

Fe(η^5 -C₅H₅)⁺ initiated construction of hexaruthenium–polypyridine complexes

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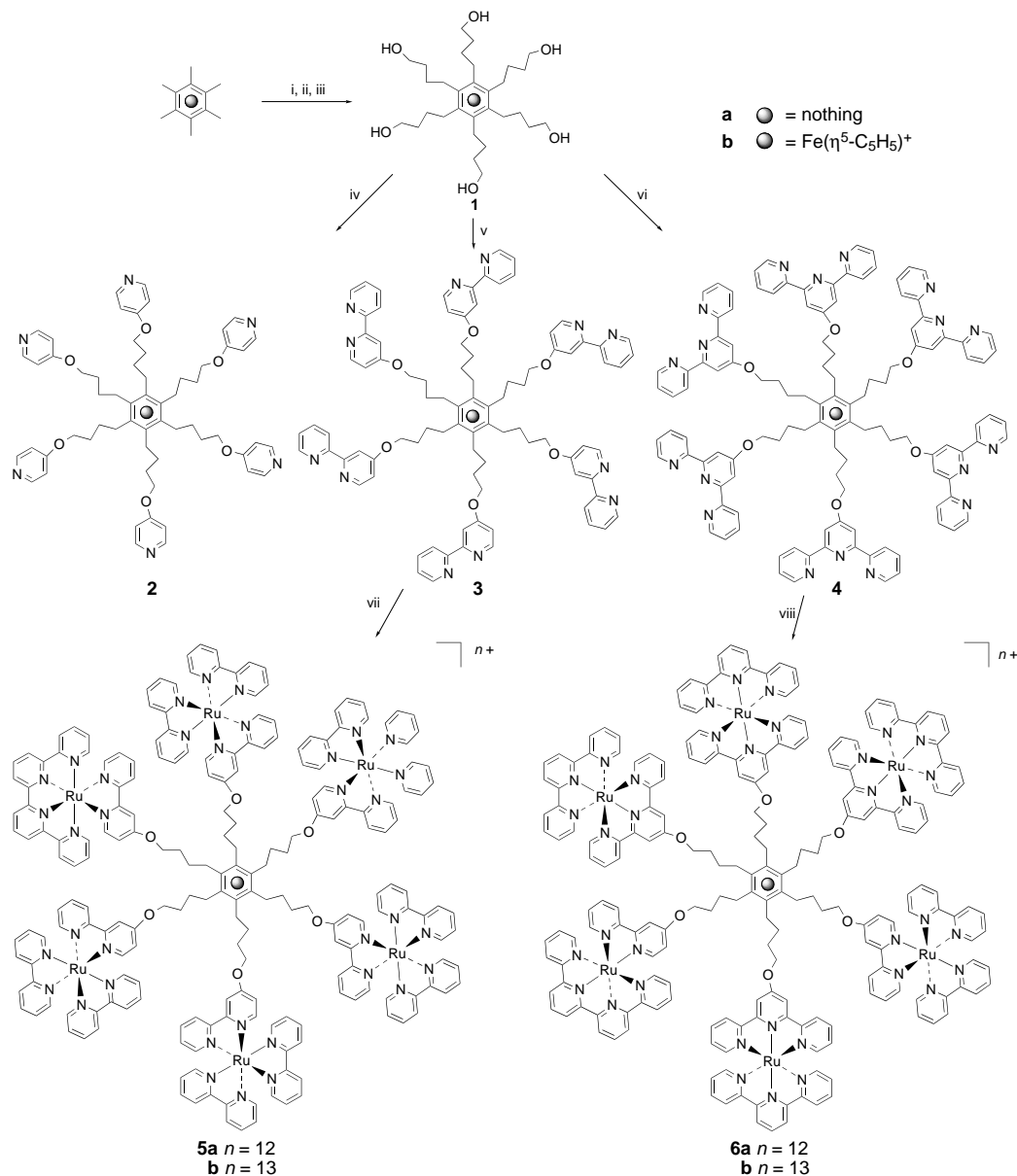
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Aromatic stars containing hexa-pyridine, -bipyridine and -terpyridine branches are synthesised with or without the central Fe(η^5 -C₅H₅)⁺ group and coordinated to ruthenium(II) polypyridine moieties to construct hexa- and hepta-nuclear hexa-bipyridine and -terpyridine complexes.

Oligopyridines have recently fascinated the supramolecular chemistry community¹ as powerful building blocks for the construction of inorganic helicates,^{2,3} antennas,⁴ metallo-stars⁵

and metallo-dendrimers⁶ containing photoactive redox sites.^{1,4,7} In this context, and given our interest in redox-active metal-lodendrimers for molecular recognition and electronics and polyelectronic redox catalysis,⁸ we have synthesized 'inorganometallic' hexaruthenium(II) bipyridine and terpyridine complexes which we are now reporting for the first time.

