Metal-Mediated Synthesis of Multidomain Ligands— A New Strategy for Metallosupramolecular Chemistry

Edwin C. Constable,* Alexander M. W. Cargill Thompson, Peter Harveson, Ludwig Macko and Margareta Zehnder

Abstract: The bridging ligand bis{4'-(2,2':6',2''-terpyridinyl)}ether (**1**) can be prepared in 69% yield from the reaction of 4'-chloro-2,2':6',2''-terpyridine (**3**) with 2,2':6',2''-terpyridin-4'(1'*H*)-one (**2**) in Me_2NCHO in the presence of KOH. More conveniently, complexes of **1** can be prepared in situ by the reaction of **2** with a ruthenium(II) complex of **3** in the presence of K_2CO_3. This methodology has been developed for the synthesis of a range of mono-, di-, tri- and hexanuclear complexes with a variety of Xtpy (Xtpy = 4'-substituted 2,2':6',2''-terpyridine) terminator ligands. The molecular structure of **1** ($a = 9.623(2)$, $b = 11.241(1)$, $c = 11.828(1)$ Å; space group $P\bar{1}$; $\alpha = 93.064(9)$, $\beta = 107.072(14)$, $\gamma = 99.088(14)°$; $Z = 2$, $R = 0.0450$, $R_w = 0.0577$) has been determined. The generality of the methodology may ultimately be limited by the sensitivity of the ether-linkage in **1** to attack by nucleophiles.

Keywords
crystal structure · polynuclear complexes · ruthenium compounds · supramolecular chemistry · terpyridines

Introduction

There is considerable interest in the design of metallosupramolecular oligomers containing known numbers of metal ions in defined spatial arrangements.[1, 2] The electronic and photophysical properties of oligopyridine complexes of d^6 transition metal ions make these particularly attractive motifs for incorporation into such multinuclear systems.[3] In particular, the possibility of intermetallic electron or energy transfer offers the potential for the design of molecular devices that will channel light energy or electrons in a defined manner. Ultimately, this might allow the design and synthesis of nano-scaled supramolecular devices for light harvesting and photoconversion.

Such molecular devices may be constructed by using multidomain ligands possessing two or more metal-binding domains addressable by two or more metal ions. The total number of metal-binding domains and the number of donor atoms within each metal-binding domain will control the topography and the growth pattern (divergent or linear) of the metallosupramolecule. The combination of correctly designed ligands with kinetically inert d^6 metal centres allows a stepwise, divergent synthesis of the metallosupramolecules that is motivationally and conceptually different from strictly self-assembling systems involving labile metal ions.[2, 4] The primary strategy which has emerged is that described by Denti and Balzani as the "complexes-as-metal, complexes-as-ligands" approach.[5] This strategy has been used widely for the synthesis of polynuclear complexes containing 2,3- and 2,5-bis(2-pyridyl)pyrazine and related ligands.[5–7] In these cases, the metal-binding domains are didentate, and termination involves a didentate ligand such as 2,2'-bipyridine or 1,10-phenanthroline. We and others have discussed previously the disadvantages inherent in the assembly of supramolecules based upon six-coordinate metals bonded to three didentate domains, and have developed a suite of ligands based upon tridentate 2,2':6',2''-terpyridine (tpy) metal-binding domains.[8–11] Ligands containing two or three tpy metal-binding domains are readily obtained in reasonable yield, and a wide variety of substituted tpy ligands is available for use as terminators; an appropriate choice of substituent in an Xtpy terminator (Xtpy = 4'-substituted 2,2':6',2''-terpyridine) allows a subtle control over the electrochemical and photophysical properties of the metal complex.[12]

As progressively higher nuclearities are reached, the divergent complexes-as-metals approach has a number of disadvantages. Firstly, it becomes increasingly difficult to specifically address only one of the metal-binding domains in a multi-domain ligand, and a protection–deprotection methodology has recently been introduced to overcome this problem.[7] Nevertheless, this is a multistep procedure with inherent disadvantages. The second problem concerns the coordination of the multidomain ligands in the higher nuclearity complexes. In our hands, the rate of coordination is competitive with that of decomplexation of the earlier generation sites. The outcome is a partial scrambling of ligands. In view of these two problems, we have developed two parallel strategies—convergent synthesis with multinuclear building blocks and in situ ligand assembly. In this paper we describe the latter approach.

Previous studies of metallosupramolecular oligomers have always relied upon the prior preparation of the metal-free multidomain ligand, even if this was obtained in a metal-directed

[*] Prof. Dr. E. C. Constable, Prof. Dr. M. Zehnder, Dr. A. M. W. Cargill Thompson, P. Harveson, L. Macko
Institut für Anorganische Chemie der Universität
Spitalstrasse 51, CH-4056 Basel (Switzerland)
Telefax: Int. code + (61)322-1554
e-mail: constable@ubaclu.unibas.ch

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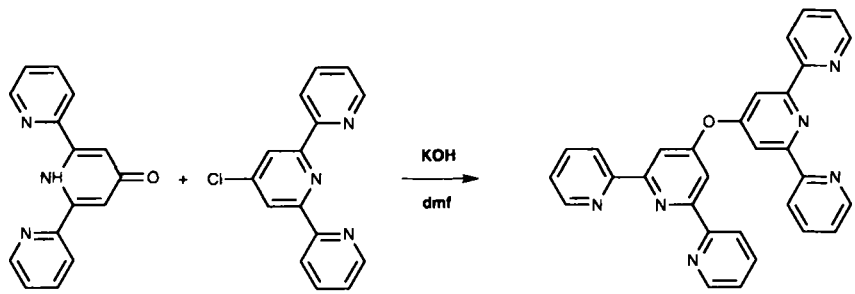
synthesis. Coordination of 4-halopyridines to transition metals activates the 4-position towards attack by nucleophiles,[9, 13, 14] and it occurred to us that if both the electrophile and the nucleophile contained metal-binding domains, that this could be developed into an in situ synthesis of multidomain ligands. Specifically, the reaction of coordinated electrophiles with a nucleophile would give a complex with a vacant metal-binding domain. In this paper we describe a new type of ligand with two tpy metal-binding domains connected through an ether linkage. This new ligand may be obtained metal-free or as a complex from an in situ synthesis. The introduction of the ether linkage results in a noncoplanar and nonlinear arrangement of the metal-binding domains.

Results and Discussion

The ligand bis{4′-(2,2′:6′,2″-terpyridinyl)}ether (**1**) could be prepared directly (Scheme 1) by the nucleophilic attack of the anion derived from 2,2′:6′,2″-terpyridin-4′(1′*H*)-one (**2**) upon 4′-chloro-2,2′:6′,2″-terpyridine (**3**). This reaction was, however, relatively slow, and for good conversions required an excess of **2** and potassium hydroxide at reflux in DMF for a number of days. After this period, the reaction mixture was cooled and quenched with water; **1** precipitated as a white solid, while **2** and its anion remained in solution. Typically, yields of the order of 70% were obtained. Recrystallisation from CH_2Cl_2/MeOH afforded analytically pure **1** as a colourless microcrystalline solid. The dinucleating ligand can be readily distinguished from **3**; in the ^{1}H NMR spectrum of a $CDCl_3$ solution, the $H^{3'}$ singlet occurs at $\delta = 8.22$ for **1** as compared to $\delta = 8.48$ for **3**. The simplicity of the remainder of the ^{1}H NMR spectrum of **1** is consistent with the two tpy environments being equivalent on the NMR timescale. The electron impact mass spectrum exhibits a molecular ion peak at $m/z = 480$.



2 **3** **1**

Scheme 1. The synthesis of the free ligand **1**.

Colourless crystals of **1** suitable for crystallographic study were grown by the slow evaporation of a chloroform/methanol solution, and the molecular structure from the X-ray determination is presented in Figure 1. A number of features are immediately apparent. Firstly, each of the tpy domains is approximately planar and exhibits a *transoid* conformation about the interannular C–C bonds, as observed in all other tpy ligands in the solid state.[8–10, 15] The tpy domains are not precisely planar, but have N-C-C-N dihedral angles in the usual range 4.0–6.0°.[8–10, 15] All bond lengths and angles within the ligand are typical. The second feature revealed by the structural analysis is

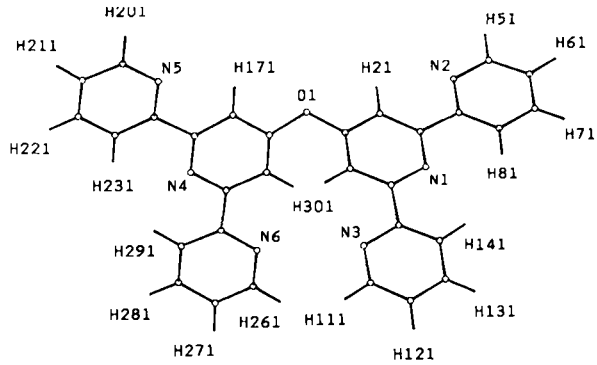


Fig. 1. The crystal structure of **1** showing the numbering scheme adopted. Selected bond lengths (Å): O(1)–C(1) 1.383(1), O(1)–C(16) 1.386(1), N(1)–C(3) 1.338(2), N(1)–C(9) 1.344(2), N(2)–C(4) 1.334(2), N(2)–C(5) 1.343(2), N(3)–C(10) 1.339(2), N(3)–C(11) 1.334(2), N(4)–C(18) 1.340(2), N(4)–C(24) 1.343(2), N(5)–C(19) 1.334(2), N(5)–C(20) 1.344(2), N(6)–C(25) 1.333(2), N(6)–C(26) 1.333(2).

that the tpy domains are not coplanar, but are skewed with respect to each other (Fig. 2). This is a natural consequence of the introduction of the approximately sp^3-hybridised ($\sphericalangle$C(1)-O(1)-C(16) = 120.0(1)°) ether spacer, and is in contrast to other structurally characterised bis(2,2′:6′,2″-terpyridine) ligands in which the tpy domains are constrained to a linear relationship.[8–10] The skewing is defined by the dihedral angles $\sphericalangle$C(30)-C(16)-O(1)-C(1) and $\sphericalangle$C(16)-O(1)-C(1)-C(15) of approximately 37°. The bond lengths C(16)–O(1) and C(1)–O(1) of 1.386(1) and 1.383(1) Å, respectively, are typical of diaryl ethers. In the solid state, the lattice is constructed such that π-stacking interactions with interplanar distances of approximately 4 Å between the tpy domains of adjacent molecules are observed (Fig. 2).

