Synthesis and Properties of Polynuclear Complexes containing {Mo(NO)[HB(dmpz)₃]Cl} Metal Centres Axially bound to a Ru(tpp) Core (dmpz = 3,5-dimethylpyrazol-1-yl; tpp = meso-5,10,15,20-tetraphenylporphyrinate)

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A series of mononuclear complexes [Mo(NO){HB(dmpz)₃}Cl(L)] [dmpz = 3,5-dimethylpyrazol-1-yl; L = a potentially bridging ligand of which one terminus (pyridyl or phenolate) is attached to the Mo and the second terminus (pyridyl) is pendant] were attached to the axial positions of a Ru(tpp) core (tpp = meso-5,10,15,20-tetraphenylporphyrinate) via the pendant pyridyl groups. By using [Ru(tpp)-(CO)(EtOH)], of which only the axial EtOH ligand is substitution labile, binuclear complexes [{(OC)(tpp)Ru}(μ-L){Mo(NO)[HB(dmpz)₃]Cl}] were prepared. With [Ru(tpp)(thf)₂] (thf = tetrahydrofuran), in which both thf ligands are labile, the trinuclear complexes [{Cl[HB(dmpz)₃](ON)Mo}-(μ-L){Ru(tpp)}(μ-L){Mo(NO)[HB(dmpz)₃]Cl}] were prepared. The new complexes have been thoroughly characterised by ¹H NMR, fast atom bombardment mass spectrometry, IR, UV/VIS and EPR spectroscopy and electrochemistry as appropriate. Weak electrochemical interactions between the molybdenum groups and the Ru(tpp) core are apparent. In the trinuclear complexes with two axial paramagnetic molybdenum groups (17 valence-electron configuration) a weak spin-exchange interaction between the two remote molybdenum centres can be detected when the intermediate bridging ligands L are 4,4'-bipyridine but not when L is 3,3'-dimethyl-4,4'-bipyridine, possibly due to an increased dihedral twist of the two bridging ligands in the latter case.

Porphyrins and metalloporphyrins are frequently used as components in supramolecular systems due to their desirable photochemical and redox properties: the principal interest in such supramolecular species is to model naturally occurring photosynthetic processes,[1] although they are also becoming popular in the design and synthesis of 'unnatural products' where the same physicochemical properties make them appealing components as building blocks for inclusion in supramolecules with specific electronic, steric and photophysical properties.[2] Almost without exception, however, the porphyrin subunit is incorporated into the supramolecule via covalent modification of the periphery, which can involve inconvenient synthetic methods, especially if only one substituent is to be attached. With the exception of one-dimensional polymers,[3] there have been few attempts to construct polymetallic species by attaching metal complexes at the axial metal sites via appropriate bridging ligands, which is perhaps surprising since this is a potentially simple route to the modular construction of high-nuclearity complexes.

We have recently prepared a series of mononuclear complexes of the {Mo(NO)[HB(dmpz)₃]Cl} moiety (dmpz = 3,5-dimethylpyrazol-1-yl) with some potentially bridging bis-(pyridyl) and pyridyl–phenol ligands; in these complexes the pyridyl terminus of the bridging ligand is free and hence available for ligation to a second metal centre.[4,5] These molybdenum complexes are of particular interest for use as building blocks in polymetallic species for two reasons: (i) they are redox active and show chemically reversible electrochemical behaviour at potentials which are sensitive to the nature of the sixth ligand and its remote substituents; (ii) EPR spectroscopy of the 17e species is a powerful diagnostic tool for examining the extent of interaction of the unpaired electron across the bridging ligand to other groups via spin–spin exchange. We describe here the use of these complexes as building blocks in the construction of some new bi- and tri-nuclear complexes, by ligation of the pendant pyridyl groups to the axial sites

of a Ru(tpp) centre (tpp = dianion of meso-5,10,15,20-tetraphenylporphyrin), and some physical properties of the new complexes.

Experimental

The apparatus and instrumentation used for the physical measurements has been described previously.[4,5] The compounds L¹,[5] [Ru(tpp)(CO)(EtOH)],[6] [{Ru(tpp)(OEt)}₂-(μ-O)]·2H₂O,[6] [Mo(NO){HB(dmpz)₃}Cl₂],[7] and the mononuclear molybdenum complexes used as building blocks (I–VII)[4,5] were prepared as described previously.

Preparations.—Monosubstituted Ru(tpp) *derivatives* **1–8**. All of these were prepared by reaction of equimolar amounts of [Ru(tpp)(CO)(EtOH)] with either L¹ (for **1**) or the appropriate pyridyl-substituted molybdenum complex (I–VII for **2–8** respectively) in CH₂Cl₂ at room temperature.[8] In a representative procedure a mixture of [Ru(tpp)(CO)(EtOH)] (75 mg, 0.095 mmol) and IV (64 mg, 0.098 mmol) in dry CH₂Cl₂ (20 cm³) was stirred overnight at room temperature under N₂. After evaporation of the solvent *in vacuo* the solid residue was purified by column chromatography on alumina (activity III) with CH₂Cl₂–hexane (3:1); the major brown fraction was collected and recrystallised from CH₂Cl₂–hexane to give **5** (129 mg, 95% yield). The yields of the other complexes varied between 70 and 98%.

