A new convergent strategy for high-nuclearity metallodendrimers

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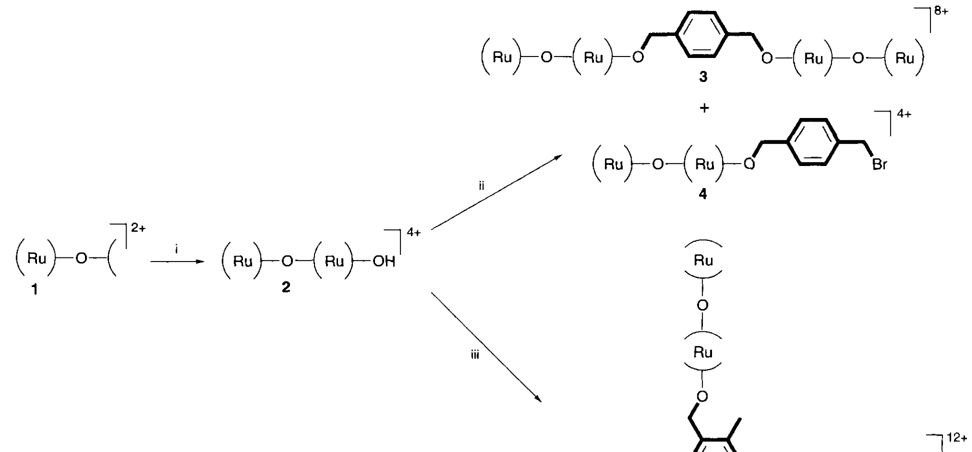
A convergent methodology for the synthesis of metallodendrimers is described in which the key step is the reaction of a *metal-complex* containing a coordinated nucleophile with a multifunctional electrophile; using this methodology, linear and starburst tetra-, hexa- and nona-ruthenium metallodendrimers are prepared.

Multinuclear metallodendrimers are of current interest as photoconversion and light-harvesting devices.[1] The stereogenic problems associated with the use of ligands based upon 2,2′-bipyridine led us[2] and others[3] to adopt the 2,2′:6′,2″-terpyridine metal-binding domain for the assembly of metallodendrimers. Synthetic problems associated with divergent approaches[4] led us to develop convergent methodologies for the preparation of homo- and hetero-nuclear systems[5] and eventually adopt a strategy in which new bridging ligands were prepared *in situ* by reactions of co-ordinated electrophiles.[6] We now extend this *ligand-reactivity* approach[7] to the convergent synthesis of metallodendrimers by the reaction of coordinated nucleophiles with multifunctional electrophiles. Specifically, we have introduced a new type of coupling methodology for the assembly of metallodendrimers involving the reaction of coordinated 4′-hydroxy-2,2′:6′,2″-terpyridine ligands with poly(bromomethyl)benzenes.