Our standard route which involves the hexa-alkylation of [Fe^{II}(η^5 -C₅H₅)(η^6 -C₆Me₆)]PF₆ using iodoalkyl derivatives under basic conditions is very successful, for instance to



Scheme 1 Synthesis of the hexaruthenium and heptametallic complexes; *Reagents and conditions*: i, Bu^tOK, allylbromide, thf; ii, if decomplexation is required: $h\nu_{\text{vis}}$, PPh₃, MeCN; iii, BH₃·thf, methylbut-2-ene, thf; then H₂O₂, OH⁻; iv, KOH, Me₂SO, 4-bromopyridine, 30 °C; v, KOH, Me₂SO, 4-chloro-2,2'-bipyridine, 30 °C; vi, KOH, Me₂SO, 4'-chloro-2,2':6'2''-terpyridine, 30 °C; vii, [Ru(bipy)₂Cl₂], ethanol, 80 °C, NH₄PF₆; viii, [Ru(terpy)Cl₃], *N*-ethylmorpholine, methanol, 80 °C, NH₄PF₆

synthesize hexaferrocene stars.⁹ However, all attempts to obtain the hexapyridine compound by direct alkylation of $[\text{Fe}^{\text{II}}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^6\text{-C}_6\text{Me}_6)]\text{PF}_6$ with 4-iodoalkyl-4'-methyl-2,2'-bipyridine in the presence of KOH and dimethoxyethane (dme) failed, apparently due to dehydrohalogenation or/and partial decomplexation of the $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{Me}_6)]^+$ complex in the presence of 2,2'-bipyridine. A new synthetic strategy was therefore required, the principle of which consisted of synthesizing the hexol before coupling the 4-chloro-2,2'-bipyridine derivative by alkoxy dehalogenation.¹⁰ Using this approach, we also synthesized the hexapyridine and hexaterpyridine compounds which were successfully hexaruthenated.

Perallylation of $[\text{Fe}^{\text{II}}(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{Me}_6)]\text{PF}_6$ eventually followed by visible photolysis, regioselective hydroboration and oxidation using H_2O_2 under basic conditions yields the hexol **1a** and the corresponding iron complex **1b**, as already known,^{9b} Scheme 1. The reaction of these two products, **1a** and **1b**, with bromo- or chloro-pyridyl compounds (4-bromopyridine, 4-chloro-2,2'-bipyridine and 4'-chloro-2,2':6',2''-terpyridine) in Me_2SO in the presence of KOH gave the associated hexasubstituted products, soluble in organic solvents and fully characterised by NMR (^1H , ^{13}C , COSY spectroscopy) and mass spectra (FAB⁺). The analytical and spectroscopic data for hexapyridine **2a**, hexabipyridine **3a**, hexaterpyridine **5a**, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{hexapyridine})]\text{PF}_6$ **2b** and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{hexaterpyridine})]\text{PF}_6$ **5b**† show the expected structures. The reaction of **1b** with 4-chloro-2,2'-bipyridine was disappointing, the expected $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ complex of the hexabipyridine **3b** was never cleanly obtained. This is probably due to a partial decomplexation of the $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{Me}_6)]^+$ complex, as mentioned above. Interestingly, this decomplexation is limited with the terpyridine derivatives, the difference with the bipyridine case being explained by steric effects. The ruthenation of **3a**, **4a** and **4b** was carried out using standard procedures with $[\text{Ru}(\text{bipy})_2\text{Cl}_2]$ and $[\text{Ru}(\text{terpy})\text{Cl}_3]$ as starting materials. The products **5a** and **6a** were then obtained and fully characterized by NMR (^1H , ^{13}C , COSY spectroscopy) and mass spectra (MALDI-TOF and electrospray, ES).

The MALDI-TOF spectra show peaks at m/z 5510.7 and 5499.1 which are assigned to (**5a** – PF_6) and (**6a** – PF_6); these results were confirmed by the ES spectra. Further evidence for the presence of the terminal $[\text{Ru}(\text{bipy})_3]^{2+}$ moieties is given by electrochemical measurements where the set of $\text{Ru}^{\text{II}}\text{--Ru}^{\text{III}}$ redox systems gives a single and reversible anodic wave at +0.82 and +0.79 V (vs. $\text{Fc}\text{--Fc}^+$) respectively. For compound **6b**, partial decomplexation of the iron core is indicated by the ES data.

We have shown that a new synthetic route for metallo-stars is open via a combination of organometallic, organic and inorganic chemistry. We are currently carrying out further studies on the construction of higher generations of functionalised dendrimers containing ruthenium polypyridine complexes at the periphery.

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Footnotes

† Preparations of 4-chloro-2,2'-bipyridine^{11a} and $[\text{Ru}(\text{terpy})\text{Cl}_3]$ ^{11b} were performed by the literature method.

