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Convergent syntheses of topologically linear heterotri- and heteropenta-nuclear complexes based upon bis{4′-(2,2′ : 6′,2″-terpyridinyl)} ether

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In situ synthesis of the oxygen-linked dinucleating compound bis{4′-(2,2′ : 6′,2″-terpyridinyl)} ether **I** by the reaction of ruthenium(II)-coordinated 4′-chloro-2,2′ : 6′,2″-terpyridine ligands with 4′-hydroxy-2,2′ : 6′,2″-terpyridine allowed the preparation of the mono- and di-nuclear *complex ligands* [(terpy)Ru(**I**)][PF$_6$]$_2$ and [(terpy)Ru(**I**)Ru(**I**)][PF$_6$]$_2$ in which **I** has one coordinated and one non-coordinated metal-binding domain. Subsequent reaction of these complex ligands with labile iron(II) or cobalt(II) salts allowed the preparation of the heterotri- and heteropenta-nuclear complexes [{(terpy)Ru(**I**)}$_2$M][PF$_6$]$_6$ and [{(terpy)Ru(**I**)Ru(**I**)}$_2$M][PF$_6$]$_{10}$ (M = Co or Fe). Spectroscopic and electrochemical studies on these novel topologically linear species are described.

Metallodendrimers, dendrimers incorporating metal sites, are an important emerging motif in supramolecular chemistry that offer the advantage of multiple reaction sites within chemically well-defined and discrete macromolecular systems.[1] Four main strategies may be identified for the inclusion of metal centres in metallodendrimers; (i) use of a metal-containing core which is then structurally developed using a divergent dendrimer synthesis or the convergent attachment of dendritic wedges, (ii) decoration of surface or inner generations of a conventionally prepared and functionalised dendrimer, (iii) incorporation of the metal centres as part of the backbone connectivity of the dendrimer and (iv) the use of the metal as the branching point within the dendrimer.[1]

Idealised dendrimers are monodispersed, but it is frequently found that higher generation dendrimers have high polydispersivities. One of the problems encountered in the synthesis of dendrimers, particularly those of higher orders, is the formation of polydispersed species in which single-site failures are propagated as failure sequences and voids in subsequent generations.[2] The growth of a dendrimer cannot be infinite and eventually the starburst limit is reached, at which surface congestion is sufficient that a monodispersed species *cannot* be formed. These considerations have led us to consider an alternative approach to conceptually similar polynuclear systems which exhibit topologically *linear* arms radiating from a central core rather than multiply branched arms.[3–14] We term these species *metallostars*.

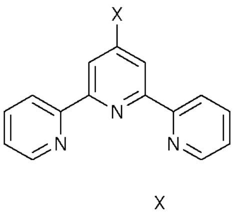
Critical concepts in dendrimer and metallodendrimer chemistry are those of successive *generations* and building blocks which are used in divergent iterative synthesis or in the preparation of dendritic wedges for convergent synthesis.[2] These concepts may be transferred to metallostars, which are expected to be closer to monodispersed and exhibit fewer or no failure sequences.

In this paper we consider methodology leading to topologically linear heteromultinuclear complexes which will subsequently be adapted for the attachment of multinuclear arms to core species in metallostar synthesis. These compounds are the linear equivalents of dendritic wedges.

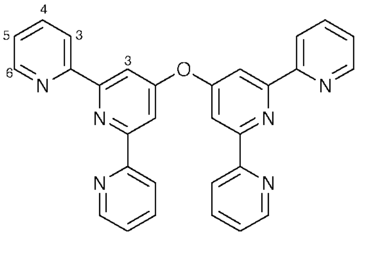
Results and discussion

Strategy

The strategy adopted for the synthesis of metallodendrimers relies upon the use of ligands containing discrete metal-binding domains which may selectively be addressed to allow the assembly of higher nuclearity systems.[13] For reasons which we have detailed elsewhere, we favour the terpy metal-binding domain over the more widely investigated 2,2′-bipy group.[14] In an extension of our earlier studies with directly linked or phenylene-spaced terpy domains, we introduced the ether linked ligand bis{4′-(2,2′ : 6′,2″-terpyridinyl)} ether **I** which contains two terpy metal-binding domains.[3] We also showed that the coordination of 4′-chloro-2,2′ : 6′,2″-terpyridine **II** to ruthenium(II) enhanced its electrophilicity and allowed the *in situ* synthesis of complexes of **I** under mild conditions by reaction with nucleophilic 4′-hydroxy-2,2′ : 6′,2″-terpyridine **III**.[3] In particular, we showed that it was possible to prepare complexes in which one of the terpy domains of **I** was coordinated to a metal whilst the other was non-coordinated. With a suite of such complexes to hand, we aimed to use the Balzani–Denti "complexes-as-metals, complexes-as-ligands"[15] approach for the preparation of multinuclear complexes. In this case, we planned to use the self-assembly reaction of complexes with non-coordinated terpy domains with labile first row transition metal salts to give heteropolynuclear systems.



	X
terpy	H
II	Cl
III	OH
IV	OEt



I

Synthesis and characterisation of ruthenated ligands

Synthesis. The reaction of the electrophilic complexes [Ru(terpy)(**II**)][PF$_6$]$_2$ **1**·2PF$_6$ and [(Ru(**II**)$_2$][PF$_6$]$_2$[16] **2**·2PF$_6$ with nucleophile **III** in MeCN in the presence of K$_2$CO$_3$ gave the complex ligands [Ru(terpy)(**I**)][PF$_6$]$_2$ **3**·2PF$_6$ and [Ru(**I**)$_2$][PF$_6$]$_2$ **4**·2PF$_6$ in acceptable yields (Scheme 1).[3] As discussed previously, these species have characteristic ^{1}H NMR

