Boron-rich metallodendrimers—mix-and-match assembly of multifunctional metallosupramolecules

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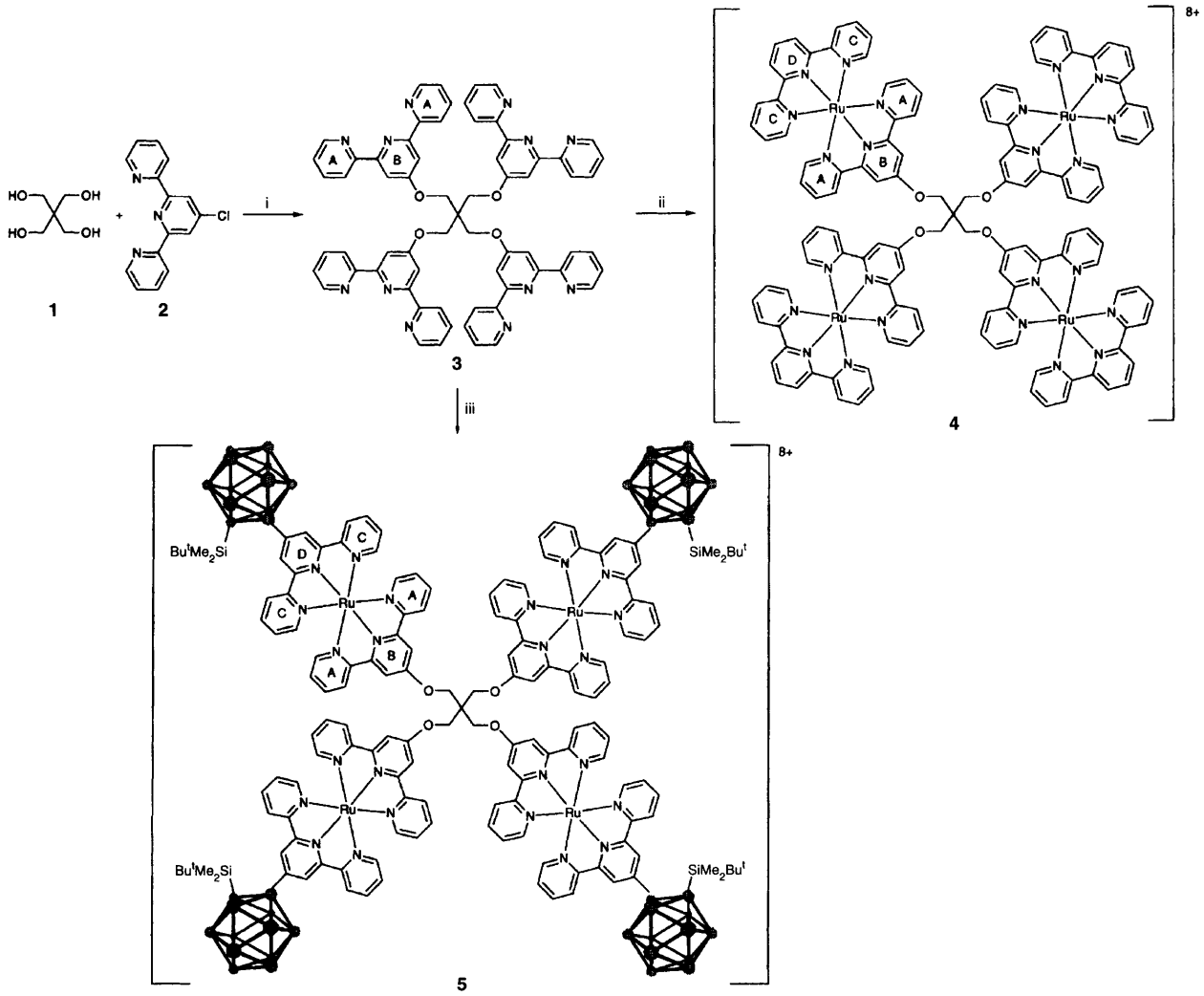
A dendritic system based upon a pentaerythritol unit bearing pendant 2,2′:6′,2″-terpyridine metal-binding domains is described; tetranuclear complexes bearing pendant carborane units are reported.