The new bridging ligand **1** may be used for the assembly of metallosupramolecules in a similar manner to other ligands containing tpy metal-binding domains that we have studied.[8–10, 16–20] For example, the reaction of a slight excess of [Ru(**4**)Cl_3] with **1** in boiling ethane-1,2-diol gave, after chromatographic workup, the dinuclear complex [(**4**)Ru(**1**)Ru(**4**)][PF_6]$_4$ as an orange solid in around 25% yield. The same product could be obtained by performing the reaction in methanol containing a little *N*-ethylmorpholine as reducing agent, but lowered yields were obtained as a result of some over-reduction to ruthenium metal. The ^{1}H NMR spectrum of this dinuclear complex is characteristic (Table 1) and exhibits a total of eleven resonances corresponding to the six environments of the terminal ligands **4** and the five of the symmetric ligand **1**.

The low yields observed in the preparation of [(**4**)Ru(**1**)-Ru(**4**)]$^{4+}$ complexes direct from **1**, combined with the lengthy reaction times involved

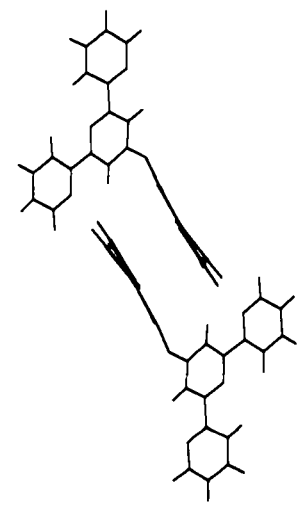
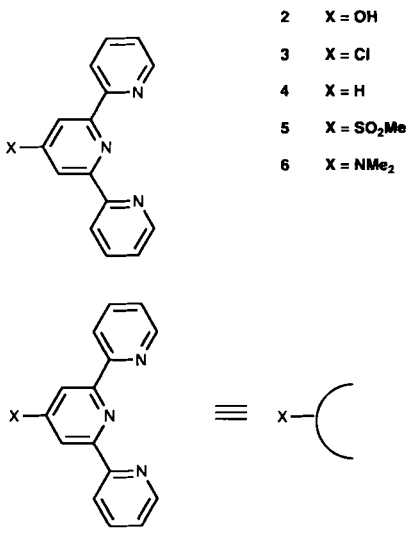


Fig. 2. An alternative view of **1** showing the skewing of the ligand and the stacking in the solid state.

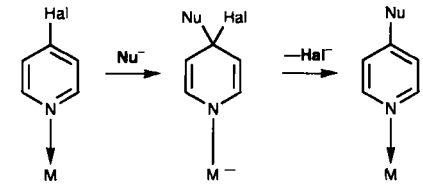
Table 1. ^{1}H NMR spectroscopic data (300 MHz, CD_3CN, 25 °C) for the complexes reported.

		(**X**tpy)						Ru(**tpy**-O-tpy)					Ru(tpy-O-**tpy**)				
		H^3 d	H^4 dd	H^5 dd	H^6 d	$H^{3'}$	$H^{4'}$	H^3 d	H^4 dd	H^5 dd	H^6 d	$H^{3'}$ s	H^3 d	H^4 dd	H^5 dd	H^6 d	$H^{3'}$ s
[(**4**)Ru(**1**)][PF_6]$_2$		8.49	7.94	7.23	7.50	8.73 d	8.39 t	8.40	7.84	7.13	7.33	8.55/8.51	8.80	8.04	7.50	8.73	8.51/8.55
[(**1**)Ru(**1**)][PF_6]$_2$								8.41	7.87	7.21	7.50 m	8.55/8.51	8.80	8.04	7.50 m	8.72	8.51/8.55
[(**4**)Ru(**1**)Ru(**4**)][PF_6]$_4$		8.53	7.97	7.27	7.60	8.77 d	8.43 t	8.57	7.94	7.21	7.41	8.81					
[(**4**)Ru(**1**)Ru(**5**)][PF_6]$_4$	**4** end	8.53	7.95 m	7.27	7.60	8.78 d	8.44 t	8.57	7.95 m	7.21 m	7.41 m	8.82					
	5 end	8.72	8.03	7.36	7.68	9.16 s	**Me** 3.52 s	8.57	7.95 m	7.21 m	7.41 m	8.82					
[(**4**)Ru(**1**)Ru(**3**)][PF_6]$_4$	**4** end	8.53	7.97 m	7.29 m	7.64 m	8.78 d	8.43 t	8.58	7.97 m	7.21 m	7.43 m	8.83					
	3 end	8.53	7.97 m	7.29 m	7.64 m	8.88 s	–	8.58	7.97 m	7.21 m	7.43 m	8.83					
		(**X**tpy)						Ru(**tpy**-O-tpy)					Ru(tpy-O-**tpy**)				
		H^3 d	H^4 dd	H^5 dd	H^6 d	$H^{3'}$	$H^{4'}$	H^3 d	H^4 dd	H^5 dd	H^6 d	$H^{3'}$ s	H^3 d	H^4 dd	H^5 dd	H^6 d	$H^{3'}$ s
[(**4**)Ru(**1**)Ru(**1**)Ru(**4**)][PF_6]$_6$		8.53	7.97	7.28	7.62	8.78 d	8.44 t	8.58	7.95	7.21	7.42	8.84	8.61	8.00	7.33	7.69	8.84
[(**3**)Ru(**1**)Ru(**1**)Ru(**3**)][PF_6]$_6$		8.53	7.98 m	7.32 m	7.64	8.88 s	–	8.57	7.98 m	7.22	7.46	8.83/8.81	8.61	7.98 m	7.32 m	7.68	8.81/8.83
[(**5**)Ru(**1**)Ru(**1**)Ru(**5**)][PF_6]$_6$		8.72	8.03	7.37	7.69	9.17 s	**Me** 3.53 s	8.59	7.96	7.20	7.40	8.86/8.84	8.62	8.00	7.33	7.69	8.84/8.86
		(**tptpy**)						(tptpy)Ru(**X**tpy)									
		H^3 d	H^4 dd	H^5 dd	H^6 d	$H^{3'}$ s	H^{Ar} s	H^3 d	H^4 dd	H^5 dd	H^6 d	$H^{3'}$	$H^{4'}$				
[{(**4**)Ru}$_3$(**7**)][PF_6]$_6$		9.04	7.99 m	7.23	7.55	9.65	9.26	8.54	7.99 m	7.23	7.43	8.79 d	8.46 t				
[{(**3**)Ru}$_3$(**7**)][PF_6]$_6$		8.89	8.00 m	7.26 m	7.58	9.48	9.23	8.54	8.00 m	7.26 m	7.48	8.90 s	–				
		(**tptpy**)Ru(botpy)						Ru(**tpy**-O-tpy)					Ru(tpy-O-**tpy**)				
		H^3 d	H^4 dd	H^5 dd	H^6 d	$H^{3'}$ s	H^{Ar} s	H^3 d	H^4 dd	H^5 dd	H^6 d	$H^{3'}$ s	H^3 d	H^4 dd	H^5 dd	H^6 d	$H^{3'}$ s
[{(**1**)Ru}$_3$(**7**)][PF_6]$_6$		8.94	8.05	7.32	7.62	9.52	9.23	8.47	7.90	7.23	7.55	8.58	8.81	8.05	7.52	8.74	8.58
		(**X**tpy)Ru(botpy)						Ru(**tpy**-O-tpy)									
		H^3 d	H^4 dd	H^5 dd	H^6 d	$H^{3'}$		H^3 d	H^4 dd	H^5 dd	H^6 d	$H^{3'}$ s					
[{(**4**)Ru(**1**)Ru}$_3$(**7**)][PF_6]$_{12}$	**7** end	8.95	8.08	7.36	7.71	9.54 s	**Ar** 9.29 s	8.63	7.99 m	7.32	7.67	8.84/8.86					
	4 end	8.54	7.99 m	7.29	7.62	8.78 d	**H**$^{4'}$ 8.44 t	8.59	7.99 m	7.22	7.43	8.86/8.84					
[{(**3**)Ru(**1**)Ru}$_3$(**7**)][PF_6]$_{12}$	**7** end	8.95	8.08	7.34 m	7.71	9.53 s	**Ar** 9.29 s	8.63	7.99 m	7.34 m	7.67	8.84/8.86					
	3 end	8.53	7.99 m	7.34 m	7.65	8.89 s	–	8.59	7.99 m	7.23	7.46	8.86/8.84					
[{(**5**)Ru(**1**)Ru}$_3$(**7**)][PF_6]$_{12}$	**7** end	8.96	8.08	7.35 m	7.69 m	9.54 s	**Ar** 9.29 s	8.63	8.00 m	7.35 m	7.69 m	8.85/8.87					
	5 end	8.73	8.00 m	7.35 m	7.69 m	9.17 s	**Me** 3.53 s	8.60	8.00 m	7.21	7.41	8.87/8.85					