Disubstituted Ru(tpp) *derivatives* **9–12**. A solution containing [{Ru(tpp)(OEt)}₂(μ-O)]·2H₂O (70 mg, 0.045 mmol) and NaBH₄ (70 mg, excess) in tetrahydrofuran (thf) (6 cm³) under N₂ was stirred at room temperature for 30 min.[6] The mixture was then passed down a short alumina column (grade I, 1 × 5 cm) with thf as eluent. The major brown band was collected. To this was added 3 equivalents of either L¹ (for **9**), I (for **10**), V (for **11**) or VI (for **12**), and the resultant mixture was stirred at room temperature under N₂ for 18 h. After evaporation of

the solvent *in vacuo* the residue was purified by column chromatography on alumina (activity III) with CH_2Cl_2–thf (98:2) and finally recrystallised from CH_2Cl_2–hexane. Yields: 55–60%.

Alternative syntheses of complexes 9 *and* 10. In a nitrogen-flushed quartz Schlenk tube fitted with a reflux jacket was placed dry toluene (50 cm³), [Ru(tpp)(CO)(EtOH)] (120 mg, 0.15 mmol), and either L¹ (80 mg, 0.38 mmol, for 9) or I (0.25 g, 0.40 mmol, for 10). The mixture was irradiated (Hanovia 500 W medium-pressure mercury vapour lamp at a distance of 15 cm from the quartz reaction vessel) under reflux for 25 h.[9] After removal of the solvent *in vacuo*, chromatography on alumina (grade III) with CH_2Cl_2, and recrystallisation of the main band from CH_2Cl_2–hexane, 9 or 10 was obtained in *ca.* 50% yield.

Results and Discussion

Preparation and Characterisation of Complexes.—Complex 1 and the binuclear Ru–Mo complexes 2–8 were prepared in high yield (70–98%) by reaction of [Ru(tpp)(CO)(EtOH)] with a slight excess of either L¹ (for 1) or the appropriate pyridyl-substituted mononuclear molybdenum complex (for 2–8) in CH_2Cl_2. The co-ordinated ethanol of [Ru(tpp)(CO)(EtOH)] is known to be substitution labile and readily replaced by a variety of axial ligands.[8] The axially disubstituted complex 9 and the trinuclear Mo–Ru–Mo complexes 10–12 were prepared by reaction of [Ru(tpp)(thf)₂] (generated *in situ* by treatment of [{Ru(tpp)(OEt)}₂(μ-O)]·2H₂O with NaBH₄)[6] with 2 equivalents of either L¹ (for 9) or the appropriate molybdenum complex (I, V, VI for 10–12 respectively), and purified in the same way. An alternative preparation for 9 and 10 involved reaction of [Ru(tpp)(CO)(EtOH)] with 2 equivalents of L¹ (for 9) or I (for 10) whilst irradiating with a mercury lamp; under these conditions the axial CO ligand of the starting material is labilised in addition to the EtOH ligand.[9] This method did not prove practicable for preparation of the trinuclear species 11 and 12 since partial decomposition of the pyridyl-substituted molybdenum fragments occurred.

