

A New Ligand for the Self Assembly of Starburst Coordination Oligomers and Polymers

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The coordination properties of the tridentate ligand 2,2':6',2''-terpyridine (tpy) make it an ideal structural unit to control the assembly of coordination oligomers and polymers, and the new ligand 1,3,5-tris[4'-(2,2':6',2''-terpyridinyl)]benzene (ttpy) has been prepared as a building block for the assembly of coordination polymers, the complex $\{[(\text{tpy})\text{Ru}]_3(\text{ttpy})\}[\text{PF}_6]_6$ having been prepared; in the trinuclear complex, the three ruthenium(II) centres are equivalent and oxidise at the same potential.

Coordination polymers and oligomers possessing specific electronic or geometric properties can be prepared by the interaction of suitably designed multidentate ligands with metal ions having specific geometrical requirements.^{1,2} The oligopyridines are ideal metal-binding functionalities to introduce into structure-inducing ligands for the preparation of coordination polymers as they form stable, non-labile complexes with a wide range of metal ions,³ and assembly of the polymers is a spontaneous self-assembly process. Although 2,2'-bipyridines possess favourable metal-binding characteristics, they give rise to stereoisomerism at six-coordinate centres. We are currently exploring the use of 2,2':6',2''-terpyridinyl functionalities as the metal-binding components of such ligands.⁴ With 4'-substituted 2,2':6',2''-terpyridines (Xtpy) no stereoisomerism problems are associated with the formation of $[\text{M}(\text{Xtpy})_2]^{n+}$ complexes, and an additional advantage of the 2,2':6',2''-terpyridinyl functionality is that the connectivity at a six-coordinate metal centre is two, and the spatial properties of the oligomers or polymers are entirely controlled by the arrangement of the 2,2':6',2''-terpyridinyl

groups in the ligand, in contrast to the complex spatial properties resulting from coordination of three 2,2'-bipyridine groups to a six-coordinate metal centre.²

We have concentrated upon this approach of controlling the connectivity at the ligand centre, and have designed a new tris (2,2':6',2''-terpyridinyl) ligand that acts as a branch point with a connectivity of three for the self-assembly of coordination polymers and oligomers containing six-coordinate metal centres. In the desired ligand 1,3,5-tris [4'-(2,2':6',2''-terpyridinyl)]benzene (ttpy), the spatial control is achieved using a 1,3,5-trisubstituted benzene spacer group. The metal-directed self-assembly results in the formation of dendrimeric systems with a close similarity to the novel materials obtained utilising more conventional organic synthetic methodology.⁵ The new ligand ttpy was prepared as indicated in Scheme 1. The key step involves the condensation of 2-acetylpyridine with benzene-1,3,5-tricarbaldehyde, which is itself prepared by the reduction of benzene-1,3,5-tricarbonyl chloride with $\text{Li}[\text{AlH}(\text{Bu}^t\text{O})_3]$,⁶ to give the tris(chalcone) in 52% yield as a white solid (¹H NMR, CDCl_3 , H_{Ar} , 8.07, s; H_{alkenic} , 7.99, d, J