in the synthesis of **1**, prompted us to investigate alternative synthetic approaches to such polynuclear species. We have previously shown that metal complexes of 4-halopyridines are activated towards nucleophilic displacement of the halogen by a



variety of nucleophiles,[9, 13, 14] and we have used the reaction of $[Fe(\mathbf{3})_2]^{2+}$ with dimethylamine for the preparation of $[Fe(\mathbf{6})_2]^{2+}$ salts.[9, 14] It is worthy of note that **3** itself reacts only extremely sluggishly with dimethylamine. The intermediate in these metal-assisted substitution reactions is thought to be stabilised by charge delocalisation to the metal centre (Scheme 2).



Scheme 2. The proposed mechanism of metal-assisted nucleophilic substitution reactions of 4-halopyridines.

Accordingly, we attempted to generate ligand **1** in situ by the reaction of **2** or its anion with complexes of ruthenium(II) with **3**. Initial attempts to react $[(\mathbf{4})Ru(\mathbf{3})]^{2+}$ salts directly with $[(\mathbf{4})Ru(\mathbf{2})]^{2+}$ salts with the intention of obtaining the dinuclear species $[(\mathbf{4})Ru(\mathbf{1})Ru(\mathbf{4})]^{4+}$ directly were unsuccessful. The reaction was attempted without success in DMSO at 60 °C in the presence of potassium hydroxide (5 equiv)[19] and in dry acetonitrile with excess potassium carbonate. The reactions were followed by thin layer chromatography (silica, H_2O/MeCN/KNO_3(aq) as mobile phase), but no dinuclear complex was produced, even after prolonged reaction times of several days. It was, however, observed that the $[(\mathbf{4})Ru(\mathbf{3})]^{2+}$ salts were converted slowly to $[(\mathbf{4})Ru(\mathbf{2})]^{2+}$ salts if the solvent used was slightly damp. We therefore concluded that though $[(\mathbf{4})Ru(\mathbf{3})]^{2+}$ may be more *activated* to attack by nucleophiles than free **3**, coordinated **2** is *deactivated* as a nucleophile by coordination to an electropositive metal centre. The logical progression was therefore to react *coordinated* **3** with deprotonated anion from **2**.

The heteroleptic mononuclear complex $[(\mathbf{4})Ru(\mathbf{3})][PF_6]_2$[9] reacted cleanly with an excess of **2** in boiling acetonitrile in the presence of potassium carbonate to give the red mononucleating *ligand* complex $[(\mathbf{4})Ru(\mathbf{1})][PF_6]_2$ in near-quantitative yield

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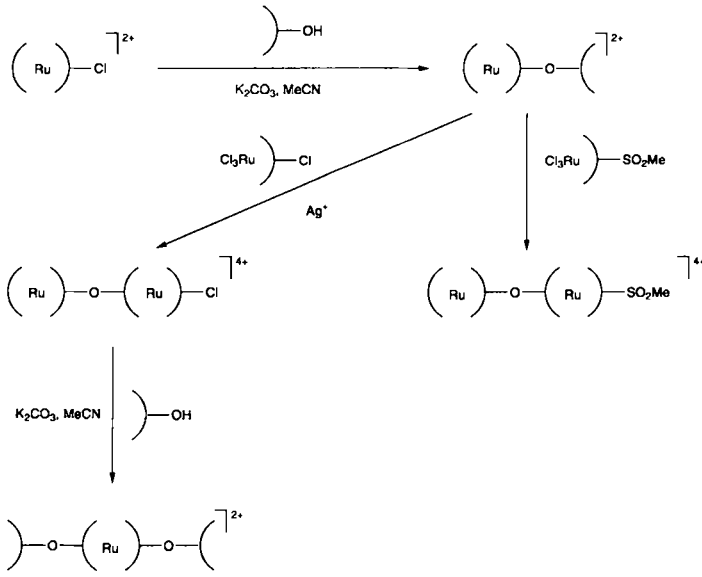
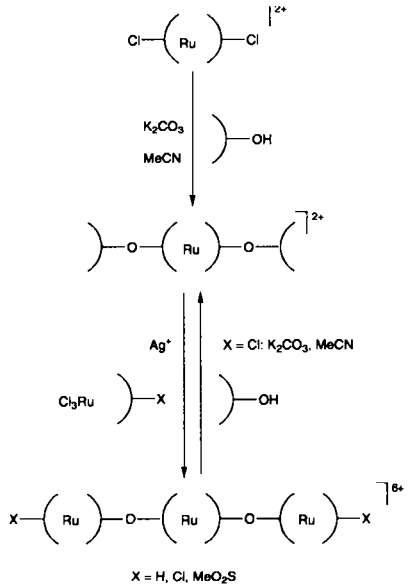


Scheme 3. The generation of complexes of **1** in situ by the route starting with the heteroleptic complex $[(\mathbf{4})Ru(\mathbf{3})][PF_6]_2$.

(Scheme 3). The reaction proceeded to completion within a few hours, and could readily be followed by TLC. The homoleptic complex $[(\mathbf{3})Ru(\mathbf{3})][PF_6]_2$ reacted similarly with an excess of **2** in the presence of base to give the dinucleating ligand species $[(\mathbf{1})Ru(\mathbf{1})][PF_6]_2$ (Scheme 4), although a longer reaction time was needed. The FAB mass spectra were in accord with the proposed formulations; peaks corresponding to the loss of one and two PF_6^- counter ions from the molecular species were observed, along with some fragmentation ions. For example, $[(\mathbf{4})Ru(\mathbf{1})][PF_6]_2$ exhibits peaks at $m/z = 960$ and 814, assigned to $[M-PF_6]^+$ and $[M-2PF_6]^+$, respectively.

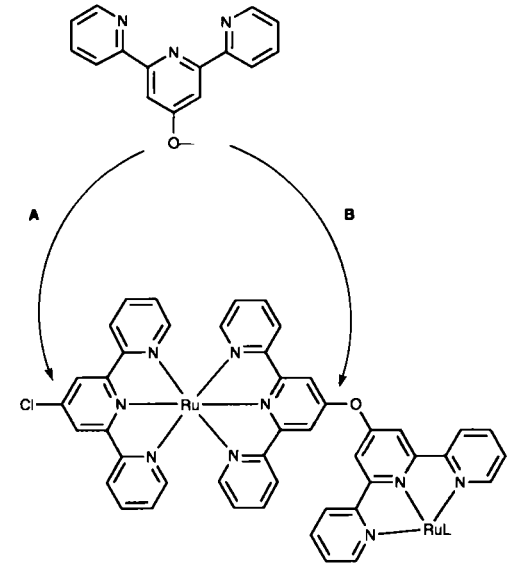
The mononuclear ligand complex $[(\mathbf{4})Ru(\mathbf{1})][PF_6]_2$ is a useful starting point for the assembly of asymmetric oligomers (Scheme 3). The reaction of $[(\mathbf{4})Ru(\mathbf{1})][PF_6]_2$ with $[Ru(\mathbf{3})Cl_3]$ or $[Ru(\mathbf{5})Cl_3]$ gave, after chromatographic purification, the red-orange dinuclear complexes $[(\mathbf{4})Ru(\mathbf{1})Ru(\mathbf{3})][PF_6]_4$ in 41% yield and $[(\mathbf{4})Ru(\mathbf{1})Ru(\mathbf{5})][PF_6]_4$ in 53% yield, respectively.



Scheme 4. The generation of complexes of **1** in situ by the route starting with the homoleptic complex $[(\mathbf{3})Ru(\mathbf{3})][PF_6]_2$.

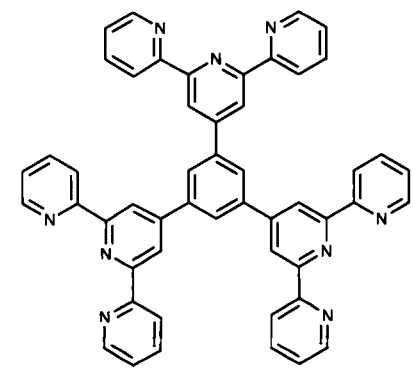
Similarly, the potentially dinucleating ligand complex $[(\mathbf{1})Ru(\mathbf{1})][PF_6]_2$ is a useful starting material for the synthesis of symmetrical trimers (Scheme 4), and reaction with two equivalents of $[Ru(\mathbf{3})Cl_3]$, $[Ru(\mathbf{4})Cl_3]$ or $[Ru(\mathbf{5})Cl_3]$ gave the trinuclear complexes $[(Xtpy)Ru(\mathbf{1})Ru(\mathbf{1})Ru(Xtpy)][PF_6]_6$ (Xtpy = **3**, **4** or **5**) in 34–38% yield. Mass spectra of these complexes were fully in accord with their proposed formulations.