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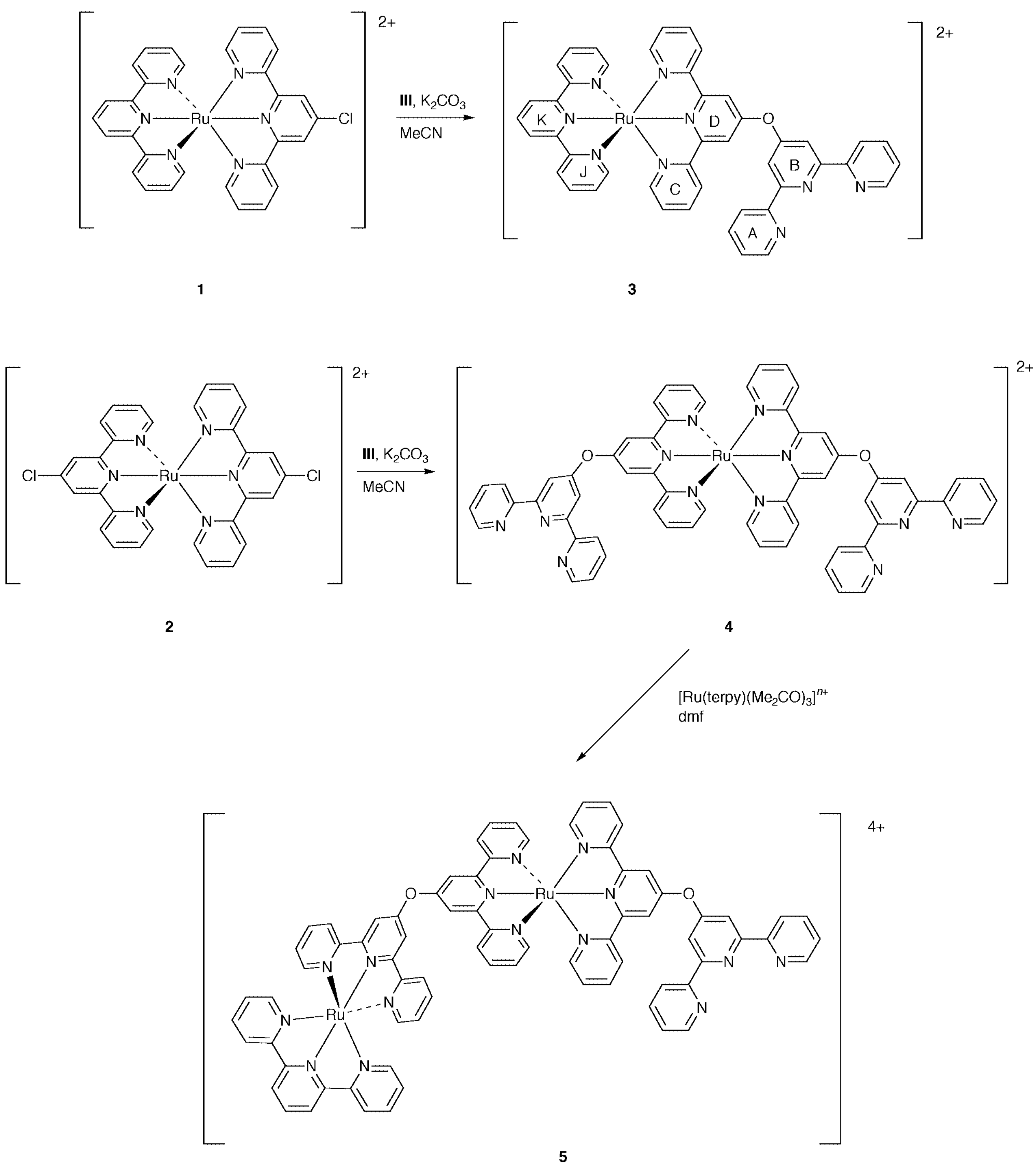


Scheme 1

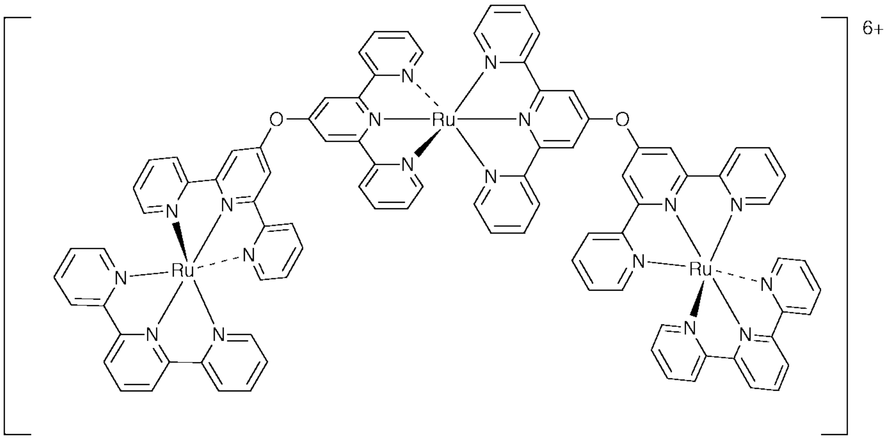
spectra associated with the terminal rings of coordinated and non-coordinated terpy domains. We note at this point that each replacement of a terpy ligand by the electron-releasing ligand **I** shifts the ruthenium(II)–ruthenium(III) potential 30–40 mV to less positive potential (+0.91, +0.87 and +0.84 V (*versus* Fc–Fc$^+$) for [Ru(terpy)$_2$][PF$_6$]$_2$, **3**·2PF$_6$ and **4**·2PF$_6$ respectively). The combination of electrochemical and ^{1}H NMR spectroscopic data allows the rapid establishment of the number and types of ligands present within these species. The complex **3** is the prototype ruthenated ligand with a non-coordinated terpy domain associated with the ligand **I**. In contrast, the complex **4** may be regarded as a ruthenated analogue of a bridging ligand, in that it contains two non-coordinated terpy metal-binding domains.