5a (89% yield): ^1H NMR [250 MHz, $(\text{CD}_3)_2\text{CO}$], δ 8.73 (d, 5 H, CHbipy 3'), 8.20 (s 1 H, CHbipy_{int} 3), 8.13 (d, 5 H, CHbipy 4'), 7.99 (d, 5 H, CHbipy 6'), 7.66 (d, 1 H, CHbipy_{int} 6), 7.52 (m, 5 H, CHbipy 5'), 7.03 (m, 1 H, CHbipy_{int} 5), 4.28 (br. s, 2 H, CH_2O), 2.67 (br. s, 2 H, CH_2Ar), 1.89 (br. s, 2 H, $\text{CH}_2\text{CH}_2\text{O}$), 1.65 (br. s, 2 H, $\text{CH}_2\text{CH}_2\text{Ar}$); ^{13}C NMR [250 MHz, $(\text{CD}_3)_2\text{CO}$], δ 167.64 (C_qO), 158.92 and 158.08 (C_q bipy), 152.96 and 152.56 (CHbipy 6 and 6'), 138.72 (CHbipy 4'), 137.40 (C_q Ar), 128.72 (CHbipy 5'), 125.22 (CHbipy 3'), 115.57 (CHbipy 5), 111.71 (CHbipy 3), 66.14 (CH_2O), 29.35, 29.05 and 25.82 (CH_2); MS (MALDI-TOF): m/z 5510.7 (M – PF_6), $\text{C}_{210}\text{H}_{186}\text{F}_{72}\text{N}_{36}\text{O}_6\text{P}_{12}\text{Ru}_6$ requires m/z 5655.97, – PF_6 m/z –5510.9.

6a (88% yield): ^1H NMR [250 MHz, $(\text{CD}_3)_2\text{CO}$], δ 8.97 (d, 2 H, CHterpy_{ext} 3'), 8.71 (m, 4 H, CHterpy 3), 8.61 (s, 2 H CHterpy_{int} 3'), 8.47

(t, 1 H, CHterpy_{ext} 4'), 7.86 (m, 4 H, CHterpy 4), 7.73 and 7.60 (d, 4 H, CHterpy 6), 7.18 (br. s, 4 H, CHterpy 5), 4.85 (br. t, 2 H, CH_2O), 3.18 (br. s, 2 H, CH_2Ar), 2.44 (br. s, 2 H, $\text{CH}_2\text{CH}_2\text{O}$), 2.16 (br. s, 2 H, CHCH_2Ar); ^{13}C NMR [250 MHz, $(\text{CD}_3)_2\text{CO}$], δ 167.00 (C_qterpyO), 159.34 and 156.84 (C_q terpy 2 and 2'), 153.57 and 153.26 (CHterpy 6), 138.77 and 137.71 (CHterpy 4 and 4'), 137.71 (C_q Ar), 128.55 (CHterpy 5), 125.5 and 125.24 (CHterpy 3), 124.72 (CHterpy_{ext} 3'), 112.18 (CHterpy_{int} 3'), 71.36 (CH_2O), 30.68, 30.25, 29.01 (CH_2); MS (MALDI-TOF): m/z 5499.1 (M – PF_6), $\text{C}_{210}\text{H}_{174}\text{F}_{72}\text{N}_{36}\text{O}_6\text{P}_{12}\text{Ru}_6$ requires m/z 5643.92, – PF_6 m/z 5498.9.

6b: ^1H NMR [250 MHz, $(\text{CD}_3)_2\text{CO}$], δ 8.95 (br. d, 12 H, CHterpy_{ext} 3'), 8.68 (br m, 24 H, CHterpy 3), 8.61 (br s, 12 H, CHterpy_{int} 3'), 8.47 (br t, 6 H, CHterpy_{ext} 4'), 7.88 (br m, 24 H, CHterpy 4), 7.72 and 7.58 (d, 24 H, CHterpy 6) 7.17 (br s, 24 H, CHterpy 5), 4.93 (br s, 5 H, C_5H_5), 4.82 (br. t, 12 H, CH_2O), 3.43 (br s, 12 H, CH_2Ar), 2.37 (br s, 12 H, $\text{CH}_2\text{CH}_2\text{O}$), 2.07 (br s, 12 H, $\text{CH}_2\text{CH}_2\text{Ar}$); ^{13}C NMR [250 MHz, $(\text{CD}_3)_2\text{CO}$], δ 166.98 (C_qterpyO), 158.32 and 155.63 (C_qterpy 2 and 2'), 152.56 and 152.07 (CHterpy 6), 138.68 and 137.75 (CHterpy_{ext} 4 and 4'), 127.56 (CHterpy 5), 124.48 and 124.18 (CHterpy 3), 123.71 (CHterpy_{ext} 3'), 111.21 (CHterpy_{int} 3'), 102.55 (C_q Ar), 78.32 (C_5H_5), 69.38 (CH_2O), 29.57, 28.86, 26.48 (CH_2). MS (ES): m/z 1333.8 (M^{4+}), 1037.6 (M^{5+}), 840.2 (M^{6+}), corresponding to a measured mass of 5911.92 (M^+), $\text{C}_{215}\text{H}_{179}\text{FeF}_{78}\text{N}_{36}\text{O}_6\text{P}_{13}\text{Ru}_6$ requires m/z 5912.37.

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