Attempts to obtain higher nuclearity complexes by this methodology, by reaction of $[(\mathbf{4})Ru(\mathbf{1})Ru(\mathbf{3})][PF_6]_4$ or $[(\mathbf{3})Ru(\mathbf{1})Ru(\mathbf{1})Ru(\mathbf{3})][PF_6]_6$ with further **2** under the usual conditions, failed to give the expected ligand complexes $[(\mathbf{4})Ru(\mathbf{1})Ru(\mathbf{1})][PF_6]_4$ and $[(\mathbf{1})Ru(\mathbf{1})Ru(\mathbf{1})Ru(\mathbf{1})][PF_6]_6$. In each case, the mononuclear ligand complex $[(\mathbf{1})Ru(\mathbf{1})][PF_6]_2$ was identified by ^1H NMR spectroscopy as a major product of the reaction. At first sight this observation appears to be at odds with the facile preparation of the dinuclear and trinuclear complexes discussed above, but this is not so. The methodology relies upon the displacement of a leaving group (chloride) by the incoming nucleophile. Cleavage of a C–O bond in ligand **1** gives an alternative leaving group, and this process appears to be competitive with attack at the C–Cl bond (Scheme 5).



Scheme 5. The competing reactions that prevent the build-up of higher nuclearity complexes.

A combination of this methodology with our existing multidomain tpy ligands allows a variety of two- and three-dimensional metallosupramolecular arrays to be assembled. For example, 1,3,5-tris{4′-(2,2′:6′,2″-terpyridinyl)}benzene (**7**) is a trinucleating ligand containing three tpy domains,[18] which can be used for the assembly of higher nuclearity complexes; the absence of ether bridges in the central core eliminates any possibilities of C–O bond cleavage upon reaction with the **2**.



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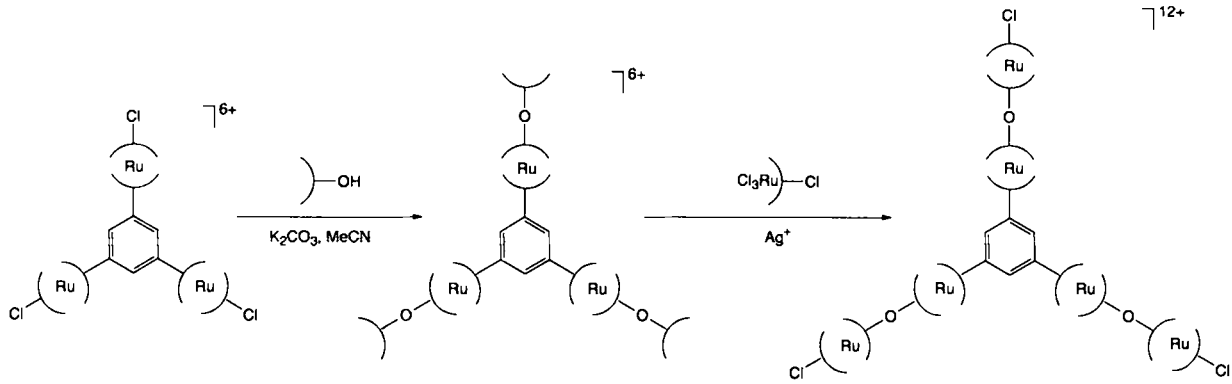

Scheme 6. The generation of complexes of **1** in situ by the route starting with the trinuclear complex $[\{(\mathbf{3})Ru\}_3(\mathbf{7})][PF_6]_2$.

The trinuclear complex $[\{(\mathbf{3})Ru\}_3(\mathbf{7})][PF_6]_6$ reacted cleanly with an excess of **2** in dry acetonitrile in the presence of potassium carbonate to give the trinucleating ligand complex $[\{(\mathbf{1})Ru\}_3(\mathbf{7})][PF_6]_6$ in 97% yield (Scheme 6). The ^1H NMR spectrum of a CD_3CN solution of this complex is quite simple, as all three ruthenium centres are identical and only sixteen resonances result from the two different coordinated tpy domains (ten resonances), the noncoordinated tpy domain (five resonances) and the central 1,3,5-trisubstituted benzene (one resonance) (Table 1).

The trinucleating ligand complex $[\{(\mathbf{1})Ru\}_3(\mathbf{7})][PF_6]_6$ could then be further treated with three equivalents of $[Ru(Xtpy)(Me_2CO)_3]^{n+}$ (Xtpy = **3**, **4** or **5**), which was generated by the reaction of $[Ru(Xtpy)Cl_3]$ with $AgBF_4$ in acetone, to give the hexanuclear complexes $[\{(Xtpy)Ru(\mathbf{1})Ru\}_3(\mathbf{7})][PF_6]_{12}$ in 27–32% isolated yield. These three hexanuclear complexes all exhibit similar ^1H NMR spectra (Table 1), which contain four sets of five or six resonances, assigned to the four tpy functionalities—the terminal Xtpy, the central **7** and the two nonequivalent ends of the **1** bridges. It is worthy of note that the solubility of these hexanuclear complexes in acetonitrile is comparable to that of the linear di- and trinuclear complexes discussed above. We have been unable to observe parent ions in the time-of-flight or FAB mass spectra of these higher nuclearity complexes.

As discussed above, attempts to further increase the nuclearity by treating the hexanuclear complex $[\{(\mathbf{3})Ru(\mathbf{1})Ru\}_3(\mathbf{7})][PF_6]_{12}$ with **2** and K_2CO_3 in acetonitrile to give the trinucleating ligand species $[\{(\mathbf{1})Ru(\mathbf{1})Ru\}_3(\mathbf{7})][PF_6]_{12}$ failed, and the hexanuclear complex fragmented. The main fragment observed in the ^1H NMR spectrum of the crude product mixture was $[(\mathbf{1})Ru(\mathbf{1})][PF_6]_2$.

^1H NMR spectroscopic studies: We have made extensive use of ^1H NMR spectroscopy in the characterisation of these compounds. Relevant data are collected in Table 1, and a brief discussion of the pertinent features now follows.

The ^1H NMR spectrum of a $\{Ru(tpy)_2\}$ moiety formed from 4′-substituted 2,2′:6′,2″-terpyridines exhibits a characteristic pattern of resonances with $\delta(H^3) > \delta(H^4) > \delta(H^6) > \delta(H^5)$, which may be readily established by COSY experiments. The position of the $H^{3'}$ resonance depends upon the nature of the X substituent in the Xtpy ligand, but is also a characteristic value. In free tpy ligands a second characteristic pattern of resonances is observed with $\delta(H^3) \approx \delta(H^6) > \delta(H^4) > \delta(H^5)$. This latter pattern also holds true for noncoordinated tpy domains when they are present in hypodentate metal complexes.[20]

The ^1H NMR spectrum of $[(\mathbf{1})Ru(\mathbf{1})][PF_6]_2$ (Table 1, Fig. 3) exhibits a total of ten resonances, which a COSY spectrum readily

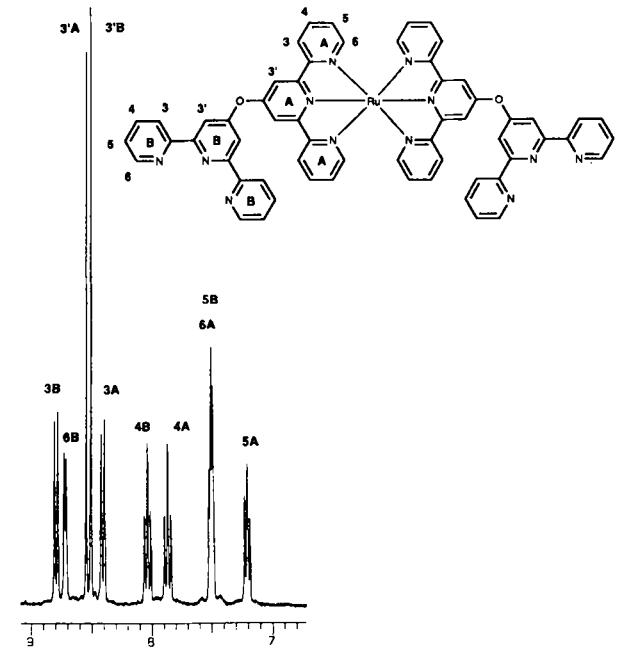

Fig. 3. The ^1H NMR spectrum (300 MHz) of a solution of $[(\mathbf{1})Ru(\mathbf{1})][PF_6]_2$ in CD_3CN showing the characteristic sequences of the resonances of the coordinated and noncoordinated tpy domains.