Attempts selectively to bind a second {Ru(terpy)} unit to complex **4**·2PF$_6$ to give [(terpy)Ru(**I**)Ru(**I**)]$^{4+}$ **5** by direct reaction with one equivalent of [Ru(terpy)Cl$_3$] under a variety of conditions were unsuccessful and resulted predominantly in the formation of the trinuclear complex [(terpy)Ru(**I**)Ru(**I**)-Ru(terpy)]$^{6+}$ **6**.[3] Treatment of an acetone suspension of [Ru-(terpy)Cl$_3$] with AgBF$_4$ gives a deep blue solution containing the solvento species [Ru(terpy)(Me$_2$CO)$_3$]$^{n+}$ ($n = 2$ or 3) which has been shown previously to be a good synthon for introducing {Ru(terpy)} units.[17] A solution of one equivalent of this complex in dmf reacted smoothly with **4**·2PF$_6$ to give after two hours a deep red reaction mixture which TLC showed only to contain minor amounts of the trinuclear complex cation **6**. Chromatographic purification gave the desired

Table 1 300 MHz ^{1}H NMR data (δ) for CD_3CN solutions of the complex ligands and heterotri- and heteropenta-nuclear complexes. All coupling constants are typical for terpy ligands and complexes.[3] No assignment of resonances to individual ruthenium-bonded rings was possible for the paramagnetic compounds **9**·6PF$_6$ and **10**·10PF$_6$

Proton	**3**·2PF$_6$	**5**·4PF$_6$	**7**·6PF$_6$	**8**·10PF$_6$	**9**·6PF$_6$	**10**·10PF$_6$
A6	8.73	8.73	7.44	7.46	114	114
A5	7.50	7.51	7.23	7.28	68[a]	68[a]
A4	8.04	8.05	7.97	7.98	67[a]	67[a]
A3	8.80	8.81	8.58	8.58	37[a]	37[a]
B3	8.55	8.57	8.92	8.95	14.2[a]	14.3[a]
C6	7.33	7.67	7.44	7.72	[b]	[c]
C5	7.13	7.19	7.25	7.35	[b]	[c]
C4	7.84	7.90	7.97	8.02	[b]	[c]
C3	8.40	8.44	8.61	8.65	10.4/8.74	10.4/8.83
D3	8.51	8.55	8.97	8.99	9.18	9.28
E6		7.67		7.70		[c]
E5		7.25		7.35		[c]
E4		7.96		8.00		[c]
E3		8.63		8.62		[c]
F3		8.90		8.82		[c]
G6		7.40		7.42		[c]
G5		7.22		7.22		[c]
G4		7.93		7.95		[c]
G3		8.62		8.61		[c]
H3		8.90		8.84		[c]
J6	7.50	7.58	7.63	7.61	[b]	
J5	7.23	7.25	7.28	7.28	[b]	
J4	7.94	7.96	7.97	7.96	[b]	
J3	8.49	8.52	8.54	8.53	10.4/8.74	10.4/8.83
K3	8.73	8.77	8.79	8.78	8.95	9.01
K4	8.39	8.43	8.45	8.44	8.55	8.55

[a] Unambiguous assignment of A5, A4, A3, B3 not possible. [b] No further assignment of resonances at δ 8.30/8.15/7.94/7.83/7.50/7.18 possible. [c] No additional assignment of broadened resonances possible.



6

dinuclear complex **5**·4PF$_6$ as an orange-red powder in 43% yield. The synthetic transformations are summarised in Scheme 1.

Characterisation. The complex **5**·4PF$_6$ exhibits peaks assigned to $\{\mathbf{5}(PF_6)_n\}^+$ ($n = 3, 2, 1$ or 0) in its MALDI-TOF (MALDI = matrix assisted laser desorption ionisation) mass spectrum, together with a fragmentation peak corresponding to $\{Ru(\mathbf{I})_2\}^+$. The ^{1}H NMR spectrum of a CD_3CN solution of **5**·4PF$_6$ is sharp and well resolved (Fig. 1a, Table 1) and exhibits a total of 26 resonances which are assigned to the five magnetically inequivalent terpy domains. Assignments were made on the basis of COSY spectroscopy and by comparison with the spectrum of **1**·2PF$_6$ and other model compounds. The most characteristic feature is the sequence of signals assigned to the non-coordinated A ring, in which H^{A6} lies about 0.1 ppm upfield of H^{A3}, whereas for the coordinated terpy rings H^6 lies 0.8–1 ppm upfield of H^3.[3] Although the two ruthenium centres are in different environments, the two expected ruthenium(II)–ruthenium(III) redox processes are not resolved by cyclic voltammetry and a single, broad wave ($E_a - E_c = 110$ mV; for ferrocene in the same solution, $E_a - E_c = 60$ mV) was observed at +0.89 V.

Synthesis and characterisation of heterotri- and heteropenta-nuclear complexes

Synthesis. Both of the complexes **3**·2PF$_6$ and **5**·4PF$_6$ possess non-coordinated terpy domains and may simply be regarded as terpy ligands. The coordination reactions to ruthenium(II) and ruthenium(III) centres described above are slow (log (k_{ex}/s^{-1}) for water exchange at ruthenium-(II) and -(III), ≈ 0.7 and −6 respectively) whereas reactions with first row transition metals (log (k_{ex}/s^{-1}) for water exchange at iron(II) or cobalt(II), ≈6.5) are expected to be fast and may reasonably be described as self-assembly processes.[18]

Treatment of MeCN solutions of complexes **3**·2PF$_6$ and **5**·4PF$_6$ with aqueous iron(II) sulfate or ammonium iron(II)

