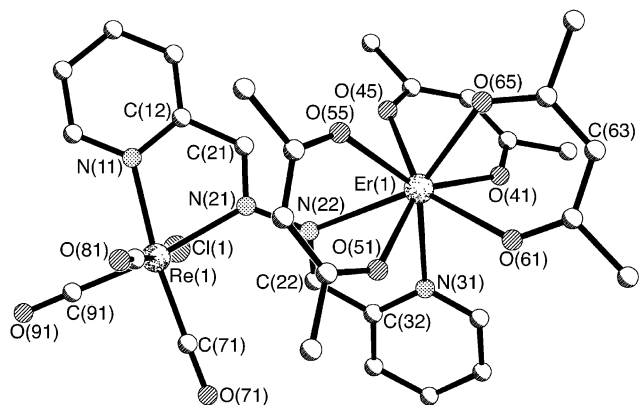
Fig. 7. Molecular structure of [Re(CO)$_3$Cl(μ-L^1)Er(hfac)$_3$] with F atoms omitted for clarity. This view emphasises the approximately square-antiprismatic geometry about the Er centre.

[Er(hfac)$_3$]·2H$_2$O were also prepared by the published method [10]. Organic reagents used for syntheses of L^3 and L^4, and metal complexes [Re(CO)$_5$Cl], were obtained from Aldrich and used as received. Electron-impact (EI) and FAB mass spectra were recorded on a VG-Autospec instrument; proton NMR spectra were recorded on a JEOL GX-270 (270 MHz) spectrometer.

Table 2
Selected bond distances (Å) for the mononuclear Re(I) complexes

[Re(CO)$_3$Cl(L^1)]	
Re(1)–C(41)	1.915(5)
Re(1)–C(31)	1.932(6)
Re(1)–C(51)	1.933(6)
Re(1)–N(11)	2.176(5)
Re(1)–N(18)	2.190(5)
Re(1)–Cl(1)	2.4775(14)
[Re(CO)$_3$Cl(L^2)]	
Re(1)–C(41)	1.913(4)
Re(1)–C(51)	1.919(4)
Re(1)–C(61)	1.919(4)
Re(1)–N(21)	2.152(3)
Re(1)–N(11)	2.176(3)
Re(1)–Cl(1)	2.4862(10)
[Re(CO)$_3$Cl(L^4)]	
Re(1)–C(61)	1.909(8)
Re(1)–C(61A)	1.911(14)
Re(1)–C(71)	1.914(4)
Re(1)–C(81)	1.918(4)
Re(1)–N(21)	2.156(3)
Re(1)–N(11)	2.167(3)
Re(1)–Cl(1)	2.446(2)
Re(1)–Cl(1A)	2.449(7)
[Re(CO)$_3$Cl(L^5)]	
Re(1)–C(41)	1.916(4)
Re(1)–C(51)	1.925(5)
Re(1)–C(61)	1.945(5)
Re(1)–N(11)	2.163(3)
Re(1)–N(21)	2.179(3)
Re(1)–Cl(1)	2.4839(11)

UV–Vis absorption spectra were recorded on a Perkin–Elmer Lambda 2 spectrometer.

3.2. Synthesis of L^3

This ligand was simply prepared by mixing together hot ethanolic solutions of 2-formylpyridine (2 equiv.) and 1,4-diaminobenzene (1 equiv.), upon which a yellow precipitate quickly formed which was filtered off, recrystallised from hot C$_2$H$_5$OH, and dried in vacuo. Yield: 95%. *Anal*. Found: C, 75.7; H, 4.9; N, 19.5. Required for C$_{18}$H$_{14}$N$_4$: C, 75.5; H, 4.9; N, 19.6%. EI MS: *m/z* 286 (*M*$^+$). ^{1}H NMR (270 MHz, CD$_2$Cl$_2$): δ 8.70 (2H, ddd, pyridyl H^6), 8.64 (2H, s, C*H*=N), 8.23 (2H, d, pyridyl H^3), 7.83 (2H, td, pyridyl H^4), 7.38 (6H, m, pyridyl H^5 and phenyl). L^3 has been prepared independently by Hannon and co-workers [11].