establishes as corresponding to two 2-pyridyl rings and two $H^{3'}$ protons. The sequence of resonances within each set allows unambiguous assignment of the coordinated and noncoordinated domains, and only the assignment of the two $H^{3'}$ protons is uncertain (Table 1). A COSY experiment was also used to assign the sixteen resonances in the ^1H NMR spectrum of $[(\mathbf{4})Ru(\mathbf{1})][PF_6]_2$ to the three tpy moieties, which were then unambiguously identified by comparison with the data for $[(\mathbf{1})Ru(\mathbf{1})][PF_6]_2$. The resonances for the terminal **4** ligand are at similar δ values to those in $[Ru(\mathbf{4})_2][PF_6]_2$.[21]

The asymmetric dinuclear complexes $[(\mathbf{4})Ru(\mathbf{1})Ru(\mathbf{3})][PF_6]_4$ and $[(\mathbf{4})Ru(\mathbf{1})Ru(\mathbf{5})][PF_6]_4$ each exhibit four sets of five coupled resonances in their ^1H NMR spectra (Table 1), arising from the four different tpy moieties present. The complex $[(\mathbf{4})Ru(\mathbf{1})Ru(\mathbf{5})][PF_6]_4$ also exhibits a singlet resonance at $\delta = 3.52$ assigned to the methyl group of the MeO_2S substituent. The symmetrical trinuclear complexes $[(Xtpy)Ru(\mathbf{1})Ru(\mathbf{1})Ru(Xtpy)][PF_6]_6$ each exhibit only three sets of tpy resonances. One set is due to the terminator ligand Xtpy (Xtpy = **3**, **4** or **5**), and the other two to the different tpy environments in the bridging **1**

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ligands. The ^{1}H NMR spectrum of [(**4**)Ru(**1**)Ru(**1**)Ru(**4**)][PF_6]$_6$ was fully assigned with the aid of a COSY experiment, and by comparison with those of the dinuclear complexes. The ^{1}H NMR spectra of the mixed-terminator ligand trinuclear complexes [(**3**)Ru(**1**)Ru(**1**)Ru(**3**)][PF_6]$_6$ and [(**5**)Ru(**1**)Ru(**1**)-Ru(**5**)][PF_6]$_6$ were fully assigned by comparison with the spectra of [(**4**)Ru(**1**)Ru(**3**)][PF_6]$_4$, [(**4**)Ru(**1**)Ru(**5**)][PF_6]$_4$ and [(**4**)Ru(**1**)-Ru(**1**)Ru(**4**)][PF_6]$_6$.

Electrochemical studies: All of the ruthenium complexes discussed above are electrochemically active, and acetonitrile solutions were studied by cyclic voltammetry; redox potential data (vs. Fc/Fc$^+$) are presented in Table 2, along with data for a number of mono- and trinuclear reference compounds. Mononuclear [(**4**)Ru(**1**)]$^{2+}$ and [(**1**)Ru(**1**)]$^{2+}$ each exhibit a reversible ruthenium(II)/(III) process and two fully reversible ligand-centred reductive processes. A comparison with redox data for model complexes suggests that the oxygen in **1** is slightly less electron-releasing than that in EtOtpy, probably as a result of the electron-releasing effect of the oxygen being divided between two tpy moieties in the case of **1**. We have discussed substituent effects on electrode potentials in such systems in detail elsewhere.[9, 12, 21] Both of the metal centres in the symmetrical dinuclear [(**4**)Ru(**1**)Ru(**4**)][PF_6]$_4$ complex undergo simultaneous and independent reversible ruthenium(II)/(III) processes, indicative of little ground-state interaction. Two overlapping and reversible ligand-centred reduction processes are observed, followed by an absorption spike. The asymmetric dinuclear complex [(**4**)Ru(**1**)Ru(**5**)][PF_6]$_4$ exhibits two reversible ruthenium(II)/(III) processes, as the strongly electron-withdrawing methylsulfonyl substituent stabilises one ruthenium(II) centre. The weakly electron-withdrawing chloro substituent on one of the terminator ligands in [(**4**)Ru(**1**)Ru(**3**)][PF_6]$_4$ shifts the potential associated with the ruthenium(II)/(III) process at the directly coordinated metal centre only marginally, and the processes for the two metal centres are not fully resolvable, but appear as a single process with a large peak-to-peak separation ($E_{anodic} - E_{cathodic}$ = 120 mV). For these and most of the other multinuclear complexes, the ligand-centred reductive processes are complicated, owing to the large number of possible ligand-centred reductive processes of similar energies. The reductive sections of the cyclic voltammograms also tend to be complicated by strong absorption spikes.

Table 2. Cyclic voltammetry data for the complexes in acetonitrile solution, with 0.1 M [nBu$_4$N][BF_4] as supporting electrolyte (E_0, V vs. Fc/Fc$^+$) [a].

	Ru(II/III)	Fc/Fc$^+$	Reductions
[(**4**)Ru(**1**)][PF_6]$_2$	0.87 (70)	(70)	−1.61 (50), −1.84 (100)
[(**1**)Ru(**1**)][PF_6]$_2$	0.84 (60)	(80)	−1.61 (60), −1.79 (80)
[(**4**)Ru(**1**)Ru(**4**)][PF_6]$_4$	0.90 (90)	(70)	−1.62 (130) [b], −1.82 [c]
[(**4**)Ru(**1**)Ru(**3**)][PF_6]$_4$	0.91 (120) [d]	(70)	−1.59 (100), −1.78 [c]
[(**4**)Ru(**1**)Ru(**5**)][PF_6]$_4$	0.89 (40), 1.01 (50)	(80)	−1.40 (50), −1.60 (70), −1.72 [c]
[(**4**)Ru(**1**)Ru(**1**)Ru(**4**)][PF_6]$_6$	0.91 (120) [d]	(80)	−1.61 (130) [d], −1.72 [c]
[(**3**)Ru(**1**)Ru(**1**)Ru(**3**)][PF_6]$_6$	0.92 (90) [d]	(70)	−1.57 (80), −1.66 [c]
[(**5**)Ru(**1**)Ru(**1**)Ru(**5**)][PF_6]$_6$	0.89 (70), 1.01 (70) [e]	(70)	−1.39 (70), −1.56 (70), −1.71 (135) [d]
[{(**1**)Ru}$_3$(**7**)][PF_6]$_6$	0.88 (50)	(70)	−1.59 (60), −1.74 (121) [d]
[{(**4**)Ru(**1**)Ru}$_3$(**7**)][PF_6]$_{12}$	0.90 (70)	(70)	[f]
[{(**3**)Ru(**1**)Ru}$_3$(**7**)][PF_6]$_{12}$	0.90 (110)	(70)	[f]
[{(**5**)Ru(**1**)Ru}$_3$(**7**)][PF_6]$_{12}$	0.87 (70), 1.02 (50)	(70)	−1.57 (60) [f]
[(**4**)Ru(**4**)][PF_6]$_2$ [g]	0.92		−1.67, −1.92
[(**4**)Ru(EtOtpy)][PF_6]$_2$ [g]	0.85		−1.73, −1.85
[(EtOtpy)Ru(EtOtpy)][PF_6]$_2$ [g]	0.74		−1.76, −1.97
[{(**4**)Ru}$_3$(**7**)][PF_6]$_6$ [h]	0.90		−1.63 [c]
[{(EtOtpy)Ru}$_3$(**7**)][PF_6]$_6$ [h]	0.83		−1.65 [c]

[a] Peak separations ($E_{anodic} - E_{cathodic}$, mV) are given in parentheses; all processes are reversible unless otherwise stated. [b] Two overlapping processes (shoulders observed, but not resolvable). [c] Semi-reversible process with absorption spike. [d] Broad process owing to the ruthenium centres in different environments being oxidised/reduced at similar potentials. [e] Two-electron process. [f] Multiple non-resolvable reductive processes. [g] Reference [9]. [h] Reference [18].

The symmetric trinuclear complexes [(**4**)Ru(**1**)Ru(**1**)Ru(**4**)]-[PF_6]$_6$ and [(**3**)Ru(**1**)Ru(**1**)Ru(**3**)][PF_6]$_6$ exhibit single broad ruthenium(II)/(III) processes, whilst [(**5**)Ru(**1**)Ru(**1**)Ru(**5**)][PF_6]$_6$ exhibits a two-electron process assigned to the two terminal ruthenium centres bearing the strongly electron-withdrawing ligand **5**, and a one-electron process assigned to the central ruthenium centre. The three chemically identical centres in the trinuclear complex [{(**1**)Ru}$_3$(**7**)][PF_6]$_6$ exhibit a single ruthenium(II)/(III) process. The hexanuclear complex [{(**5**)Ru(**1**)-Ru}$_3$(**7**)][PF_6]$_{12}$ has two different ruthenium environments. The three terminal ruthenium centres coordinated to the electron-withdrawing ligand **5** show a single ruthenium(II)/(III) process at +1.02 V, while the three central ruthenium centres show another single reversible ruthenium(II)/(III) process at + 0.87 V, effectively the same potential as observed for the trinuclear complex [{(**1**)Ru}$_3$(**7**)][PF_6]$_6$. Multiple ligand-centred reductive processes are observed, although only one at −1.57 V is fully resolved. The hexanuclear complexes [{(**4**)Ru(**1**)Ru}$_3$(**7**)][PF_6]$_{12}$ and [{(**3**)Ru(**1**)Ru}$_3$(**7**)][PF_6]$_{12}$ both exhibit single broad ruthenium(II)/(III) processes at + 0.90 V. All three of the hexanuclear complexes decompose on successive reductive cycles.