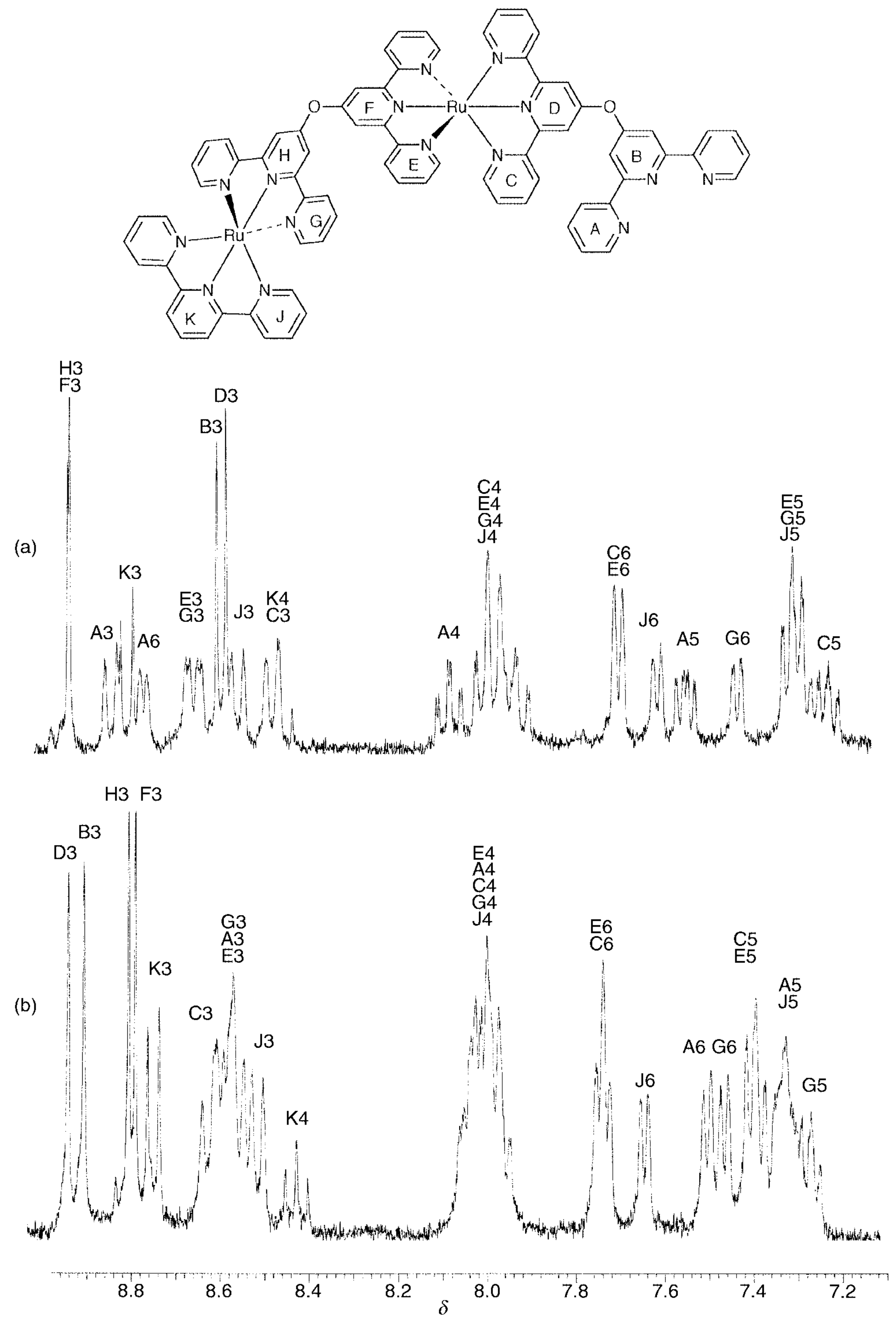
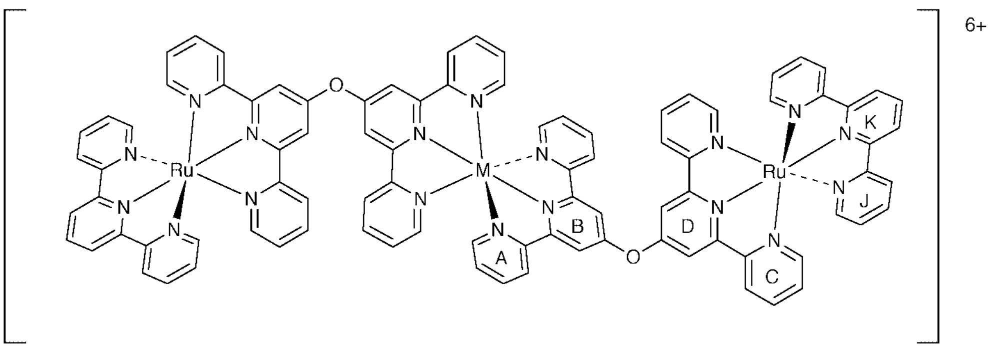


Fig. 1 300 MHz ^{1}H NMR spectra of CD_3CN solutions of (a) the diruthenated complex ligand **5**·$4PF_6$ and (b) the pentanuclear iron(II) complex **8**·$10PF_6$ showing assignments.