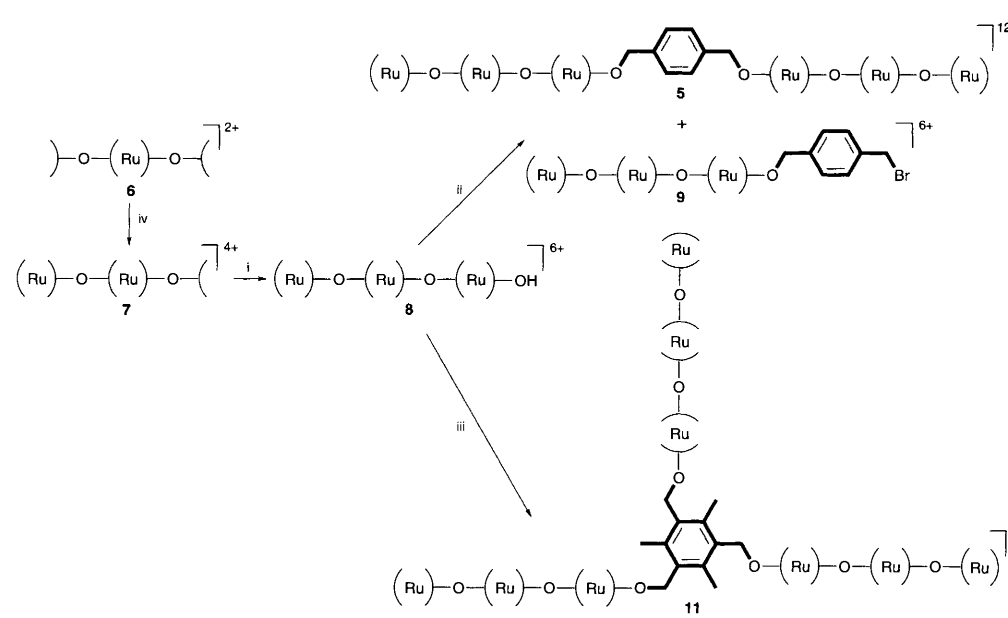
The *complex ligand* [(tpy)Ru(botpy)]$^{2+}$ **1**[6] [tpy = 2,2′:6′,2″-terpyridine; botpy = bis(2,2′:6′,2″-terpyridinyl) ether] which is a mononuclear species containing a vacant metal-binding domain was treated with [(HOtpy)RuCl$_3$] [HOtpy = 2,2′:6′,2″-terpyridin-4′(1′*H*)-one] (prepared directly from the reaction of commercial ruthenium trichloride with HOtpy in ethanol) in methanol in the presence of *N*-ethylmorpholine to give the complex [(tpy)Ru(botpy)Ru(HOtpy)]$^{4+}$ **2**, isolated as its red PF$_6^-$ salt [*m/z* 1455 (**2**, 2PF$_6$), 1311 (**2**, PF$_6$) and 1168 (**2**)] in 70% yield (Scheme 1). This complex contains an HOtpy ligand which may be deprotonated and used as a nucleophile. The convergent strategy is now illustrated by the reaction of **2** with 1,4-bis(bromomethyl)benzene in acetonitrile in the presence of K$_2$CO$_3$ to give the tetranuclear complex [(tpy)Ru(botpy)Ru(btob)Ru(botpy)Ru(tpy)]$^{8+}$ **3** [btob = 1,4-bis(2,2′:6′,2″-terpyridin-4′-oxy)benzene], which was isolated as the red PF$_6^-$ salt [*m/z* 3447 (**3**, 7PF$_6$)] in 33% yield, together with small amounts of the dinuclear intermediate **4**. The tetranuclear complex **3** contains two ruthenium environments and exhibits *two* ruthenium(II)–ruthenium(III) processes (+0.91 and +0.80 V *vs.* Fc/Fc$^+$) in the cyclic voltammogram of its PF$_6^-$ salt, in contrast to the dinuclear precursor **2** (PF$_6$)$_2$ which exhibits a single reversible process at +0.87 V. The ^{1}H NMR spectrum of a CD$_3$CN solution of **3** (PF$_6$)$_8$ exhibits a singlet at δ 5.75 assigned to the methylene group in addition to a complex set of overlapping signals in the aromatic region.

The corresponding hexanuclear complex **5** is also readily prepared by this approach (Scheme 2). The reaction of [Ru(tpy)Cl$_3$] with AgBF$_4$ in acetone gives an intermediate solvento species, which reacts with [(botpy)Ru(botpy)]$^{2+}$ **6**[6] in dmf to give the new dinuclear *complex ligand* [(tpy)Ru(botpy)Ru(botpy)]$^{4+}$ **7** in 34% yield [isolated as the hexafluorophosphate salt, *m/z* 1830 (**6**, 3PF$_6$), 1687 (**6**, 2PF$_6$), 1545 (**6**, PF$_6$) and 1402 (**6**)]. Subsequent reaction of [(tpy)Ru(botpy)Ru(botpy)]$^{4+}$ with [RuCl$_3$(HOtpy)] in methanol in the presence of *N*-ethylmorpholine gave trinuclear [(tpy)Ru(botpy)Ru(botpy)Ru(HOtpy)]$^{6+}$ **8** [*m/z* 2327 (**8**, 4PF$_6$), 2187 (**8**, 3PF$_6$) and 2043 (**8**, 2PF$_6$) for the PF$_6^-$ salt] in 63% yield. The coupling of [(tpy)Ru(botpy)Ru(botpy)Ru(HOtpy)]$^{6+}$ with 1,4-bis(bromomethyl)benzene in acetonitrile in the presence of K$_2$CO$_3$ gave the hexanuclear complex [(tpy)Ru(botpy)Ru(botpy)Ru(btob)Ru(botpy)Ru(botpy)Ru(tpy)]$^{12+}$ **5** isolated in 15% yield as the red PF$_6^-$ salt [*m/z* 5193 (**5**, 11PF$_6$), 5051 (**5**, 10PF$_6$)] together with 32% of the trinuclear intermediate **9**.