The complexes were all characterised by elemental analysis, IR and fast-atom bombardment (FAB) mass spectroscopy
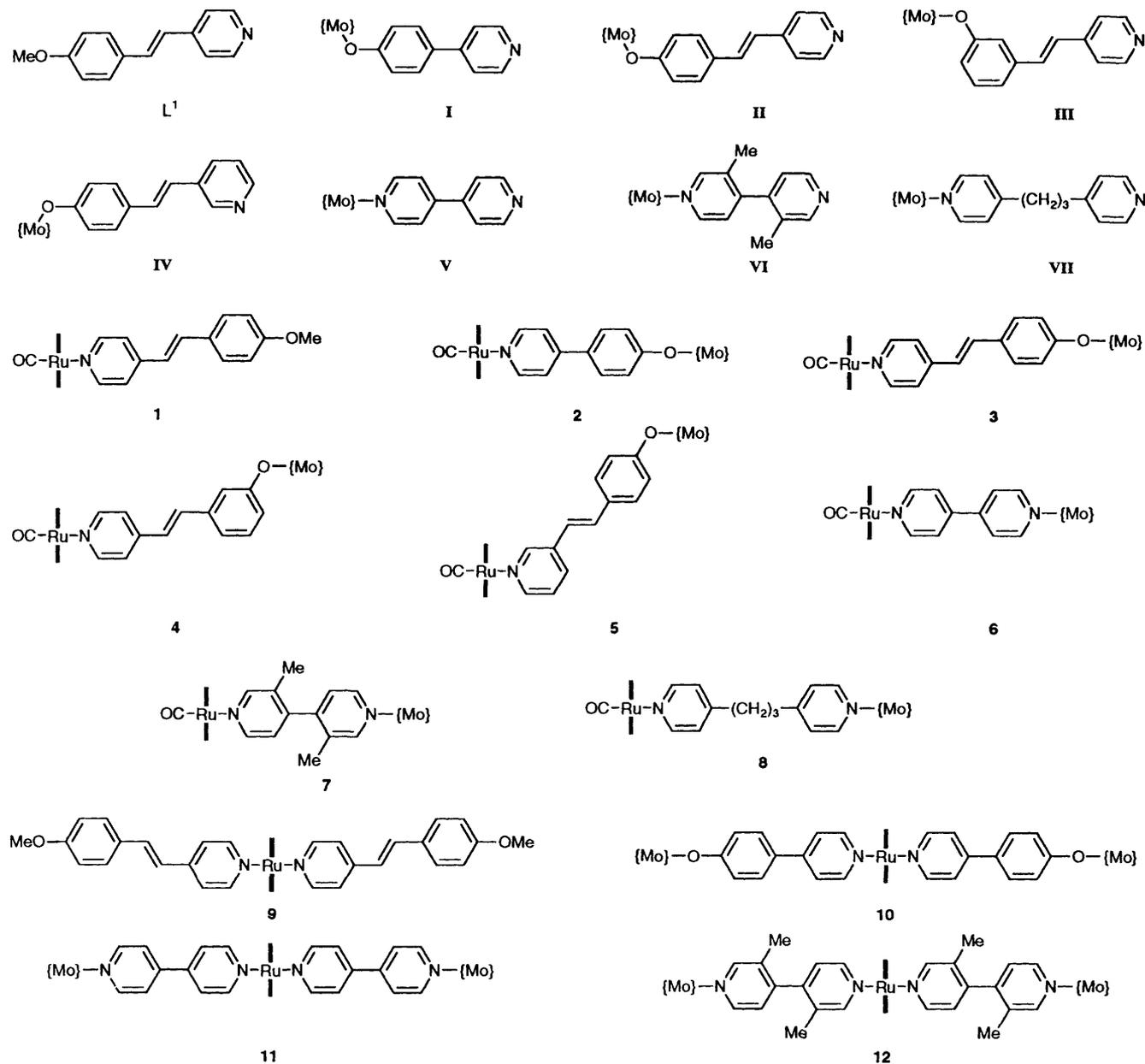
{Mo} = Mo(NO)[HB(dmpz)₃]Cl

Vertical lines represent the tpp ligand viewed edge-on

(Table 1). In the FAB mass spectra all complexes exhibited a molecular ion peak cluster at the appropriate mass, together with fragments due to loss of axial groups and detachment of monodentate ligands (NO, Cl) from the molybdenum centres. The IR spectra show characteristic CO vibrations for the carbonyl ligand bound to the Ru(tpp) core in the mono-substituted Ru(tpp) derivatives, and NO vibrations for the axial molybdenum fragments, at *ca.* 1685 cm⁻¹ for the phenoxy-substituted molybdenum centres of *ca.* 1610 cm⁻¹ for the pyridyl-substituted ones.[5]

In addition, ¹H NMR spectra were recorded for the dia-magnetic complexes (Table 2). As well as complexes 1 and 9, which bear one or two axial L¹ ligands respectively on the Ru(tpp) core, the phenoxy-substituted molybdenum centres of 2–5 and 10 are diamagnetic due to their 16 valence-electron configuration (the pyridyl-substituted molybdenum centres have 17 valence electrons).[5] These ¹H NMR data have some interesting features. First, the *o*-protons (H² and H⁶) for the peripheral phenyl rings on the tpp core are inequivalent when the ruthenium bears two different axial substituents (complexes 1–5).[8] The phenyl rings are twisted perpendicular to the porphyrin plane, such that H² and H⁶ lie on opposite faces of that plane and will be pointing directly towards the (different) axial substituents. In the most extreme case (complex 5) the chemical shifts of H² and H⁶ differ by nearly 0.5 ppm. The effect is not apparent for the *m*-protons (H³ and H⁵) which are coincident in all cases. Secondly, the ring current of the aromatic porphyrin system results in electronic shielding of the protons on the axial ligand, which decreases steadily with distance; this is a common phenomenon in axially substituted porphyrin complexes. Thus for 1 the upfield shift of the ligand protons on co-ordination varies from 7.07 ppm for the protons nearest the ring, pyridyl H² and H⁶, to 0.17 ppm for the terminal methyl group. For 5, substitution of the pyridyl ring in the 3 position results in four separate pyridyl signals each of intensity 1 H, rather than (as for all of the others) two obvious doublets each of intensity 2 H. In this case these protons were difficult to assign since, in addition to the more complex pattern and weaker signals, the signals from the H² and H⁶ protons appeared to suffer from quadrupolar broadening caused by the adjacent N atom. The appearance of these two signals and the coupling patterns of the other two from the pyridyl ring (which may be second order) varied unpredictably between spectra of otherwise well characterised samples, so these assignments should be regarded as tentative. All other signals in the NMR spectrum of 5 could be assigned readily and all other analytical data for 5 are as expected.