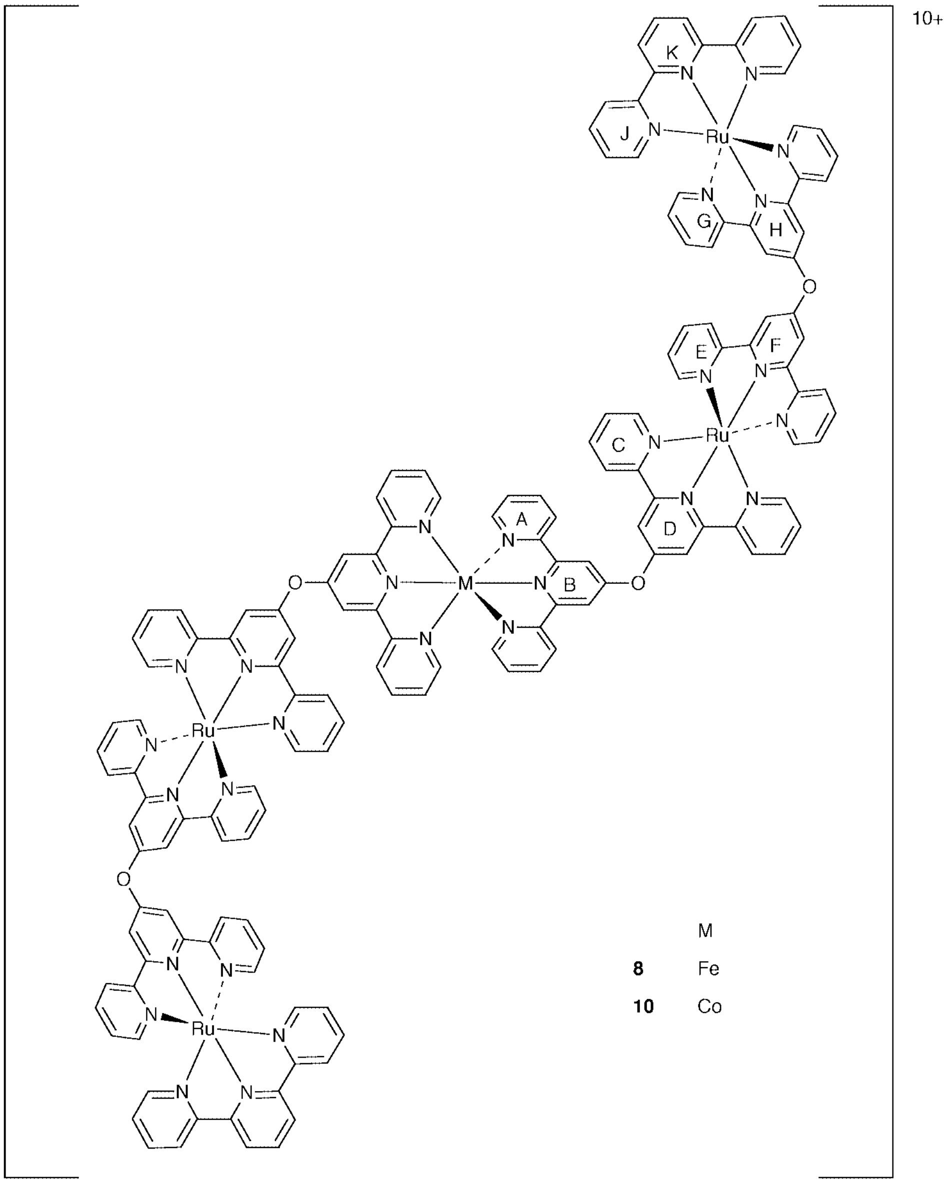
sulfate resulted in an immediate change from orange-red to red-purple and the addition of $[NH_4][PF_6]$ gave red-purple precipitates of the heteropolynuclear complexes $[\{(\text{terpy})\text{Ru}(\mathbf{I})\}_2\text{Fe}][PF_6]_6$ **7**·$6PF_6$ and $[\{(\text{terpy})\text{Ru}(\mathbf{I})\text{Ru}(\mathbf{I})\}_2\text{Fe}][PF_6]_{10}$ **8**·$10PF_6$ respectively. Similarly, reaction of **3**·$2PF_6$ and **5**·$4PF_6$ with cobalt(II) acetate in aqueous MeCN gave orange solutions from which the complexes $[\{(\text{terpy})\text{Ru}(\mathbf{I})\}_2\text{Co}][PF_6]_6$ **9**·$6PF_6$ and $[\{(\text{terpy})\text{Ru}(\mathbf{I})\text{Ru}(\mathbf{I})\}_2\text{Co}][PF_6]_{10}$ **10**·$10PF_6$ were isolated as beautiful orange-red solids. Typical yields were in the range 65–80%.

Characterisation. Primary characterisation of the complexes was by MALDI-TOF MS which has been found to be very effective for multinuclear compounds of this type. The trinuclear species **7**·$6PF_6$ and **9**·$6PF_6$ exhibited strong peaks assigned to $\{P(PF_6)_n\}^+$ ($n = 4$ or 3; P = **7** or **9**) together with fragmentation peaks corresponding to $\{\{(\text{terpy})\text{Ru}(\mathbf{I})\}\text{M}(\mathbf{I})(PF_6)_2\}^+$ (M = Co or Fe). Similarly, the pentanuclear species **8**·$10PF_6$ and **10**·$10PF_6$ each exhibited peaks assigned to $\{P(PF_6)_n\}^+$ ($n = 8$, 7 or 6; P = **8** or **10**). Although satisfactory microanalytical results were obtained for the trinuclear complexes, the pentanuclear complexes consistently gave results which were 2–5% low in carbon, a phenomenon that we have noted before with high-nuclearity ruthenium systems and which we ascribe to the formation of ruthenium carbides.

In the case of the iron(II) complexes, there is a noticeable



	M
7	Fe
9	Co



	M
8	Fe
10	Co

colour change upon coordination and the electronic spectra exhibit, in addition to ligand-centred transitions, both iron- and ruthenium-centred MLCT bands. The iron-centred MLCT absorptions (λ_{max} 559 and 554 nm for **7**·6PF$_6$ and **8**·10PF$_6$ respectively) correspond to that of the model compound [Fe(**IV**)$_2$][PF$_6$]$_2$ (λ_{max} 557 nm) whilst the ruthenium-centred transitions (λ_{max} 481 and 486 nm for **7**·6PF$_6$ and **8**·10PF$_6$ respectively) are close to those of the starting complex ligands (λ_{max} 479 and 488 nm for **3**·2PF$_6$ and **5**·4PF$_6$ respectively). For the cobalt(II) complexes, only the ruthenium-centred absorptions are observed and are found at essentially the same energy as those of the iron compounds (λ_{max} 480 and 485 nm for **9**·6PF$_6$ and **10**·10PF$_6$ respectively). Although the MLCT bands are composites of a series of overlapping absorp-