The methodology is not limited to the bringing together of only two polynuclear metal units. As an example of the extention of the approach, the synthesis of starburst hexanuclear



Scheme 1 *Reagents and conditions*: i, [Ru(HOtpy)Cl$_3$], MeOH, *N*-ethylmorpholine, reflux; ii, 1,4-bis(bromomethyl)benzene, MeCN, K$_2$CO$_3$; iii, 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene, MeCN, K$_2$CO$_3$; iv, [Ru(typ)Cl$_3$], AgBF$_4$



Scheme 2 *Reagents and conditions*: i, [Ru(HOtpy)Cl_3], MeOH, *N*-ethylmorpholine, reflux; ii, 1,4-bis(bromomethyl)benzene, MeCN, K_2CO_3; iii, 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene, MeCN, K_2CO_3; iv, [Ru(typ)Cl_3], $AgBF_4$

and nonanuclear complexes is described. The key building block is 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene, prepared by the bromomethylation of mesitylene with paraformaldehyde and potassium bromide in H_2SO_4–acetic acid.[8] The reaction of the nucleophilic dinuclear complex **2** with 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene under the usual conditions gave the hexanuclear complex $[\{(tpy)Ru(botpy)Ru\}_3(ttob)]^{12+}$ **10** [ttob = 1,3,5-tris(2,2′:6′.2″-terpyridin-4′-oxy)-2,4,6-trimethylbenzene], isolated in 15% yield as its PF_6^- salt [*m*/*z* 5245 (**10**, $11PF_6$), 5102 (**9**, $10PF_6$) and 4951 (**10**, $9PF_6$)]. The aromatic region of the ^1H NMR spectrum of this salt is complex, but the aliphatic region contains singlets at δ 5.97 (6 H) and δ 2.92 (9 H) assigned to the methylene and the methyl protons respectively Finally, the nonanuclear complex $[\{(tpy)Ru(botpy)Ru(botpy)Ru\}_3(ttob)]^{18+}$ **11** was obtained from the reaction of the trinuclear nucleophilic complex **8** with 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene in the presence of K_2CO_3 in acetonitrile. The compound was isolated as its octadeca(hexafluorophosphate) salt in 80% yield after chromatography. The nonanuclear complex exhibited peaks at *m*/*z* 7881 (**11**, $17PF_6$, F) and 7333 (**11**, $16PF_6$, F) together with a variety of other fragmentation ions. Preliminary results have also shown that an octadecaruthenium complex is obtained in a precisely similar manner by the reaction of **8** with hexakis-(bromomethyl)benzene.

The solubility of all of the polynuclear complexes described above is dictated by the counter-ion. The chloride salts are water and methanol soluble, whilst the PF_6^- salts are acetonitrile and acetone soluble. The ^1H NMR spectra of all of the complexes are sharp and well-resolved, and in general, the resonances associated with a particular molecular fragment are not particularly sensitive to the nuclearity of the complex. The *complex ligands* which contain a non coordinated tpy domain exhibit particularly characteristic spectra, as we have noted previously.[9] In particular, H^6 of a non coordinated tpy domain lies to lower field than H^6 in a coordinated ligand; for example, in **7** $(PF_6)_4$, H^6 of the non coordinated domain is found at δ 8.73, whilst the other H^6 resonances are found at δ 7.58, 7.40, 7.67 and 7.69. All of the complexes were obtained as chemically pure species after chromatography over silica using acetonitrile–aqueous KNO_3 mobile phases, and were fully characterised by conventional methods. All mass spectrometric measurements were made using the TOF MALDI technique. In general, the electrochemical results for these higher nuclearity complexes were disappointing. In most cases, only a single rather broad process could be observed in the cyclic voltammograms of the PF_6^- salts (for example, **7** shows a single broad process at +0.88 V with $E_a - E_c$ = 104 mV). Further studies of the electrochemical properties are underway, but are hampered by the observation that complexes containing btob or ttob ligands adsorb strongly to glassy carbon or platinum electrode surfaces.

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