3.3. Synthesis of L^4

A mixture of 2-acetylpyridine (3.0 g, 25 mmol), 1,4-diaminobenzene (1.34 g, 12 mmol) and toluenesulphonic acid (0.1 g, catalytic amount) was refluxed in dry, degassed toluene (40 cm^3) for 1 h. The reaction mixture was then evaporated to dryness to leave a brownish-red mixture of oil and crystals. The mixture was extracted with boiling hexane, giving a yellow extract and leaving a dark coloured residue. The hexane extract was evaporated to dryness to give mixture of oil and crystals. This residue was recrystallized twice from the minimum amount of C$_2$H$_5$OH to give 1.01 g (26%) of the ligand L^4 as a bright yellow solid. This ligand should be stored at 0 °C to prevent its discoloration. *Anal*. Found: C, 77.1; H, 5.6; N, 17.9. Required for C$_{20}$H$_{18}$N$_4$: C, 76.4; H, 5.8; N, 17.8%. EI MS: *m/z* 314 (*M*$^+$). NMR (270 MHz, CD$_2$Cl$_2$): δ 8.64 (2H, ddd, pyridyl H^6), 8.28 (2H, d, pyridyl H^3), 7.80 (2H, td, pyridyl H^4), 7.38 (2H, ddd, pyridyl H^5), 6.85 (4H, s, phenyl), 2.39 (6H, s, Me). L^4 has been prepared independently by Hannon and co-workers [11].

3.4. Synthesis of [Re(CO)$_3$Cl(L^1)]

A mixture of [Re(CO)$_5$Cl] (130 mg, 0.36 mmol) and L^1 (114 mg, 0.54 mmol, excess) in dry, degassed toluene/CH$_2$Cl$_2$ (30 cm^3, 3:1 v/v) was heated to reflux for 4 h under N$_2$. During the reaction, the solution gradually changed colour from yellow to deep red, and a brownish-red precipitate formed. The solution was then cooled to 0 °C, and the precipitate was filtered off, washed with hexane and ether, and vacuum dried to give 136 mg (73%) of pure [Re(CO)$_3$Cl(L^1)]. Decomposition of the complex was observed when column chromatography on alumina was attempted. *Anal*. Found: C, 34.7; H, 1.6; N, 10.4. Required for C$_{15}$H$_{10}$ClN$_4$O$_3$Re: C, 34.9; H, 2.0; N, 10.9%. FAB

Table 3
Selected bond distances (Å) and angles (°) for the dinuclear complexes [Re(CO)$_3$Cl(L^1)Yb(hfac)$_3$]: Ln = Er (left) or Yb (right)