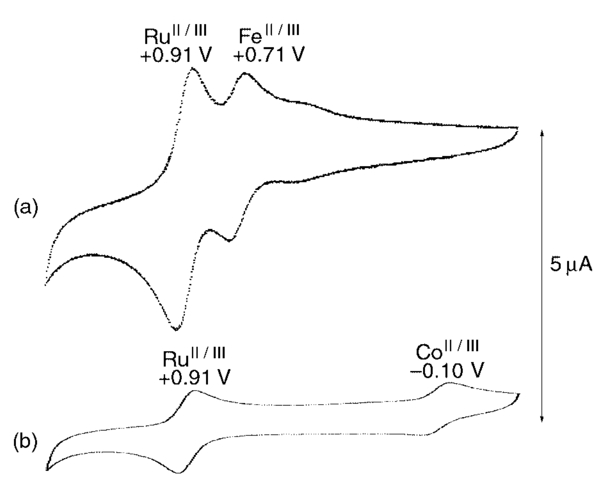


Fig. 2 Cyclic voltammograms of complexes (a) **7**·6PF$_6$ and (b) **9**·6PF$_6$. In each case, the solvent was degassed MeCN containing 0.1 M [Bu$^n_4$N][BF$_4$] as supporting electrolyte; scan rate 20 mV s^{-1}, reference internal Fc/Fc$^+$.

tions, the absorption coefficients correlate surprisingly well with the number of {Ru(terpy)$_2$} motifs in the complex (for the monoruthenium species **3**·2PF$_6$, $\varepsilon = 17.3 \times 10^3$ dm^3 mol^{-1} cm^{-1}, for the diruthenium species **5**·4PF$_6$, **7**·6PF$_6$ and **9**·6PF$_6$, $\varepsilon/10^3 = 32.9$, 36.8, 39.3 dm^3 mol^{-1} cm^{-1} respectively and for the tetraruthenium compounds **8**·10PF$_6$ and **10**·10PF$_6$, $\varepsilon/10^3 =$ 78.9 and 82.4 dm^3 mol^{-1} cm^{-1}).

The electrochemical properties of the complexes were investigated with a view to quantifying metal–metal interactions within these systems. Although the ether bridges are formally expected to be insulating, in contrast to phenylene-linked species studied previously the presence of charged substituents on the ligands is expected to have an influence on the redox properties of the central heteroatom. This question is of particular relevance to our related studies on polynuclear dendrimers and metallostars where we routinely find that only outer generation metal centres may electrochemically be addressed. The heterotrinuclear complexes both exhibit two metal-centred redox processes. The complex **7**·6PF$_6$ shows a two electron ruthenium(II)–ruthenium(III) process at +0.91 V (no resolved splitting) and a one electron iron(II)–iron(III) process at +0.71 V, whilst **9**·6PF$_6$ also shows a two electron ruthenium(II)–ruthenium(III) process at +0.91 V (no resolved splitting) and a one electron cobalt(II)–cobalt(III) process at −0.10 V (Fig. 2). In both complexes the ruthenium(II)–ruthenium(III) processes were apparently near-reversible ($E_a - E_c = 60$–80 mV) and more or less independent of scan rate (20 to 80 mV s^{-1}). Assuming that the two ruthenium centres are non-interacting, then a simple statistical treatment predicts a separation in the formal reduction potentials for the redox process at each centre of (RT/F) ln 4 or 36 mV at 298 K with a cyclic voltammetric response resembling a one electron process (*i.e.* $E_a - E_c = 59$ mV).[19] The iron(II)–iron(III) potential is shifted about 100 mV to more positive potential than for the model compound [Fe(**IV**)$_2$][PF$_6$]$_2$ (+0.60 V), consistent with the presence of the charged substituents on the ligands destabilising the iron(III) state.

In the pentanuclear complexes **8**·10PF$_6$ and **10**·10PF$_6$ the situation is somewhat different. Once again, single ruthenium(II)–ruthenium(III) processes are observed at +0.89 and +0.91 V respectively, and, although multiple processes are not resolved, there is a significant broadening ($E_a - E_c = 150$ and 190 mV respectively). Assuming that (i) there is no interaction between the ruthenium centres and (ii) that the inner and outer generation ruthenium centres are electrochemically equivalent, the generalised treatment of Bard and co-workers[20] for n non-interacting centres leads to a difference in the formal redox potentials of the first and last process of ($2RT/F$) ln n, or in our case with $n = 4$ of about 70 mV at 298 K, compatible with the observed voltammograms. In the case of **8**·10PF$_6$ a very poorly resolved iron(II)–iron(III) process is observed as a weak shoulder on the ruthenium(II)–ruthenium(III) wave with a potential close to that of **7**·6PF$_6$. For **10**·10PF$_6$ a very poorly reversible and weak cobalt(II)–cobalt(III) process is observed close to 0 V. The increasing lack of reversibility at inner generation metal sites has been discussed previously[21] and these new compounds appear to fit into the general trend, in accord with our previous observations on cobaltahexaruthenametallastars.[6]

The ruthenium(II)–ruthenium(III) potentials in both the tri- and penta-nuclear complexes are somewhat (≈50 mV) more positive than those in the starting complex ligands, as expected on the basis of the higher charges. In each case, two quasi-reversible ligand-centred reductions were also observed at ≈−1.6 and ≈−1.8 V.

The ^{1}H NMR spectra of these complexes (Table 1) are well resolved and show characteristic changes upon coordination of the pendant terpy domains of **3**·2PF$_6$ or **5**·4PF$_6$ to iron(II) or cobalt(II). The spectra of **3**·2PF$_6$ or **5**·4PF$_6$ in CD$_3$CN closely resemble one another, with the only significant difference being observed for H^{C6}, which lies over a terpy ring in **3**·2PF$_6$ but over a **I** ligand in **5**·4PF$_6$. As mentioned above, the A rings are characteristic with a sequence A3–A6–A4–A5 and chemical shifts ≈ δ 8.80–8.73–8.04–7.50, typical of a non-coordinated terpy domain. Upon reaction of **3**·2PF$_6$ or **5**·4PF$_6$ with iron(II) to give **7**·6PF$_6$ or **8**·10PF$_6$ the sequence of the A ring resonances changes to A3–A4–A6–A5, with A6 undergoing a large upfield shift to δ 7.44 and A5 shifting upfield by ≈0.25 ppm, primarily as a result of the shielding from the second terpy domain coordinated to the iron(II) centre. A significant shift of 0.4 ppm is associated with D3 which is sensitive to changes in the adjacent metal-binding domain, whilst the upfield shift of A3 is a result of van der Waals deshielding that is a consequence of the adoption of the *cis* conformation in a coordinated terpy domain. In general the changes observed upon formation of the tri- and penta-nuclear complexes are similar. The only other significant changes are associated with the C ring protons which generally experience small downfield shifts as a result of the increased localised charge density. The ^{1}H NMR spectra of **5**·4PF$_6$ and **8**·10PF$_6$ are compared in Fig. 1a and 1b respectively.