The dendrimer or arborol approach permits the selective and effective introduction of repeated functional motifs into supramolecules.[1] We[2] and others[3] have developed approaches in which key growth steps involve metal–donor atom interactions as opposed to carbon–carbon or carbon–heteroatom bond formation. Such metallodendrimers may bear multiple functionality at inner generations or at the surface generation. The design of water soluble boron-rich dendritic systems is of interest in the field of boron neutron capture therapy[4] and inner generation boron-functionalised dendrimers have recently been described.[5] We now report the use of metallosupramolecular methodology for the synthesis of surface-generation boron cluster functionalised metallodendrimers.

Our chosen starting point was pentaerythrytol **1** which bears four identical nucleophilic side-chains. The reaction of **1** with 4′-chloro-2,2′:6′,2″-terpyridine **2**[6] in Me_2SO in the presence of KOH gave compound **3** (FABMS *m/z* 1062) as a white solid in 77% yield (Scheme 1). Although the free ligand **3** is extremely insoluble in most organic solvents, protonation leads to species which are freely soluble in water, D_2O or other protic solvents and whose ^1H NMR spectra confirm that reaction of all the side-



Scheme 1 *Reagents and conditions*: i, KOH, Me_2SO; ii, [Ru(tpy)Cl_3], *N*-ethylmorpholine, $HOCH_2CH_2OH$; iii, [Ru(sicarbtpy)Cl_3], *N*-ethylmorpholine, $HOCHCH_2OH$

chains is complete and that the four CH_2Otpy (tpy = 2,2′:6′,2″-terpyridine) groups are equivalent.† A singlet at δ 4.07 indicates that the two protons of each potentially diastereotopic methylene group are equivalent.

Compound **3** contains four tpy metal-binding domains and is the key species for the assembly of the metallodendrimer. As a test of the growth reaction we reacted **3** with $[Ru(tpy)Cl_3]$ in ethane-1,2-diol at 120 °C. The deep red solution obtained after 12 h was worked up and the tetranuclear complex $\mathbf{4}[PF_6]_8$ was obtained in 30% yield after chromatographic purification. The ^1H NMR spectrum of a CD_3CN solution of $\mathbf{4}[PF_6]_8$ immediately indicates the very high symmetry of the product, and clearly shows that a $\{Ru(tpy)_2\}$ moiety is attached to each of the four chains.‡ The CH_2 groups appear as a sharp singlet at δ 5.53, again providing support for the high symmetry of the product. The spectrum was fully assigned by COSY spectroscopy. The chemical shifts of the protons attached to the C and D rings of the terminal tpy ligands are comparable to those of model $[Ru(tpy)(ROtpy)]^{2+}$ (ROtpy = 4′-alkoxy-2,2′:6′,2″-terpyridine) complexes.[7] Further evidence for the equivalence of the terminal $\{Ru(tpy)_2\}$ domains comes from the observation of a single fully reversible Ru^{II}–Ru^{III} process at +0.816 V {*cf.* $[Ru(tpy)(EtOtpy)]^{2+}$, +0.834 V,[7] potentials quoted *vs.* Fc–Fc^+). We thus assign an E' value of 0.357 V to the dendrimer.§

Finally, we investigated the reaction of **3** with the carbaboranyl-functionalised complex, $[Ru(sicarbtpy)Cl_3]$ {sicarbtpy = 4′-[2-(*tert*-butyldimethylsilyl)-1,2-carbaboranyl]-2,2′:6′,2″-terpyridine).[8] After reaction in ethane-1,2-diol at 120 °C the tetranuclear complex $\mathbf{5}[PF_6]_8$ was isolated in 31% yield. The ^1H NMR spectrum of a CD_3CN solution of $\mathbf{5}[PF_6]_8$ confirmed the high symmetry of the product and showed that a ruthenium terminator group had been attached to each of the chains.¶ However, the introduction of the sterically demanding protected carbaboranyl group has the effect of conformationally constraining the tetranuclear complex; the diastereotopic methylene groups appear as an AB multiplet shifted considerably with respect to the position of the single CH_2 resonance observed in $\mathbf{4}^{8+}$. This conformational restriction is also observed in the carbaboranyl group, and in contrast to the ^1H NMR spectra of free ligand or $[Ru(tpy)(sicarbtpy)]^{2+}$ the two methyl groups on the silyl protecting group are magnetically non-equivalent.[8] The spectrum was fully assigned by COSY NMR spectroscopy and the presence of the intact *closo*-carbaborane was confirmed by ^{11}B NMR spectroscopy. Despite the observation of the diastereotopic methylene and methyl groups, the terminal $\{Ru(tpy)_2\}$ domains are equivalent and a single fully reversible Ru^{II}–Ru^{III} process is observed at +0.789 V. A view of the complex is presented in Fig. 1 in which the various domains are emphasised.