Bond distances			
Er(1)–O(61)	2.287(3)	Yb(1)–O(61)	2.274(4)
Er(1)–O(45)	2.294(3)	Yb(1)–O(55)	2.276(3)
Er(1)–O(55)	2.294(3)	Yb(1)–O(51)	2.276(4)
Er(1)–O(41)	2.295(3)	Yb(1)–O(45)	2.281(3)
Er(1)–O(51)	2.307(3)	Yb(1)–O(41)	2.293(4)
Er(1)–O(65)	2.309(3)	Yb(1)–O(65)	2.305(4)
Er(1)–N(31)	2.494(4)	Yb(1)–N(31)	2.472(4)
Er(1)–N(22)	2.627(3)	Yb(1)–N(22)	2.617(4)
Re(1)–C(81)	1.901(5)	Re(1)–C(91)	1.912(6)
Re(1)–C(71)	1.919(5)	Re(1)–C(71)	1.919(6)
Re(1)–C(91)	1.924(5)	Re(1)–C(81)	1.919(6)
Re(1)–N(11)	2.169(4)	Re(1)–N(11)	2.178(4)
Re(1)–N(21)	2.178(3)	Re(1)–N(21)	2.186(4)
Re(1)–Cl(1)	2.4676(12)	Re(1)–Cl(1)	2.4717(14)
Bond angles			
O(61)–Er(1)–O(45)	144.04(11)	O(61)–Yb(1)–O(55)	144.52(13)
O(61)–Er(1)–O(55)	120.17(11)	O(61)–Yb(1)–O(51)	75.00(14)
O(45)–Er(1)–O(55)	79.34(10)	O(55)–Yb(1)–O(51)	73.76(13)
O(61)–Er(1)–O(41)	74.89(11)	O(61)–Yb(1)–O(45)	119.76(14)
O(45)–Er(1)–O(41)	73.47(11)	O(55)–Yb(1)–O(45)	79.07(12)
O(55)–Er(1)–O(41)	144.52(12)	O(51)–Yb(1)–O(45)	143.95(13)
O(61)–Er(1)–O(51)	72.80(12)	O(61)–Yb(1)–O(41)	72.57(14)
O(45)–Er(1)–O(51)	142.96(10)	O(55)–Yb(1)–O(41)	142.74(13)
O(55)–Er(1)–O(51)	74.02(11)	O(51)–Yb(1)–O(41)	139.65(14)
O(41)–Er(1)–O(51)	139.90(11)	O(45)–Yb(1)–O(41)	74.72(12)
O(61)–Er(1)–O(65)	73.97(11)	O(61)–Yb(1)–O(65)	74.26(13)
O(45)–Er(1)–O(65)	83.05(10)	O(55)–Yb(1)–O(65)	82.87(12)
O(55)–Er(1)–O(65)	76.62(10)	O(51)–Yb(1)–O(65)	77.40(13)
O(41)–Er(1)–O(65)	77.84(11)	O(45)–Yb(1)–O(65)	76.10(13)
O(51)–Er(1)–O(65)	114.44(11)	O(41)–Yb(1)–O(65)	115.18(13)
O(61)–Er(1)–N(31)	78.94(12)	O(61)–Yb(1)–N(31)	79.25(14)
O(45)–Er(1)–N(31)	107.52(11)	O(55)–Yb(1)–N(31)	107.26(14)
O(55)–Er(1)–N(31)	137.81(11)	O(51)–Yb(1)–N(31)	73.61(14)
O(41)–Er(1)–N(31)	73.42(12)	O(45)–Yb(1)–N(31)	138.30(13)
O(51)–Er(1)–N(31)	77.61(12)	O(41)–Yb(1)–N(31)	77.31(14)
O(65)–Er(1)–N(31)	144.64(11)	O(65)–Yb(1)–N(31)	144.80(13)
O(61)–Er(1)–N(22)	133.87(11)	O(61)–Yb(1)–N(22)	133.86(13)
O(45)–Er(1)–N(22)	76.91(10)	O(55)–Yb(1)–N(22)	76.71(12)
O(55)–Er(1)–N(22)	77.28(11)	O(51)–Yb(1)–N(22)	117.59(13)
O(41)–Er(1)–N(22)	117.05(11)	O(45)–Yb(1)–N(22)	77.51(13)
O(51)–Er(1)–N(22)	72.50(11)	O(41)–Yb(1)–N(22)	72.14(13)
O(65)–Er(1)–N(22)	149.53(10)	O(65)–Yb(1)–N(22)	149.16(13)
N(31)–Er(1)–N(22)	64.67(11)	N(31)–Yb(1)–N(22)	64.75(13)

MS: m/z 539 (25%, {M+Na}$^+$); 516 (12%, M^+); 479 (18%, {M−Cl}$^+$). IR (CH$_2$Cl$_2$), cm^{-1}: 2028, 1929, 1907. UV–Vis (CH$_2$Cl$_2$), λ_{max} (nm) (ε, M^{-1} cm^{-1}): 437 (3070), 312 (20600). X-ray quality crystals were grown by slow evaporation of a CH$_2$Cl$_2$/hexane solution of the complex.