The cobalt(II) complexes **9**·6PF$_6$ and **10**·10PF$_6$ contain a d^7 metal centre and will be paramagnetic regardless of the spin state or geometry. In the solid state, [Co(terpy)$_2$]$^{2+}$ complexes are often spin-crossover species with a spin state determined by lattice effects involving solvent or counter ion. The introduction of substituents into the 6 position of the terpy results in high-spin complexes, but ligands with 4′ substituents such as **I** behave much as terpy itself.[22] The ^{1}H NMR spectra of paramagnetic complexes often exhibit unusual features.[23] We have previously shown that the paramagnetically shifted spectra observed for cobalt(II) complexes with oligopyridines are diagnostic and may be used to establish coordination modes and to investigate dynamic processes.[6,24,25] In this case, the ^{1}H NMR spectra provide unambiguous evidence for the binding of the non-coordinated terpy domains to cobalt(II). In addition to a mass of poorly resolved peaks in the "normal" δ 7–10 region, each complex also exhibits five resonances which are paramagnetically shifted downfield. The ^{1}H NMR spectrum of the downfield region of a CD$_3$CN solution of **9**·6PF$_6$ is presented in Fig. 3; the spectrum exhibits peaks at δ 114, 68, 67, 37 and 14.2 assigned to the A and B ring protons. To all intents and purposes, the downfield region of **10**·10PF$_6$ was identical (Table 1). Full assignment was not possible as the peaks are considerably broadened and all attempts at correlation spectroscopy failed. The spectra confirm the coordination of the pendant terpy domain to the cobalt.

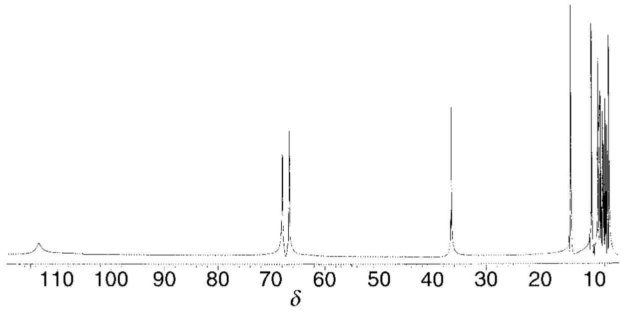


Fig. 3 300 MHz ^{1}H NMR spectrum of a CD_3CN solution of the paramagnetic trinuclear cobalt(II) complex **9**·10PF$_6$.

Conclusion

We have shown that the reaction of ruthenated terpy ligands with labile first row transition metal salts leads to the formation of heteropolynuclear complexes in an efficient self-assembly process. The metal centres behave essentially as independent units and there is no evidence for ground state electronic communication through ether bridges in complexes of ligand **I**. We are currently extending these observations to the synthesis of heteropolynuclear metallostars.

Experimental

General

The ^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini 300 or Bruker AC250 spectrometers, FAB mass spectra on a VG 70–250 spectrometer with 3-nitrobenzyl alcohol as the matrix, MALDI-TOF mass spectra on a PerSeptive Biosystems Voyager-RP Biospectrometry Workstation using a variety of matrices, IR spectra on a Genesis Series FTIR spectrophotometer with the samples in compressed KBr disks and electronic spectra using a Perkin-Elmer Lambda 19 spectrophotometer. Electrochemical measurements were performed using an EcoChemie Autolab PGSTAT 20 potentiostat and a conventional three electrode configuration. Glassy carbon working and platinum auxiliary electrodes were used with an Ag–AgCl reference electrode. Freshly distilled HPLC grade MeCN was used as solvent. The base electrolyte was 0.1 M $[Bu^n{}_4N][BF_4]$, recrystallised from ethanol–water and rigorously dried before use. Potentials are quoted *versus* the ferrocene–ferrocenium couple (Fc–Fc$^+$, 0.0 V; found at ≈+0.56 V *vs.* NHE and ≈+0.319 V *vs.* SCE although these comparisons are not exact due to unknown liquid junction potentials between the MeCN solution of ferrocene and the aqueous reference electrodes), and all potentials were referenced to internal ferrocene added at the end of each experiment. The compounds **II**,[26] **III**,[26] **1**·2PF$_6$,[16] and **2**·2PF$_6$,[16] **3**·2PF$_6$[3] and **4**·2PF$_6$[3] were prepared by the literature methods.

Preparations

[(terpy)Ru(I)Ru(I)][PF$_6$]$_4$ 5·4PF$_6$. A mixture of [Ru(terpy)Cl$_3$] (150 mg, 0.34 mmol) and AgBF$_4$ (199 mg, 1.02 mmol) in Me_2CO (60 cm^3) was heated to reflux for 2 h to give a blue solution containing solid AgCl; this was filtered to remove AgCl and the filtrate reduced to dryness and then redissolved in dmf (40 cm^3). The blue solution so obtained was added dropwise over 40 min to a solution of complex **2**·2PF$_6$ (460 mg, 0.34 mmol) in dmf (40 cm^3) maintained at 80 °C and then the reaction mixture was heated at reflux for 2 h. The resulting red solution was cooled and treated with H_2O (150 cm^3) and methanolic $[NH_4][PF_6]$ to precipitate a fine red solid which was filtered off. The solid was redissolved in the minimum volume of MeCN and purified by column chromatography (SiO_2, MeCN-saturated aqueous KNO_3–H_2O 7:1:0.5 v/v). The major orange fraction was collected, treated with H_2O (15 cm^3) and methanolic $[NH_4][PF_6]$ and reduced in volume *in vacuo* to precipitate the complex. Recrystallisation from 1:1 MeCN–H_2O afforded **5**·4PF$_6$ as an orange-red solid (288 mg, 43%) (Found: C, 44.4; H, 3.0; N, 10.8. $C_{75}H_{51}F_{24}N_{15}O_2P_4Ru_2$ requires C, 45.6; H, 2.6; N, 10.6%); *m*/*z* (MALDI-TOF) 1829 {M − PF$_6$}, 1686 {M − 2PF$_6$}, 1538 {M − 3PF$_6$}, 1393 {M − 4PF$_6$} and 1065 {Ru(**I**)$_2$}; λ_{max}/nm (MeCN) 240 (ε/dm^3 mol^{-1} cm^{-1} 79 500), 278 (94 900), 289 (94 400), 304 (112 000) and 488 (50 700).