Electronic spectra: The electronic spectra of these highly coloured complexes were recorded in MeCN solution. All complexes exhibited a lowest energy metal-to-ligand charge transfer (MLCT) transition with λ_{max} between 479 and 493 nm (Table 3); the higher nuclearity complexes exhibited maxima at the lower energy end of this range. The narrowness of this range is indicative of the adjacent metal centres having little influence upon each other and contrasts with considerable bathochromic shifts between mono-, di- and trinuclear complexes of the directly linked ligand 6′,6″-bis(2-pyridyl)-2,2′:4,4″:2″,2‴-quaterpyridine.[15, 18, 21] The extinction coefficients for the dinuclear complexes ($\varepsilon = 35.3-37.5 \times 10^3$ dm^3 mol^{-1} cm^{-1}) and trinuclear complexes ($\varepsilon = 58.6-69.8 \times 10^3$ dm^3 mol^{-1} cm^{-1}) are respectively approximately two and three times the values observed for the mononuclear building blocks [(**4**)Ru(**1**)][PF_6]$_2$ ($\varepsilon = 17.3 \times 10^3$ dm^3 mol^{-1} cm^{-1}) and [(**1**)Ru(**1**)][PF_6]$_2$ ($\varepsilon = 19.7 \times 10^3$ dm^3 mol^{-1} cm^{-1}). The extinction coefficients for the

Table 3. Electronic spectroscopic data for the complexes in acetonitrile solution (λ_{max}, nm, ε, 10^3 dm^3 mol^{-1} cm^{-1}; sh = shoulder).

	LC				MLCT
[(**4**)Ru(**1**)][PF_6]$_2$	241 (55.1)	273 (66.1)		305 (72.4)	479 (17.3)
[(**1**)Ru(**1**)][PF_6]$_2$	241 (83.6)	276 (96.3)		302 (86.1)	484 (19.7)
[(**4**)Ru(**1**)Ru(**4**)][PF_6]$_4$	240 (63.4)	272 (77.9)		306 (118)	482 (35.3)
[(**4**)Ru(**1**)Ru(**3**)][PF_6]$_4$	239 (73.0)	274 (82.4)		305 (117)	484 (37.5)
[(**4**)Ru(**1**)Ru(**5**)][PF_6]$_4$	240 (61.1)	276 (83.1)		306 (107)	488 (37.3)
[(**4**)Ru(**1**)Ru(**1**)Ru(**4**)][PF_6]$_6$	241 (101)	278 (126)		305 (183)	486 (58.6)
[(**3**)Ru(**1**)Ru(**1**)Ru(**3**)][PF_6]$_6$	239 (115)	277 (136)	289 (135)	305 (178)	488 (60.8)
[(**5**)Ru(**1**)Ru(**1**)Ru(**5**)][PF_6]$_6$	240 (95.9)	277 (159)	286 (137)	305 (165)	492 (69.8)
[{(**1**)Ru}$_3$(**7**)][PF_6]$_6$	241 (176)	sh	289 (264)	sh	492 (84.7)
[{(**4**)Ru(**1**)Ru}$_3$(**7**)][PF_6]$_{12}$	240 (210)	sh	291 (335)	305 (374)	491 (140)
[{(**3**)Ru(**1**)Ru}$_3$(**7**)][PF_6]$_{12}$	239 (233)	sh	290 (341)	305 (386)	492 (154)
[{(**5**)Ru(**1**)Ru}$_3$(**7**)][PF_6]$_{12}$	235 (208)	sh	288 (339)	304 (352)	493 (163)

hexanuclear complexes built up from **7** are larger ($\varepsilon = 140-163 \times 10^3$ dm^3 mol^{-1} cm^{-1}) as a result of the conjugated central trinucleating **7** ligand. A number of higher energy ligand-centred (LC) processes are also observed for all of the complexes, with the characteristically small variations in λ_{max} from one complex to the next.

Conclusions

We have introduced the ligand **1** as a new bridging species for the preparation of metallosupramolecules. The free ligand is readily prepared by conventional methods, and complexes may be prepared from free **1** in a divergent manner. A powerful new methodology in which **1** ligands are prepared in situ by metal-directed reactions has been established. By this methodology, complexes with up to six metal centres have been prepared in a specific and convenient manner. Unfortunately, higher nuclearity species are not accessible directly from this methodology, as a result of competing metal-directed reactions. However, we are currently extending the methodology by combining the ether-forming reactions dicussed in this paper with other metal-directed reactions of coordinated ligands (alkylation, imine formation, etc.) to give a suite of in situ ligand extention processes that can be used sequentially. The ligand **1** is an effective "insulating" ligand and allows little electronic communication between linked metal centres.

Experimental Procedure

Procedure: ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer. Electron impact and positive-ion fast atom bombardment mass spectra were recorded on a VG 70-250 instrument, with 4-nitrobenzyl alcohol as matrix in the case of FAB spectra. Electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT 20 potentiostat. A conventional three-electrode configuration was used, with platinum bead working and auxiliary electrodes and an Ag/AgCl reference. Acetonitrile, freshly distilled from P_4O_{10}, was used as solvent in all cases. The base electrolyte was 0.1 M [nBu$_4$N][BF$_4$], recrystallised twice from ethanol/water and thoroughly dried in vacuo over P_4O_{10}. Potentials are quoted vs. the ferrocene/ferrocenium couple ($Fc/Fc^+ = 0.0$ V), and all potentials were referenced to internal ferrocene added at the end of each experiment.

The ligands 2,2′:6′,2″-terpyridine (**4**) [22], 2,2′:6′,2″-terpyridin-4′(1′*H*)-one (**2**) [9,17], 4′-chloro-2,2′:6′,2″-terpyridine (**3**) [9,17] and 4′-methylsulfonyl-2,2′:6′,2″-terpyridine (**5**) [23] were prepared by the literature methods, as were the complexes [Ru(**4**)Cl$_3$] [9], [Ru(**3**)Cl$_3$] [9] and [Ru(**5**)Cl$_3$] [20]. The homoleptic complex [(**3**)Ru(**3**)][PF$_6$]$_2$ [9], the heteroleptic complex [(**4**)Ru(**3**)][PF$_6$]$_2$ [9] and the trinuclear complex [{(**3**)Ru}$_3$(**7**)][PF$_6$]$_6$ [18] were prepared as we have previously reported; to remove any trace impurities, the latter two were chromatographed on silica (with acetonitrile, saturated aqueous KNO$_3$ and water (14:2:1 v/v) as the eluent phase) prior to use.

Bis{4′-(2,2′:6′,2″-terpyridinyl)}ether (1): **3** (300 mg, 1.12 mmol), **2** (420 mg, 1.69 mmol) and KOH (600 mg, excess) were heated at reflux for 4 d in *N,N*-dimethylformamide (DMF, 20 mL). The reaction mixture was then cooled, water (80 mL) added, and the resulting suspension allowed to stand for 10 min. The white precipitate was collected by filtration and washed with water. Concentration of a solution of the precipitate in CH_2Cl_2/MeOH afforded **1** as a colourless microcrystalline solid (370 mg, 69%). M.p. 238–240 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.63$ (8H, m; H^3, H^6), 8.22 (4H, s; H$^{3'}$), 7.85 (4H, dd; H^4), 7.31 (4H, dd; H^5); MS (EI): *m/z*: 402 [$M^+ - C_5H_4N$], 480 [M^+]; $C_{30}H_{20}N_6O$: calcd C 75.0, H 4.2, N 17.5; found C 74.8, H 4.3, N 17.3.

[(4)Ru(1)Ru(4)][PF$_6$]$_4$: [Ru(**4**)Cl$_3$] (100 mg, 0.227 mmol) and **1** (48 mg, 0.100 mmol) were heated to reflux for 30 min in ethane-1,2-diol (15 mL). The deep orange reaction mixture was cooled, and water and excess methanolic NH_4PF_6 were added to precipitate the crude complex. This was collected on Celite, redissolved in MeCN, and the resulting solution was reduced in volume to ca. 3 mL and chromatographed on silica with a mixture of MeCN, saturated aqueous KNO_3 and water (14:2:1 v/v) as the eluent phase. The second main orange product band was collected as fractions, whose purities were checked by TLC. The combined product fractions were precipitated as the PF_6^- salt by addition of excess methanolic NH_4PF_6 and water (10 mL) followed by reduction in volume. Recrystallisation from aqueous acetonitrile afforded [(**4**)Ru(**1**)Ru(**4**)][PF$_6$]$_4$ as a red-orange powder (44 mg, 25%), which was dried in vacuo. MS (FAB, ^{102}Ru): *m/z*: 583 [(**4**)Ru(**2**)$^+$], 1440 [$M^+ - 2PF_6$], 1585 [$M^+ - PF_6$]; $Ru_2C_{60}H_{42}N_{12}OP_4F_{24}$: calcd C 41.7, H 2.5, N 9.7; found C 41.5, H 2.9, N, 9.5.