3.5. Synthesis of [Re(CO)$_3$Cl(L^2)]

A mixture of [Re(CO)$_5$Cl] (83 mg, 0.23 mmol) and L^2 (158 mg, 0.66 mmol, excess) in degassed hexane (30 cm^3) was heated to reflux for 4 h under N$_2$, during which time an orange precipitate formed. The solution was filtered

while hot, and the precipitate was washed with hexane and ether and vacuum dried to give 83 mg (66%) of orange [Re(CO)$_3$Cl(L^2)]. The complex obtained was analytically pure, however, if necessary it could be additionally purified by column chromatography on alumina eluting with CH$_2$Cl$_2$. *Anal*. Found: C, 37.8; H, 2.2; N, 9.9. Required for C$_{17}$H$_{14}$ClN$_4$O$_3$Re: C, 37.5; H, 2.6; N, 10.3%. FAB MS: m/z 568 (8%, {M+Na}$^+$); 545 (13%, M^+); 509 (100%, {M−Cl}$^+$). Successive loss of the three CO and the chloride ligands was also apparent. IR (CH$_2$Cl$_2$), cm^{-1}: 2025, 1927, 1900. UV–Vis (CH$_2$Cl$_2$), λ_{max} (nm) (ε, M^{-1} cm^{-1}): 402 (4260), 289 (19100). X-ray quality crystals were grown by slow evaporation of a CH$_2$Cl$_2$/hexane solution of the complex.

3.6. Synthesis of [Re(CO)$_3$Cl(L^3)] and of [Re(CO)$_3$Cl(L^5)]

A mixture of [Re(CO)$_5$Cl] (73 mg, 0.20 mmol) and L^3 (277 mg, 0.97 mmol, excess) were heated at 60–65 °C for 6 h in dry degassed toluene (30 cm^3) under N$_2$. The relatively low temperature and the large excess of ligand are necessary to prevent formation of the undesired dinuclear complex. During the course of reaction a dark orange precipitate formed. The reaction mixture was cooled to room temperature (r.t.); the precipitate was filtered off, and washed with hexane and ether to give 80 mg (67%) of [Re(CO)$_3$Cl(L^3)]. *Anal*. Found: C, 42.6; H, 2.0; N, 9.4. Required for C$_{21}$H$_{14}$ClN$_4$O$_3$Re: C, 42.6; H, 2.4; N, 9.5%. FAB MS: m/z 593 (26%, {M+H}$^+$), 557 (23%, {M−Cl}$^+$). IR (CH$_2$Cl$_2$), cm^{-1}: 2026, 1928, 1902. UV–Vis (CH$_2$Cl$_2$), λ_{max} (nm) (ε, M^{-1} cm^{-1}): 365 (16500), 275 (sh) (20600), 250 (sh) (22500).

[Re(CO)$_3$Cl(L^3)] was usually obtained pure by this method, but in one case was slightly contaminated with the dinuclear complex so was subjected to column chromatography. A 129 mg sample of crude [Re(CO)$_3$Cl(L^3)] was dissolved in THF and loaded on to an alumina column. Elution with acetone/CH$_2$Cl$_2$ (1:4) gave a main orange band which after evaporation afforded 30 mg of a red product which proved to be the decomposition product [Re(CO)$_3$Cl(L^5)]. *Anal*. Found: C, 35.7; H, 2.1; N, 7.5. Required for C$_{15}$H$_{11}$ClN$_3$O$_3$Re: C, 35.8; H, 2.2; N, 8.4%. FAB MS: m/z 526 (6%, {M+Na}$^+$), 503 (20%, M^+), 468 (38%, {M−Cl}$^+$). X-ray quality crystals were grown by slow evaporation of a THF/heptane solution of the complex.

3.7. Synthesis of [Re(CO)$_3$Cl(L^4)]

A mixture of [Re(CO)$_5$Cl] (100 mg, 0.28 mmol) and L^4 (174 mg, 0.55 mmol, excess) in dry degassed dry hexane (90 cm^3) was heated to reflux for 4 h under N$_2$, during which time an orange precipitate formed. The reaction mixture was filtered while hot, and the pre-

cipitate was washed with hexane and ether to give 132 mg (77%) of bright orange [Re(CO)$_3$Cl(L^4)]. The complex could be handled in air, however, it is recommended to store it under N$_2$ and at 0 °C, because a change of colour from bright orange to brownish-orange was observed after 1 month of storage in air at r.t. *Anal*. Found: C, 44.7; H, 2.7; N, 8.9. Required for C$_{23}$H$_{18}$ClN$_4$O$_3$Re: C, 44.6; H, 2.9; N, 9.0%. FAB MS: *m/z* 643 (12%, {*M*+Na}$^+$), 621 (8%, *M*$^+$), 585 (18%, {*M*−Cl}$^+$). UV–Vis (CH$_2$Cl$_2$), λ_{max} (nm) (ε, M^{-1} cm^{-1}): 407 (sh) (5300), 341 (6050), 271 (sh) (27500), 237 (36300). X-ray quality crystals were grown by slow evaporation of a THF/heptane solution of the complex.