Electrochemical Properties.—The complexes were examined by cyclic and square-wave voltammetry; the results are summarised in Table 3. Redox processes centred on both the Ru(tpp) and molybdenum fragments are apparent in the positions to be expected for the component parts.[4,5,10,11] All of the axially monosubstituted Ru(tpp) derivatives 1–8 display two characteristic oxidations (columns C and D) of the Ru(tpp) unit, each of which only varies within a narrow range. The first oxidation is known to be ligand-based[12,13] whereas the second is a Ruᴵᴵ–Ruᴵᴵᴵ couple.[11] In a few cases we observed a third oxidation (column E) at the limit of the solvent window. The peak potentials were occasionally difficult to measure by cyclic voltammetry since they are in the region where the solvent begins to break down, but clearly defined peak potentials could be measured from square-wave voltammograms. We have found no mention of a third oxidation for [Ru(tpp)(CO)L] complexes in the literature. Since two ring-based oxidations and a metal-based oxidation are in principle possible, this third oxidation must be the second porphyrin-ring-based oxidation. The reduction (column A), by comparison with many other tpp complexes, is also ring-based.[12]

For complexes 2–5 the characteristic 16e/17e reduction of the phenolate-substituted molybdenum centre is in column F, whilst for 6–8 the 17e/18e reductions and 17e/16e oxidations of the pyridyl-substituted molybdenum fragments are in columns G and H respectively. The molybdenum based reduction potentials for 2–5 are between 130 and 160 mV more negative than those of the isolated mononuclear complexes I–IV. Co-ordination of the pendant pyridyl group of the latter to the Ru(tpp) core therefore results in an increase in electron density at the molybdenum centre, implying that the axial pyridyl ligand is acting as an effective π acceptor from the Ru(tpp) core, an unsurprising result, although in contrast to our earlier observation that the pyridyl terminus of I–IV can act as a π donor in other circumstances *via* internal phenolate-to-pyridyl charge transfer.[5]

For complexes 6–8 the potentials of the molybdenum-based reductions (column G) vary widely according to the degree of unsaturation of the bridging ligand; we believe that the added electron is significantly delocalised on to the pyridyl ligand and so will be sensitive to the nature of remote substituents, and the dihedral twist between the two halves of the briding ligand in the case of 7.[4] In contrast the oxidation (column H) is more metal-localised and therefore varies much less.

Attachment of a second axial pyridyl ligand to the Ru(tpp) core in complexes 9–12 has a marked effect on its electrochemistry since a pyridyl ligand stabilises a high oxidation state of the central metal much more effectively than does the carbonyl ligand which it replaces.[12] The Ruᴵᴵ–Ruᴵᴵᴵ couple (column B) is shifted cathodically by approximately 1 V

Table 1 Analytical, IR and mass spectroscopic data for the new complexes

	Analysis (%)*			IR/cm⁻¹		FAB mass
Complex	C	H	N	NO	CO	spectrum,* *m/z*
1	74.3 (74.4)	4.7 (4.3)	6.9 (7.3)	—	1942	953 (953)
2	62.1 (62.2)	4.9 (4.3)	12.1 (12.3)	1686	1942	1371 (1371)
3	62.8 (62.8)	4.7 (4.3)	11.3 (12.0)	1687	1942	1397 (1397)
4	62.9 (62.8)	4.3 (4.3)	11.8 (12.0)	1687	1940	1396 (1397)
5	63.4 (62.8)	4.4 (4.3)	11.9 (12.0)	1684	1942	1395 (1397)
6	62.0 (62.0)	4.2 (4.3)	13.6 (13.4)	1608	1946	1359 (1357)
7	62.6 (62.5)	4.4 (4.5)	12.8 (13.2)	1606	1945	1384 (1385)
8	62.9 (62.7)	4.6 (4.6)	12.9 (13.0)	1615	1943	1399 (1399)
9	76.1 (76.1)	4.9 (4.8)	7.4 (7.4)	—	—	1136 (1136)
10	58.6 (58.5)	4.6 (4.5)	14.5 (14.2)	1686	—	1973 (1971)
11	58.3 (58.1)	4.5 (4.6)	15.6 (15.9)	1610	—	1943 (1943)
12	58.3 (58.9)	4.9 (4.9)	15.3 (15.4)	1610	—	2000 (1999)

* Calculated values in parentheses.