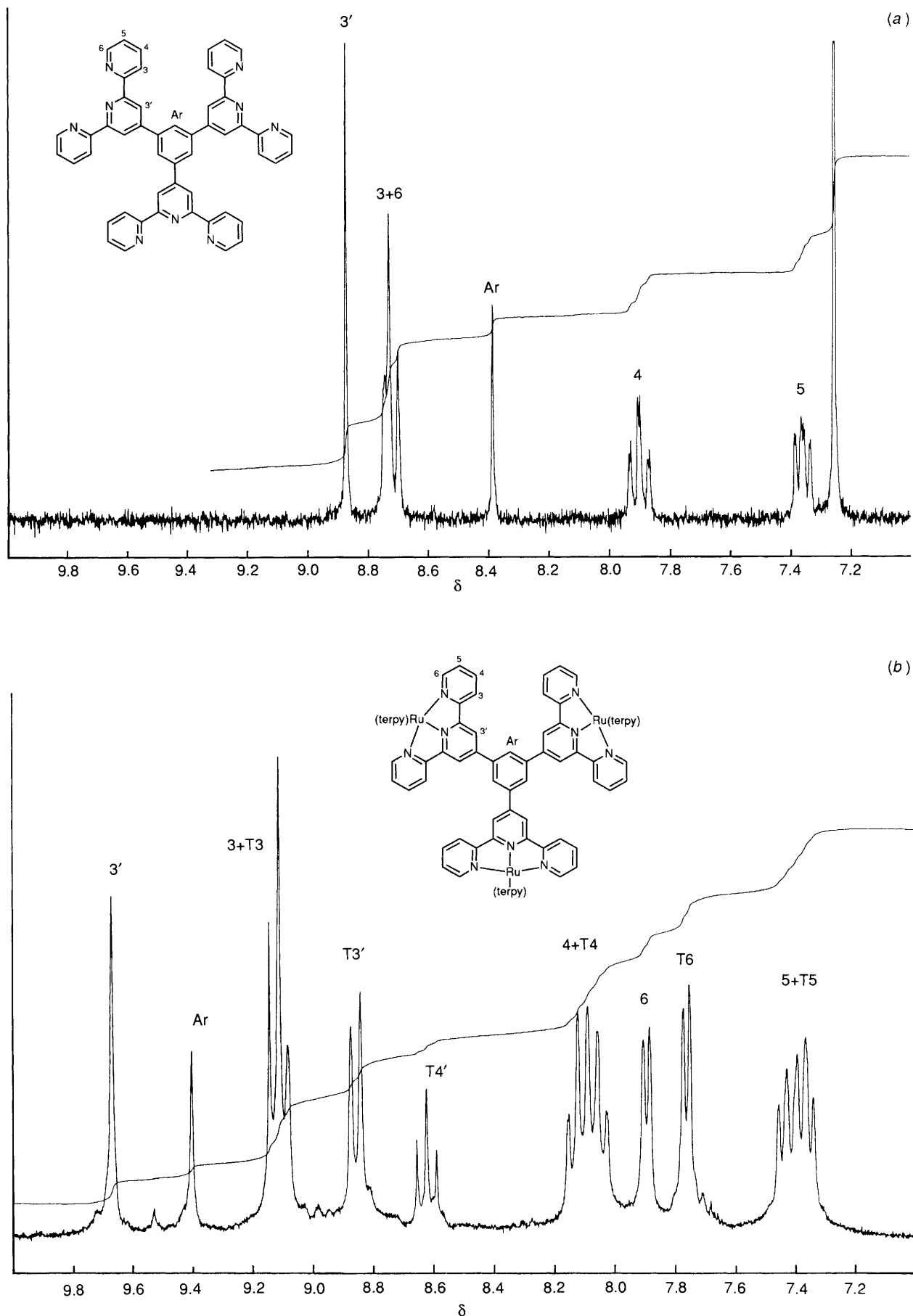
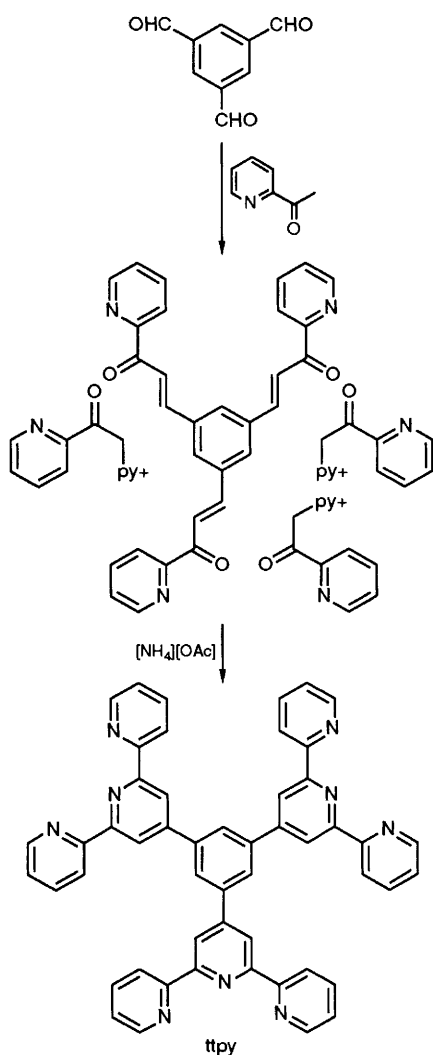


Fig. 1 250 MHz ^1H NMR spectra of (a) ttpy in CDCl_3 and (b) $[(\text{ttpy})\text{Ru}]_3(\text{ttpy})[\text{PF}_6]_6$ in CD_3COCD_3 . The peaks denoted T in spectrum (b) refer to the unsubstituted 2,2':6',2''-terpyridine ligand.