3.8. Syntheses of [Re(CO)$_3$Cl(μ-L^1)Ln(hfac)$_3$] (Ln = Yb, Er)

These were all prepared by slow evaporation of a mixed C$_6$H$_6$–heptane solution (1:1, total volume 10–15 cm^3) containing equimolar amounts of [Re(CO)$_3$Cl(L^1)] and the appropriate [Ln(hfac)$_3$]·2H$_2$O (typically, 0.1 mmol). After 10–14 days large, dark red crystals of the adducts formed in approximately 90% yield. Data for [Re(CO)$_3$Cl(μ-L^1)Er(hfac)$_3$] follow. [Re(CO)$_3$Cl(L^1)] (40 mg, 78 μmol) and [Er(hfac)$_3$]·2H$_2$O (64 mg, 78 μmol) gave 94 mg (93% yield) of the dinuclear product. *Anal*. Found: C, 27.6; H, 1.0; N, 4.3. Required for C$_{30}$H$_{13}$ClErF$_{18}$N$_4$O$_9$Re: C, 27.9; H, 0.9; N, 4.3%. IR (CH$_2$Cl$_2$), cm^{-1}: 2032, 1931 (asymmetric peak). UV–Vis (CH$_2$Cl$_2$), λ_{max} (nm) (ε, M^{-1} cm^{-1}): 457 (2570), 293 (51800).

3.9. X-ray crystallography

Details of the crystal, data collection and refinement parameters for the new structures are summarised in Table 1. In each case, structure solution and refinement used the SHELX package (version 5.03) comprising SHELXS-97 [12] and SHELXL-97 [13]; absorption corrections were applied to the data using SADABS [14]. H atoms were included in calculated positions with isotropic thermal parameters, and refined as riding atoms. In [Re(CO)$_3$Cl(L^4)], the Cl ligand and the CO group *trans* to it [C(61) and O(61)] were mutually disordered, with each group being present in lone location with a site occupancy of 75% and the other with a site occupancy of 25%. Geometric restraints were used to ensure that the Re–Cl, Re–C and C–O separations in the major and minor disorder components were similar to one another. The atoms involved in the minor component of the CO disorder [atoms C(61)A and O(61)A] gave unreasonable anisotropic thermal parameters and were accordingly refined isotropically. The structural determinations of the remaining mononuclear complexes [Re(CO)$_3$Cl(L^n)] (*n* = 1, 2, 5) were straightforward; large residual electron-density peaks close to

the metal centre for the complex with L^1 are associated with absorption effects and are not chemically significant. For both dinuclear complexes [Re(CO)$_3$Cl(μ-L^1)Ln(hfac)$_3$] the thermal parameters associated with the F atoms on the CF$_3$ groups are considerably larger than for all other non-H atoms due to the facile rotational motion of these groups.

3.10. Luminescence studies

Luminescence spectra were obtained from air-equilibrated dilute solutions (2 × 10^{-5} M) of the investigated complexes by using a Spex Fluorolog II spectrofluorimeter, equipped with a Hamamatsu R928 phototube. The spectra were uncorrected, and the determination of the luminescence quantum yield, Φ was done with reference to [Ru(bpy)$_3$]$^{2+}$ as a standard (Φ = 0.028 in air-equilibrated water) and by using a procedure illustrated elsewhere [2]. Luminescence lifetimes were obtained using an IBH single-photon counting spectrometer equipped with a nitrogen-filled thyratron gated lamp (λ_{exc} 337 or 358 nm). The uncertainty in band maximum and lifetime values is within 2 nm and 8%, respectively.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 197699–197704. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.ac.uk; or www: http://www.ccdc.cam.ac.uk).

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