Table 2 Proton NMR data (δ, J/Hz) for the new complexes

	tpp			HB(dmpz)$_3$	
	pyrrole	phenyl	Bridging ligand	pyrazolyl	methyl
1[a]	8.61 (8 H, s)	8.24–8.21 (4 H, m, H^2) 8.08–8.03 (4 H, m, H^6) 7.73–7.65 (12 H, m, H^3, H^4, H^5)	6.95 (2 H, d, J = 9.0, Ph H^3, H^5) 6.64 (2 H, d, J = 9.0, Ph H^2, H^6) 6.25 (1 H, d, J = 16, CH=) 5.70 (1 H, d, J = 16, CH=) 5.22 (2 H, d, J = 6.8, py H^3, H^5) 3.67 (3 H, s, OCH$_3$) 1.45 (2 H, d, J = 6.8, py H^2, H^6)		
2[a]	8.62 (8 H, s)	8.25–8.22 (4 H, m, H^2) 8.08 (4 H, d, J = 6.6, H^6) 7.74–7.64 (12 H, m, H^3, H^4, H^5)	6.93 (2 H, d, J = 8.8, Ph H^3, H^5) 6.67 (2 H, d, J = 8.8, Ph H^2, H^6) 5.44 (2 H, d, J = 6.8, py H^3, H^5) 1.55 (2 H, d, J = 6.8, py H^2, H^6)	5.85, 5.76, 5.65 (all 1 H, s)	2.43, 2.34, 2.33, 2.30, 1.96, 1.73 (all 3 H, s)
3[a]	8.61 (8 H, s)	8.24–8.21 (4 H, m, H^2) 8.09–8.02 (4 H, m, H^6) 7.73–7.61 (12 H, m, H^3, H^4, H^5)	7.08 (4 H, s, Ph H^2, H^3, H^5, H^6) 6.35 (1 H, d, J = 15.9, CH=) 5.80 (1 H, d, J = 15.9, CH=) 5.25 (2 H, d, J = 6.6, py H^3, H^5) 1.47 (2 H, d, J = 6.6, py H^2, H^6)	5.88, 5.80, 5.68 (all 1 H, s)	2.48, 2.33, 2.03, 1.88 (all 3 H, s), 2.36 (6 H, s)
4[b]	8.64 (8 H, s)	8.25–8.23 (4 H, m, H^2) 8.01–7.99 (4 H, m, H^6) 7.76–7.69 (12 H, m, H^3, H^4, H^5)	7.17 (1 H, t, J = 7.7, Ph H^5) 7.06 (1 H, d, J = 7.8, Ph H^4) 6.99 (1 H, s, Ph H^2) 6.84 (1 H, d, J = 7.5, Ph H^6) 6.40 (1 H, d, J = 16.2, CH=) 5.99 (1 H, d, J = 16.2, CH=) 5.44 (py H^3, H^5)[c] 1.46 (2 H, d, J = 6.6, py H^2, H^6)	5.93, 5.83, 5.72 (all 1 H, s)	2.42, 2.38, 2.36, 2.35, 1.98, 1.81 (all 3 H, s)
5[b]	8.56 (8 H, s)	8.54–8.53 (4 H, m, H^2) 8.16–8.00 (4 H, m, H^6) 7.67–7.57 (12 H, m, H^3, H^4, H^5)	7.03 (2 H, d, J = 8.8, Ph H^3, H^5) 6.95 (2 H, d, J = 8.8, Ph H^2, H^6) 6.29 (1 H, d, J = 16.3, CH=) 5.80 (1 H, d, J = 16.3, CH=) 1.53 (1 H, br s, py H^2 or H^6)[d] 1.46 (1 H, d, J = 6.6, py H^4)[d] 1.26 (1 H, br s, py H^6 or H^2)[d] 0.82–0.92 (1 H, m, py H^5)[d]	5.83, 5.76, 5.62 (all 1 H, s)	2.35, 2.28, 2.26, 2.25, 1.99, 1.76 (all 3 H, s)
9[b]	8.01–7.98 (8 H, m)	7.63–7.61 (20 H, m, all Ph protons)	7.03 (4 H, d, J = 8.9, Ph H^3, H^5) 6.68 (4 H, d, J = 8.9, Ph H^2, H^6) 6.29 (4 H, d, J = 16, CH=) 5.99 (4 H, d, J = 16, CH=) 5.52 (4 H, d, J = 5.0, py H^3, H^5) 3.68 (6 H, s, OCH$_3$) 2.35 (4 H, d, J = 5.0, py H^2, H^6)		
10[b]	8.00–7.95 (8 H, m)	7.60–7.54 (20 H, m, all Ph protons)	6.88 (4 H, d, J = 9.0, Ph H^3, H^5) 6.75 (4 H, d, J = 8.9, Ph H^2, H^6) 5.42 (4 H, d, J = 6.4, py H^3, H^5) 2.42 (4 H, J = 6.8, py H^2, H^6)	5.84, 5.76, 5.62 (all 2 H, s)	2.35, 2.29, 2.27, 2.26 (all 6 H, s), 2.28 (12 H, s)

[a] Spectrum recorded in CDCl$_3$. [b] Spectrum recorded in CD$_2$Cl$_2$. [c] Partly obscured by residual protons in the solvent, so J value and integral cannot be determined. [d] Tentative assignment; see text.

compared to that of the Ru(tpp)(CO)(pyridyl) complexes, and the first ring-based oxidations are shifted anodically typically by 0.4 V. In some cases an additional oxidation wave, which we again assume to be ring-based, is visible at the limit of the solvent window. The redox potentials of the molybdenum fragments are in the expected positions, and correspond to two coincident one-electron transfers. The electrochemical interaction between the two molybdenum centres of **10–12** is sufficiently weak that the two processes are not resolved, and a single broad wave of approximately twice the intensity of that of the Ru(tpp)-based processes occurs in each case. Fig. 1 shows the cyclic and square-wave voltammograms of **7** and **11** as typical examples.