Scheme 1

16 Hz; H_{alkenic} , 8.42, d, J 16 Hz; 6-H, 8.79, d; 3-H, 8.22, d; 4-H, 7.90, dd; 5-H, 7.53, dd; IR, ν_{CO} 1678 cm^{-1} ; m.p. > 240 °C). Reaction of this tris(chalcone) with 2-(2-pyridyl)-2-oxoethylpyridinium iodide (pyridacylpyridinium iodide) in the presence of ammonium acetate under Krohnke conditions⁷ resulted in the formation of the desired ttpy ligand as a yellow solid in 30–35% yield [positive fast atom bombardment (FAB) mass spectrum, m/z 771; IR, 1584, 1384, 793 cm^{-1}]. The ligand is surprisingly soluble in organic solvents, which is in direct contrast to very insoluble compounds such as 2,2':6',2'':6'':2''':6''':2''''-sexipyridine.⁸ We believe that this is a result of the ligand adopting a non-planar conformation in the solid state, leading to less efficient stacking in the crystal lattice. The ^1H NMR spectrum of a CDCl_3 solution of ttpy is presented in Fig. 1(a) and exhibits only six proton environments, demonstrating the high molecular symmetry on the ^1H NMR spectroscopic timescale.

The reaction of the new ttpy ligand with $[\text{Ru}(\text{tpy})\text{Cl}_3]$ in methanol in the presence of *N*-ethylmorpholine proceeds smoothly to give a deep orange solution, from which the orange-red trinuclear complex $[\{(\text{tpy})\text{Ru}\}_3(\text{ttpy})][\text{PF}_6]_6$ is

precipitated upon the dropwise addition of $[\text{NH}_4][\text{PF}_6]$. This same trinuclear complex is obtained with ratios of ttpy to $[\text{Ru}(\text{tpy})\text{Cl}_3]$ of 1:1 and 1:3; we have no explanation for this observation at present, and all attempts to obtain mononuclear or dinuclear complexes have been unsuccessful. The trinuclear complex exhibits intense clusters of ions at m/z 2355 and 2210 ($[\{(\text{tpy})\text{Ru}\}_3(\text{ttpy})][\text{PF}_6]_4$ and $[\{(\text{tpy})\text{Ru}\}_3(\text{ttpy})][\text{PF}_6]_3$ respectively) in its FAB mass spectrum each showing the expected isotopomer distributions. The ^1H NMR spectrum of a CD_3COCD_3 solution of the trinuclear complex is presented in Fig. 1(b). Once again, the spectrum is sharp and well resolved, and illustrates the high symmetry of the compound on the ^1H NMR spectroscopic time-scale. The three tpy ligands are chemically and magnetically equivalent, as are each of the 2,2':6',2''-terpyridinyl groups of the ttpy ligand. The resonances assigned to the tpy ligands are almost unshifted with respect to the analogous protons in $[\text{Ru}(\text{tpy})_2]^{2+}$.⁴ The complex is electrochemically active and a cyclic voltammogram exhibits a single fully reversible oxidation process at +0.90 V, a reversible reduction at -1.68 V and an irreversible process at -1.83 V (MeCN solution, $[\text{Bu}^n\text{N}][\text{PF}_6]$ supporting electrolyte, all potentials are quoted *versus* internal Fc/Fc^+). No further oxidation processes were observed. These redox processes are comparable with those observed for $[\text{Ru}(\text{tpy})(\text{Phtpy})]^{2+}$ (0.91, -1.66, -1.94 V).⁴ The oxidation of all three metal centres at a common potential is somewhat disappointing, and indicates that there is little or no electronic communication between the metal centres. This is compatible with a structure in which the 2,2':6',2''-terpyridinyl groups bonded to the central spacer benzene ring are orthogonal to it.

Simply mixing methanolic solutions of ttpy with solutions containing iron(II) results in immediate precipitation of completely insoluble deep blue-purple polymers. We are currently investigating these coordination polymers, which molecular modelling studies suggest contain large supercycles.

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