[{(terpy)Ru(I)}$_2$Fe][PF$_6$]$_6$ 7·6PF$_6$. A solution of $FeSO_4·7H_2O$ (8 mg, 0.03 mmol) in H_2O (10 cm^3) was added dropwise over 45 min to complex **3**·2PF$_6$ (44 mg, 0.039 mmol) in MeCN (20 cm^3). The red-purple solution was stirred at room temperature for a further 1 h and then methanolic $[NH_4][PF_6]$ was added and the volume reduced *in vacuo* to precipitate **7**·6PF$_6$. This was recrystallised from 1:1 H_2O–MeCN, collected by filtration, washed with H_2O and dried *in vacuo* to give the trinuclear complex **7**·6PF$_6$ as a red-purple powder (35 mg, 68%) (Found: C, 40.1; H, 2.6; N, 9.5. $C_{90}H_{62}F_{36}FeN_{18}O_2P_6Ru_2·6H_2O$ requires C, 40.6; H, 2.8; N, 9.5%); *m*/*z* (MALDI-TOF) 2264 {M − 2PF$_6$}, 2123 {M − 3PF$_6$}, 1978 {M − 4PF$_6$} and 1643 {(terpy)Ru(**I**)Fe(**I**)(PF$_6$)$_2$}; λ_{max}/nm (MeCN) 241 (ε/dm^3 mol^{-1} cm^{-1} 105 000), 277 (121 000), 288 (126 000), 306 (153 000), 481 (36 800) and 559 (18 200).

[{(terpy)Ru(I)Ru(I)}$_2$Fe][PF$_6$]$_{10}$ 8·10PF$_6$. A solution (1 cm^3) of $[NH_4]_2Fe(SO_4)_2·6H_2O$ (29 mg, 0.075 mmol) in H_2O (10 cm^3) was added to a solution of complex **5**·4PF$_6$ (30 mg, 0.015 mmol) in MeCN (15 cm^3) and the resulting mixture stirred at room temperature for 1 h after which methanolic $[NH_4][PF_6]$ was added and the volume reduced *in vacuo* to give a red-purple precipitate which was collected by filtration, washed with water and diethyl ether, and then dried *in vacuo*. Recrystallisation from 1:1 Me_2CO–H_2O gave **8**·10PF$_6$ as a deep red powder (26 mg, 81%); *m*/*z* (MALDI-TOF) 4019 {M − 2PF$_6$}, 3860 {M − 3PF$_6$}, 3725 {M − 4PF$_6$} and 1887 {(terpy)Ru(**I**)Ru(**I**)Fe(PF$_6$)$_3$}; λ_{max}/nm (MeCN) 241 (ε/dm^3 mol^{-1} cm^{-1} 174 000), 278 (214 000), 288 (236 000), 305 (263 000), 486 (78 900) and 554 (27 700).

[{(terpy)Ru(I)}$_2$Co][PF$_6$]$_6$ 9·6PF$_6$. Solutions of complex **3**·2PF$_6$ (83 mg, 0.075 mmol) in MeCN (10 cm^3) and $Co(OAc)_2·4H_2O$ (9 mg, 0.0375 mmol) in H_2O (10 cm^3) were mixed and heated to reflux for 3 h. The reaction mixture was cooled and treated with H_2O (10 cm^3) and methanolic $[NH_4][PF_6]$ to give an orange solid which was filtered off. Recrystallisation from 1:1 MeCN–H_2O gave **9**·6PF$_6$ as an orange powder (72 mg, 75%) (Found: C, 41.8; H, 2.8; N, 9.9. $C_{90}H_{62}CoF_{36}N_{18}O_2P_6Ru_2$ requires C, 42.3; H, 2.4; N, 9.9%); *m*/*z* (MALDI-TOF) 2268 {M − 2PF$_6$}, 2123 {M − 3PF$_6$} and 1641 {(terpy)Ru(**I**)Co(**I**)(PF$_6$)$_2$}; λ_{max}/nm (MeCN) 240 (ε/dm^3 mol^{-1} cm^{-1} 114 000), 274 (129 000), 287 (129 000), 306 (160 000) and 480 (39 300).

[{(terpy)Ru(I)Ru(I)}$_2$Co][PF$_6$]$_{10}$ 10·10PF$_6$. A solution (1 cm^3) of $Co(OAc)_2·4H_2O$ (19 mg, 0.075 mmol) in H_2O (10 cm^3) was added to complex **5**·4PF$_6$ (30 mg, 0.015 mmol) in MeCN (10 cm^3) and the mixture heated to reflux for 3 h to give an orange solution that was cooled and treated with H_2O (10 cm^3) and methanolic $[NH_4][PF_6]$ to give an orange solid. This was collected by filtration, washed with water, dried *in vacuo* and recrystallised from 1:1 Me_2CO–H_2O to give **10**·10PF$_6$ as an orange-brown powder (22 mg, 68%); *m*/*z* (MALDI-TOF) 4009 {M − 2PF$_6$}, 3867 {M − 3PF$_6$}, 3722 {M − 4PF$_6$} and 1888 {(terpy)Ru(**I**)Ru(**I**)Co(PF$_6$)$_3$}; λ_{max}/nm (MeCN) 241 (ε/dm^3 mol^{-1} cm^{-1} 195 000), 278 (228 000), 288 (239 000), 304 (278 000) and 485 (82 400).

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