Comparison of the Ru^{II}–Ru^{III} couples of complexes **10–12** (column B) shows that in **11** and **12** the Ru^{II} is harder to oxidise than in **10** by about 90 mV; there is a corresponding cathodic shift of the molybdenum-based reductions by 140 mV compared to the mononuclear fragment **1**, which confirms that the 16-electron axial molybdenum groups of **10** are better electron acceptors than are the 17-electron axial molybdenum groups of **11** and **12**.

UV/VIS Spectroscopy.—Details of the electronic spectra are summarised in Table 4. For the monosubstituted complexes of type [Ru(tpp)(CO)L] **1–8** the expected intense Soret band (*ca*. 411 nm) and the weaker β and α bands (*ca*. 532 and 566 nm) are all present and in their expected positions, which do not vary significantly between the complexes.[8,10,13,14] The ratio of the intensities of the α and β bands has been taken to be an indication of the strength of the interaction of the axial ligand with the Ru(tpp) core.[14] For **1** and **3** the ratios ϵ_α : ϵ_β are 0.23 and 0.46 : 1 respectively, indicating that the electron-accepting molybdenum fragment present in **3** strengthens the interaction of the axial pyridyl ligand with the Ru(tpp) core; this is consistent with the electrochemical effects described earlier. Likewise, changing the axial fragment from a 16-electron molybdenum phenolate to a 17-electron molybdenum pyridyl results in a noticeable decrease in the ϵ_α : ϵ_β ratio, particularly for **7** and **8**, back to approximately the value for **1**. In some cases for **1–8** an additional transition is observed just below 500 nm which is not always resolved; this has been noted before.[10,14] The three bands in the UV region (*ca*. 240, 280 and 320 nm), not

Table 3 Electrochemical data for the new complexes[a]

Complex	A	B	C	D	E	F	G	H
1	-2.03 (90)		+0.37 (80)	+0.91 (90)	+1.08 (90)			
2	-2.04 (90)		+0.37 (120)	+0.83 (140)	+1.26[b]	-0.83 (80)		
3	-2.05 (100)		+0.36 (90)	+0.96[b]		-0.85 (100)		
4	-2.07 (90)		+0.38 (90)	+0.93 (130)		-0.87 (100)		
5	-2.05 (80)		+0.36 (80)	+0.93 (140)	+1.09[b]	-0.86 (90)		
6	-2.07 (100)		+0.40 (90)	+0.89 (90)			-1.62 (90)	+0.10 (80)
7	-2.08 (120)		+0.39 (130)	+0.91 (140)			-1.92 (120)	+0.08 (120)
8	-2.17 (80)		+0.33 (100)	+0.85 (100)			-2.06 (80)	+0.01 (100)
9		-0.31 (140)	+0.81 (180)					
10	-2.04 (80)	-0.25 (100)	+0.81 (70)			-0.84 (100)[c]		
11	-2.48[b]	-0.12 (70)	+0.78 (70)		+1.20 (90)		-1.71 (180)[c]	+0.08 (80)[c]
12	-2.44[b]	-0.16 (90)	+0.83 (100)		+1.22 (150)		-1.99 (180)[c]	+0.08 (90)[c]

[a] Cyclic and square-wave voltammograms were recorded in CH_2Cl_2–0.1 mol dm^{-3} [NBu$_4$][PF$_6$] at a scan rate of 0.2 V s^{-1}. Potentials are in V vs. the ferrocene–ferrocenium couple; peak–peak separations ΔE_p where available are given in parentheses. Columns: A, porphyrin ring reduction; B, Ru^{II}–Ru^{III} couple for Ru(tpp)(pyridyl)$_2$ complexes; C, porphyrin ring-based oxidation; D, Ru^{II}–Ru^{III} couple for Ru(tpp)(CO)(pyridyl) complexes; E, possibly the second ring-based oxidation, see text; F, 16e/17e couples for phenolate-substituted molybdenum centres; G, 17e/18e couples for pyridyl-substituted molybdenum centres; H, 17e/16e couples for pyridyl-substituted molybdenum centres. [b] Half-wave potential determined from square-wave voltammogram, so ΔE_p not available. [c] Two coincident one-electron transfers (to two molybdenum centres).

Table 4 Electronic and EPR spectral data for the new complexes

λ_{max}/nm $(10^{-3}\ \varepsilon/dm^3\ mol^{-1}\ cm^{-1})^a$

Complex				Soret band		β band	α band			$g_{iso}(A_{Mo}/mT)$[b]
1	239 (33)		322 (32)	412 (212)		532 (15)	567 (3.4)			
2			306 (30)	412 (238)	492 (11)	532 (24)	566 (7.8)			1.969 (5.0)
3	234 (55)		320 (44)	412 (210)	492 (15)	533 (28)	564 (13)			1.969 (5.0)
4			313 (47)	412 (217)		532 (20)	565 (7.0)			1.968 (5.0)
5			321 (21)	411 (158)	500 (6.7)	532 (15)	565 (4.9)			1.969 (5.0)
6	246 (50)		310 (sh)	411 (203)	497 (sh)	531 (18)	564 (5.9)	594 (2.6)[c]	648 (1.0)[d]	1.981 (4.8)
7	245 (104)	273 (sh)	310 (sh)	412 (410)		531 (44)	566 (9.5)	600 (1.6)[c]		1.978 (4.9)
8	240 (48)	277 (33)	308 (28)	412 (233)	494 (sh)	532 (19)	566 (5.0)	600 (sh)[c]		1.978 (4.9)
9		294 (81)	331 (103)	410 (215)		506 (67)				
10			290 (71)	410 (162)	476 (sh)[e]	503 (48)			784 (6.9)[d]	1.980[f]
11	247 (51)	278 (48)		408 (88), 418 (118)		507 (20)			584 (16)[d]	1.979[f]
12		276 (42)	317 (sh)	410 (63), 420 (67)		503 (16)				1.978 (4.8)