[(4)Ru(1)][PF$_6$]$_2$: The heteroleptic complex [(**4**)Ru(**3**)][PF$_6$]$_2$ (200 mg, 0.224 mmol), **2** (73 mg, 0.293 mmol) and K_2CO_3 (100 mg, excess) were heated at reflux for 3 h in acetonitrile (25 mL). On cooling, water (50 mL) was added along with a little methanolic NH_4PF_6, and the resulting red-orange precipitate was collected. Recrystallisation from aqueous acetonitrile afforded analytically pure [(**4**)Ru(**1**)][PF$_6$]$_2$ as a red powder in 96% yield (237 mg). MS (FAB, ^{102}Ru): *m/z*: 583 [(**4**)Ru(**2**)$^+$], 814 [$M^+ - 2PF_6$], 960 [$M^+ - PF_6$]; $RuC_{45}H_{31}N_9OP_2F_{12}$: calcd C 48.9, H 2.8, N 11.4; found C 48.7, H 3.3, N, 10.9.

[(1)Ru(1)][PF$_6$]$_2$: This complex was prepared similarly to [(**4**)Ru(**1**)][PF$_6$]$_2$ by heating [(**3**)Ru(**3**)][PF$_6$]$_2$ (93 mg, 0.100 mmol), **2** (75 mg, 0.301 mmol) and K_2CO_3 (50 mg, excess) for 16 h in acetonitrile (10 mL). [(**1**)Ru(**1**)][PF$_6$]$_2$ was obtained as an orange-brown powder in 88% yield (120 mg). MS (FAB, ^{102}Ru): *m/z*: 830 [(**1**)Ru(**2**)$^+$], 1062 [$M^+ - 2PF_6$], 1207 [$M^+ - PF_6$]; $RuC_{60}H_{40}N_{12}O_2P_2F_{12}$: calcd C 53.3, H 3.1, N 12.4; found C 52.9, H 3.3, N, 12.2.

[(4)Ru(1)Ru(5)][PF$_6$]$_4$: [(**4**)Ru(**1**)][PF$_6$]$_2$ (120 mg, 0.109 mmol) and [Ru(**5**)Cl$_3$] (120 mg, 0.231 mmol) were heated at reflux for 1 h in ethane-1,2-diol (10 mL). Preparation and workup as for [(**4**)Ru(**1**)Ru(**4**)][PF$_6$]$_4$ above. [(**4**)Ru(**1**)Ru(**5**)][PF$_6$]$_4$ was obtained as a red-brown powder (105 mg, 53%). MS (FAB, ^{102}Ru): *m/z*: 583 [(**4**)Ru(**2**)$^+$], 661 [(**5**)Ru(**2**)$^+$], 1518 [$M^+ - 2PF_6$], 1662 [$M^+ - PF_6$]; $Ru_2C_{61}H_{44}N_{12}O_3SP_4F_{24}$: calcd C 40.5, H 2.5, N 9.3; found C 39.4, H 2.8, N, 8.9.

[(4)Ru(1)Ru(3)][PF$_6$]$_4$: [Ru(**3**)Cl$_3$] (86 mg, 0.181 mmol) and $AgBF_4$ (106 mg, 0.544 mmol) were heated to reflux for 2 h in acetone (40 mL). The resulting blue suspension was filtered through Celite and then reduced to dryness. The ligand complex [(**4**)Ru(**1**)][PF$_6$]$_2$ (190 mg, 0.172 mmol) dissolved in DMF (30 mL) was added, and the mixture heated at reflux for 30 min. The red-orange solution was then cooled, and water (60 mL) and excess methanolic NH_4PF_6 were added. The crude precipitate was collected, redissolved in MeCN, the solution reduced to minimum volume, and chromatographed over silica as above. Recrystallisation from aqueous acetonitrile afforded the asymmetric binuclear complex [(**4**)Ru(**1**)Ru(**3**)][PF$_6$]$_4$ as a red-brown powder (125 mg, 41%), which was dried in vacuo. MS (FAB, ^{102}Ru): *m/z*: 583 [(**4**)Ru(**2**)$^+$], 617 [(**3**)Ru(**2**)$^+$], 1476 [$M^+ - 2PF_6$], 1619 [$M^+ - PF_6$]; $Ru_2C_{60}H_{41}N_{12}OClP_4F_{24}$: calcd C 40.9, H 2.3, N 9.5; found C 40.2, H 2.5, N, 9.4.

[(4)Ru(1)Ru(1)Ru(4)][PF$_6$]$_6$: [Ru(**4**)Cl$_3$] (54 mg, 0.123 mmol) and $AgBF_4$ (72 mg, 0.369 mmol) were heated to reflux for 2 h in acetone (40 mL). The resulting blue suspension was filtered through Celite and then reduced to dryness. The binucleating ligand complex [(**1**)Ru(**1**)][PF$_6$]$_2$ (83 mg, 0.061 mmol) and DMF (20 mL) were added, and the mixture heated at reflux for 3 h. The red-orange solution was then cooled, and water (40 mL) and excess methanolic NH_4PF_6 were added. The crude product was collected, redissolved in MeCN, reduced to minimum volume, and chromatographed over silica as above. Recrystallisation from aqueous acetonitrile gave the trinuclear complex [(**4**)Ru(**1**)Ru(**1**)Ru(**4**)][PF$_6$]$_6$ as an analytically pure red-brown powder (55 mg, 34%). $Ru_3C_{90}H_{62}N_{18}O_2P_6F_{36}$: calcd C 41.6, H 2.4, N 9.7; found C 40.5, H 2.7, N, 9.4.

[(5)Ru(1)Ru(1)Ru(5)][PF$_6$]$_6$: As above from [Ru(**5**)Cl$_3$] (86 mg, 0.166 mmol), $AgBF_4$ (97 mg, 0.497 mmol) and [(**1**)Ru(**1**)][PF$_6$]$_2$ (80 mg, 0.059 mmol). Recrystallisation from aqueous acetonitrile gave the trinuclear complex [(**5**)Ru(**1**)Ru(**1**)Ru(**5**)][PF$_6$]$_6$ as an analytically pure red-brown powder (61 mg, 38%). $Ru_3C_{92}H_{66}N_{18}O_6S_2P_6F_{36}\cdot 6H_2O$: calcd C 38.5, H 2.7, N 8.8; found C 38.5, H 2.8, N, 8.7.

[(3)Ru(1)Ru(1)Ru(3)][PF$_6$]$_6$: The binucleating ligand complex [(**1**)Ru(**1**)][PF$_6$]$_2$ (280 mg, 0.207 mmol) and [Ru(**3**)Cl$_3$] (286 mg, 0.602 mmol) were heated to reflux for 1 h in ethane-1,2-diol (40 mL). Workup and chromatographic purification were performed as for [(**4**)Ru(**1**)Ru(**4**)][PF$_6$]$_4$ above; the second main orange product band was collected (the first orange fraction was [Ru(**3**)$_2$][PF$_6$]$_2$), and its purity checked by TLC (silica, eluent system as above). Anion metathesis with NH_4PF_6, followed by recrystallisation from aqueous acetonitrile gave the trinuclear complex [(**3**)Ru(**1**)Ru(**1**)Ru(**3**)][PF$_6$]$_6$ as an analytically pure red-brown powder (188 mg, 34%). $Ru_3C_{90}H_{60}N_{18}O_2Cl_2P_6F_{36}$: calcd C 40.5, H 2.3, N 9.4; found C 40.2, H 2.8, N, 8.9.

[{(1)Ru}$_3$(7)][PF$_6$]$_6$: The symmetrical trinuclear complex [{(**3**)Ru}$_3$(**7**)][PF$_6$]$_6$ (125 mg, 0.046 mmol), **2** (300 mg, 1.20 mmol) and K_2CO_3 (600 mg, excess) were heated at reflux for 16 h in dry acetonitrile (25 mL). After this time, the reaction mixture was cooled and then precipitated by the addition of water (20 mL) and excess methanolic NH_4PF_6. Following recrystallisation from aqueous acetonitrile, [{(**1**)Ru}$_3$(**7**)][PF$_6$]$_6$ was obtained as a brown powder in 97% yield (149 mg). $Ru_3C_{141}H_{93}N_{27}O_3P_6F_{36}$: calcd C 50.0, H 2.8, N 11.2; found C 49.5, H 3.1, N, 11.0.

[{(4)Ru(1)Ru}$_3$(7)][PF$_6$]$_{12}$: [Ru(**4**)Cl$_3$] (17 mg, 0.039 mmol) and $AgBF_4$ (23 mg, 0.118 mmol) were heated at reflux for 2 h in acetone (20 mL). The resulting blue

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suspension was filtered through Celite and then reduced to dryness. The trinucleating ligand complex $[\{(1)Ru\}_3(7)][PF_6]_2$ (40 mg, 0.012 mmol) and DMF (20 mL) were added, and the mixture heated to reflux for 2 h. The red-orange solution was then cooled, and water (40 mL) and excess methanolic NH_4PF_6 were added. The crude product was collected, redissolved in MeCN, the solution reduced to minimum volume and chromatographed over silica as above. Recrystallisation from aqueous acetonitrile gave the hexanuclear complex $[\{(4)Ru(1)Ru\}_3(7)][PF_6]_{12}$ as an analytically pure red-brown powder (19 mg, 31%). $Ru_6C_{186}H_{126}N_{36}O_3P_{12}F_{72}$: calcd C 42.5, H 2.4, N 9.6; found C 42.6, H 3.0, N, 9.1.