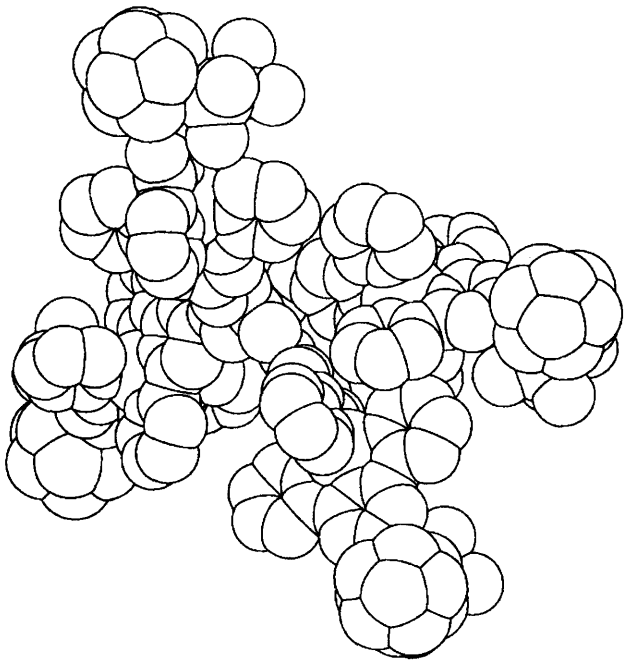


Fig. 1 Energy-minimised structure of the cation **5** (Molecular Simulations Cerius^{2TM} software, Universal Force Field). Hydrogen atoms have been omitted for clarity.

We are currently extending these studies to the formation of higher nuclearity first-generation complexes and to second-generation functionalised species.

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Footnotes

† Compound **3**. ^1H NMR (D_2O–DCl): δ 7.86 (d, 2 H, H^{6A}), 7.77 (d, 2 H, H^{3A}), 7.64, t (2 H, H^{4A}), 7.28 (s, 2 H, $H^{3B/5B}$), 7.10 (td, 2 H, H^{5A}), 4.07 (s, 2 H, CH_2).

‡ Compound $\mathbf{4}[PF_6]_8$. TOF MS: *m/z* 2828, $\mathbf{4}[PF_6]_3F$; 3015, $\mathbf{4}[PF_6]_4F_2$. ^1H NMR (CD_3CN): δ 8.81 (s, 2 H, H^{3B}), 8.74 (d, 2 H, H^{3D}), 8.67 (d, 2 H, H^{3A}), 8.48 (d, 2 H, H^{3C}), 8.37 (t, 1 H, H^{4D}), 7.88 (m, 4 H, H^{4C+4A}), 7.52 (d, 2 H, H^{6C}), 7.33 (dd, 2 H, H^{6A}), 7.15 (td, 2 H, H^{5C}), 7.13 (td, 2 H, H^{5A}), 5.53 (s, 2 H, CH_2).

§ This is a convenient parameter for the quantification of electronic effects in tpy ligands. E' (Xtpy) = $0.5(E°$ $[Ru(Xtpy)_2]^{2+})$. For heteroleptic complexes $[Ru(Xtpy)(Ytpy)]^{2+}$, $E° = E'(Xtpy) + E'(Ytpy)$.

¶ Compound $\mathbf{5}[PF_6]_8$. TOF MS: *m/z* 3420, **5**. ^1H NMR (CD_3CN): δ 8.70 (s, 2 H, H^{3B}) 8.35 (d, 2 H, H^{3D}), 8.53 (d, 2 H, $H^{3A/3C}$), 8.48 (d, 2 H, $H^{3C/3A}$), 7.88 (m, 4 H, H^{4A}), 7.38 (dd, 2 H, H^{6A}), 7.21 (td, 2 H, H^{6C}), 7.22, (td, 2 H, H^{5A}), 7.14 (td, 2 H, H^{5C}), 4.08, 4.59 (AB, 2 H, CH_2), 0.95 (s, 9 H, Bu^t), −0.05 (s, 3 H, CH_3), −0.21 (s, 3 H, CH_3). ^{11}B NMR (δ 0 for $BF_3{\cdot}OEt_2$) (CD_3CN): δ −3.6 (1B); −7.4 (2B), −13.4 (1B), −16.4 (4B), −29.7 (1B), −32.4 (1B).

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