[a] Electronic spectra recorded in CH_2Cl_2. [b] The EPR spectra were recorded at room temperature in CH_2Cl_2–thf (1:1). [c] Molybdenum-to-pyridyl m.l.c.t. process. [d] Nature of process unknown. [e] Phenolate-to-molybdenum l.m.c.t. process. [f] Second-order spectrum; see text.

all of which are resolved for all complexes, we assign to a combination of π–π* transitions within the axial ligands and the N, L and M bands characteristic of metalloporphyrins.[13] The phenolate-to-molybdenum (ligand-to-metal) charge-transfer (l.m.c.t.) bands expected for 2–5 (between 460 and 530 nm)[5] are not explicitly resolved but comparison of the spectra of 1 and 3 shows that the absorbance in the relevant region, between the Soret and β bands, is higher in the latter case [Fig. 2(a) and (b)]. Finally for the pyridyl-substituted molybdenum centres of 6–8 we expect a weak molybdenum-to-pyridyl (metal-to-ligand) charge-transfer (m.l.c.t.) band in the 500–600 nm region, the exact position depending on the nature of the substituent attached to the pyridyl ring. These are apparent for 6–8 at about 600 nm in each case. The nature of the additional weak band at 648 nm for 6 is unknown.

Attachment of a second axial pyridyl ligand to the Ru(tpp) core in complexes 9–12 results in a shift of the β band from ca. 530 to ca. 500 nm and the appearance of a long 'tail' extending through the red end of the visible spectrum.[8,13] The α band becomes an ill defined shoulder. Also, a shoulder becomes apparent on the Soret band which, for 11 and 12, becomes split into two clearly defined maxima; this is due to the appearance of vibrational fine structure on the electronic transition.[13] For 10 the expected phenolate-to-molybdenum l.m.c.t. band is visible as a shoulder at 476 nm, and there is also a broad

peak at 784 nm which extends out well into the IR region, the nature of which is uncertain [Fig. 2(c)]. For 11 [Fig. 2(d)] there is an unexpectedly intense, broad transition at 584 nm, which is in the region characteristic of molybdenum-to-pyridyl m.l.c.t. transitions but an order of magnitude more intense than usual (cf. 6–8). This transition is absent for 12.[4]

EPR Spectroscopy.—Details of the solution EPR spectra are summarised in Table 4. The molybdenum centres which are co-ordinated by a pyridyl ligand (in 6–8, 11 and 12) have 17 valence electrons and are therefore one-electron paramagnets. The phenolate-substituted molybdenum centres (in complexes 2–5 and 10) have 16 valence electrons and are diamagnetic, but may be reduced to the 17-electron configuration by reaction with cobaltocene; the reduced species thus generated are stable for several hours under nitrogen. For the Ru(tpp) derivatives bearing one axial molybdenum substituent (2–8) the EPR spectra are consistent with the single unpaired electron being localised on the molybdenum, since the EPR parameters (g_{iso} ca. 1.97 and 1.98 for the phenolate-substituted and pyridyl-substituted molybdenum fragments respectively; hyperfine coupling A_{Mo} ca. 5 mT) are identical to those commonly found for simple mononuclear molybdenum complexes.[4,5]

The situation for complexes 10–12, with two axial molybdenum groups, is rather different. The spectra for 10 (in its
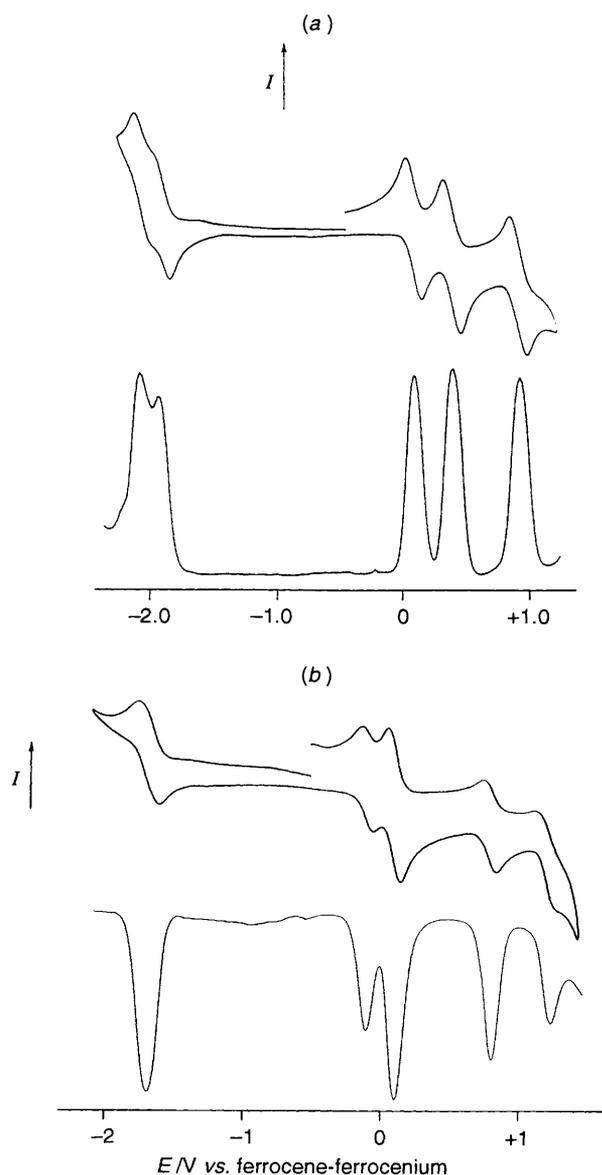
Fig. 1 Cyclic and square-wave voltammograms of (a) complex 7 and (b) 11