$[\{(3)Ru(1)Ru\}_3(7)][PF_6]_{12}$: As above from $[Ru(3)Cl_3]$ (84 mg, 0.177 mmol), $AgBF_4$ (104 mg, 0.533 mmol) and $[\{(1)Ru\}_3(7)][PF_6]_2$ (120 mg, 0.036 mmol). Recrystallisation from aqueous acetonitrile gave the hexanuclear complex $[\{(3)Ru(1)Ru\}_3(7)][PF_6]_{12}$ as an analytically pure brown powder (52 mg, 27%). $Ru_3C_{186}H_{123}N_{36}O_3Cl_3P_{12}F_{72}\cdot 12H_2O$: calcd C 40.0, H 2.6, N 9.0; found C 39.8, H 2.6, N, 9.0.

$[\{(5)Ru(1)Ru\}_3(7)][PF_6]_{12}$: As above from $[Ru(5)Cl_3]$ (46 mg, 0.089 mmol), $AgBF_4$ (52 mg, 0.266 mmol) and $[\{(1)Ru\}_3(7)][PF_6]_2$ (60 mg, 0.018 mmol). Recrystallisation from aqueous acetonitrile gave the hexanuclear complex $[\{(5)Ru(1)Ru\}_3(7)][PF_6]_{12}$ as an analytically pure brown powder (31 mg, 32%). $Ru_6C_{189}H_{132}N_{36}O_9S_3P_{12}F_{72}\cdot 12H_2O$: calcd C 39.7, H 2.7, N 8.8; found C 39.6, H 2.7, N, 8.8.

Crystal structure determination: Colourless crystals of **1** were obtained by the slow evaporation of a chloroform/methanol solution. $C_{30}H_{20}N_6O$, $M = 480.53$, triclinic, space group $P\bar{1}$, $a = 9.623(2)$, $b = 11.240(1)$, $c = 11.828(1)$ Å; $\alpha = 93.065(9)$, $\beta = 107.071(14)$, $\gamma = 99.088(14)°$; $V = 1200.99(38)$ Å^3, $\mu = 6.373$ cm^{-1}, $Z = 2$, $D_{calcd} = 1.329$ g cm^{-3}, $F(000) = 500$. The unit-cell parameters and reflection intensities were measured with the $\omega/2\theta$ scan mode for a crystal of dimensions $0.16 \times 0.27 \times 0.49$ mm with graphite-monochromated $Cu_{K\alpha}$ radiation, $\lambda = 1.54178$ Å. Of 5176 unique reflections, 3736 were used in the structure solution. The non-hydrogen atoms of the molecule were located by direct methods (SIR92) [24]; all subsequent calculations were performed with CRYSTALS [25]. A Chebychev weighting scheme was applied [26]. All hydrogen atoms were included in idealised positions with C–H distances. The non-hydrogen atoms were refined with anisotropic displacement parameters, and the hydrogen atoms with group isotropic displacement parameters. At final convergence, $R = 0.0451$, $R_w = 0.0581$ for 335 parameters. Maximum and minimum residual electron densities in the final difference map were + 0.18 and − 0.18 e Å^{-3}, respectively. Further details of the crystal structure investigation may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK), on quoting the full journal citation.

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[1] E. C. Constable, *Chem. Ind.* **1994**, 56; *Chem. Brit.* **1995**, *31*, 33.
[2] E. C. Constable, *Prog. Inorg. Chem.* **1994**, *42*, 67.
[3] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85; K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, London, **1991**; V. Balzani, F. Barigelletti, F. De Cola, *Top. Curr. Chem.* **1990**, *158*, 31; G. J. Karvanos, *Photoinduced Electron Transfer*, VCH, Weinheim, **1993**; V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, **1991**.
[4] E. C. Constable, *Tetrahedron*, **1992**, *48*, 10013.
[5] G. Denti, S. Serroni, S. Campagna, A. Juris, M. Ciano, V. Balzani, in *Perspectives in Coordination Chemistry* (Eds.: A. F. Williams, C. Floriani, A. E. Merbach), HCAV and VCH, Basel and Weinheim, **1992**, p. 153 and references therein.
[6] J. D. Petersen, L. W. Morgan, I. Hsu, M. A. Billadeau, S. E. Ronco, *Coord. Chem. Rev.* **1991**, *111*, 319; J. D. Petersen, S. L. Gahan, S. C. Rasmussen, S. E. Ronco, *Coord. Chem. Rev.* **1994**, *132*, 15.
[7] S. Serroni, G. Denti, *Inorg. Chem.* **1992**, *31*, 4251.
[8] E. C. Constable, A. M. W. Cargill Thompson, D. A. Tocher in *Supramolecular Chemistry* (Eds.: V. Balzani and L. De Cola), Klewer, Dordrecht, **1992**, p. 219.
[9] E. C. Constable, A. M. W. Cargill Thompson, D. A. Tocher, *New J. Chem.* **1992**, *16*, 855.
[10] E. C. Constable, A. M. W. Cargill Thompson, D. A. Tocher, *Supramol. Chem.* **1993**, *3*, 9; *Macromol. Symposia*, **1994**, *77*, 219; E. C. Constable, A. M. W. Cargill Thompson, D. A. Tocher, *Polymer Preprints*, **1993**, *34*, 110.
[11] J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, *Chem. Rev.* **1994**, *94*, 993 and references therein.
[12] N. Armaroli, V. Balzani, E. C. Constable, M. Maestri, A. M. W. Cargill Thompson, *Polyhedron*, **1992**, *11*, 2707.
[13] E. C. Constable, *Inorg. Chim. Acta*, **1984**, *82*, 53; E. C. Constable, *Inorg. Chim. Acta*, **1986**, *117*, L33; E. C. Constable, T. A. Leese, *Inorg. Chim. Acta*, **1988**, *146*, 55.
[14] E. C. Constable in *Inorganic Experiments* (Ed.: J. D. Woolins), VCH, Weinheim, **1994**, p. 189.
[15] C. A. Bessel, R. F. See, M. R. Churchill, K. J. Takeuchi, *J. Chem. Soc. Dalton Trans.* **1992**, 3223; E. C. Constable, J. Lewis, M. C. Liptrot, P. R. Raithby, *Inorg. Chim. Acta*, **1990**, *178*, 47; E. C. Constable, F. K. Khan, P. R. Raithby, V. E. Marquez, *Acta Crystallogr.* **1992**, *48*, 932.
[16] E. C. Constable, M. D. Ward, *J. Chem. Soc. Dalton Trans.* **1990**, 1405.
[17] F. Barigelletti, L. Flamigni, V. Balzani, J.-P. Collin, J.-P. Sauvage, A. Sour, E. C. Constable, A. M. W. Cargill Thompson, *J. Chem. Soc. Chem. Commun.* **1993**, 942; E. C. Constable, A. M. W. Cargill Thompson, S. Greulich, *J. Chem. Soc. Chem. Commun.* **1993**, 1444; F. Barigelletti, L. Flamigni, V. Balzani, J.-P. Collin, J.-P. Sauvage, A. Sour, E. C. Constable, A. M. W. Cargill Thompson, *Coord. Chem. Rev.* **1994**, *132*, 209; E. C. Constable, A. M. W. Cargill Thompson *Supramol. Chem.* **1994**, *7*, 95; E. C. Constable, in *Transition Metals in Supramolecular Chemistry* (Eds.: L. Fabbrizzi and A. Poggi), Kluwer, Dordrecht, **1994**, 81; F. Barigelletti, L. Flamigni, V. Balzani, J.-P. Collin, J.-P. Sauvage, A. Sour, E. C. Constable, A. M. W. Cargill Thompson, *J. Am. Chem. Soc.* **1994**, *116*, 7692.
[18] E. C. Constable, A. M. W. Cargill Thompson, *J. Chem. Soc. Dalton Trans.* **1992**, 3467; *J. Chem. Soc. Chem. Commun.* **1992**, 617.
[19] G. R. Newkome, F. Cardullo, E. C. Constable C. N. Moorefield, A. M. W. Cargill Thompson, *J. Chem. Soc. Chem. Commun.* **1993**, 925.
[20] E. C. Constable, A. M. W. Cargill Thompson, *J. Chem. Soc. Dalton Trans*, **1995**, 1615.
[21] E. C. Constable, A. M. W. Cargill Thompson, *J. Chem. Soc. Dalton Trans.* **1994**, 1409.
[22] D. L. Jameson, L. E. Guise, L. E. *Tetrahedron Lett.* **1991**, *32*, 1999.
[23] K. T. Potts, M. J. Cipullo, P. Ralli, G. Theodoridis, *J. Org. Chem.* **1982**, *47*, 3027.
[24] SIR 92, C. Giacovazzo, University of Bari, **1992**.
[25] CRYSTALS, Issue 9, D. Watkin; Chemical Crystallography Laboratory, Oxford, **1990**.
[26] J. R. Carruthers, D. J. Watkin, *Acta Crystallogr. Sect. A*, **1979**, *35*, 698.