Fig. 2 Electronic spectra of (a) complex 1, (b) 3, (c) 10 and (d) 11 in CH_2Cl_2

doubly reduced form) and 11 [Fig. 3(b)] both suggest an intermediate exchange interaction ($|J| \approx A_{Mo}$) since their EPR spectra are not similar to either of the two simple extremes ($|J|$ very small, resulting in effectively isolated mononuclear fragments, or $|J| \gg A_{Mo}$, resulting in a typical 'fast exchange' spectrum [4,5,15,16]) but have additional peaks and irregular hyperfine separations. In contrast, for 12 [Fig. 3(a)] the spectrum is similar to those of mononuclear complexes, with a sextet hyperfine pattern and $A_{Mo} \approx 5$ mT. Dissociation of one of the axial molybdenum groups would give this result but we found no evidence for such dissociation from the electrochemical measurements. If complex 11 is on the borderline between 'fast' and 'slow' exchange, then the appearance of the EPR spectrum will be sensitive to small variations in the value of $|J|$. It appears that the larger dihedral twist of the bridging ligands in 12 reduces the exchange interaction sufficiently to give a spectrum characteristic of isolated molybdenum fragments. This is the first indication we have had that, in binuclear complexes exhibiting spin–spin exchange, the magnitude of $|J|$ may be sensitive to the conformation of the bridging ligand as well as its length.[16]

Conclusion
We have prepared a series of polynuclear, bimetallic complexes in which one or two molybdenum complexes bearing a pendant pyridyl group are attached to the axial positions of a Ru(tpp) core. The complexes were thoroughly characterised by a variety of methods, and represent unusual examples of the stepwise assembly of polynuclear complexes using 'off the shelf' building blocks, a methodology of importance in the area of supramolecular chemistry. The electrochemical and electronic spectroscopic properties indicate that the axial molybdenum centres interact slightly with the Ru(tpp) core. There is some evidence that the spin–spin exchange interaction between two paramagnetic molybdenum centres on either side of the Ru(tpp) core in the trinuclear complexes may be modified by the dihedral twist angle of the axial bridging ligands. Photochemical studies on these complexes are underway and will be reported in due course.
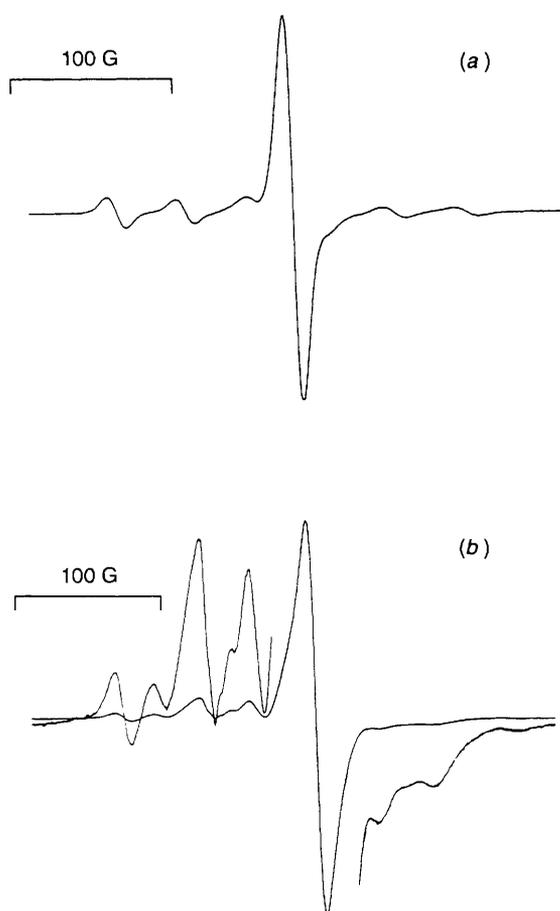
Fig. 3 Solution EPR spectra of (a) complex **12** and (b) **11** in CH_2Cl_2–thf; $G = 10^{-4}$ T

Acknowledgements

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