

Pyridine-based dendritic wedges with a specific metal ion coordination site and their palladium(II) complexes

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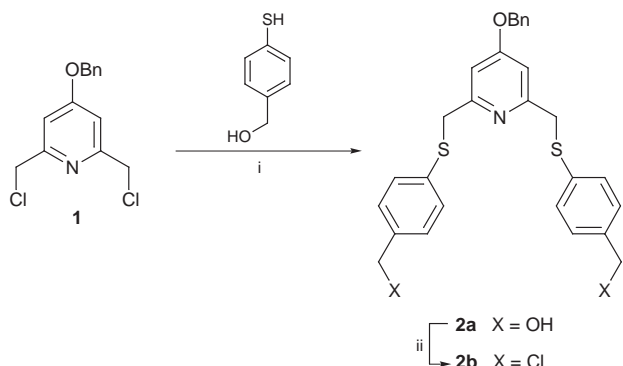
The 2,6-di(thiomethyl)pyridine sub-unit has been incorporated into pyridine-based dendritic structures providing a series of dendritic wedges, which readily form Pd^{II} complexes.

The incorporation of metal centres into a dendritic structure is a challenging idea aimed at generating materials with potentially useful features.^{1–3} Numerous dendrimers, which contain coordination sites on the outer surface,⁴ within the macrostructure throughout all layers,⁵ and at the inner core⁶ have been prepared. In contrast, except for scant coordination studies,⁷ very little has been done about the construction of dendrimers with specific coordination centres within the dendritic wedges and their reaction with metal substrates. In particular, no report has yet appeared on the synthesis of dendrimers with a pyridine-based skeleton incorporating a specific coordination site for platinum-group metals.

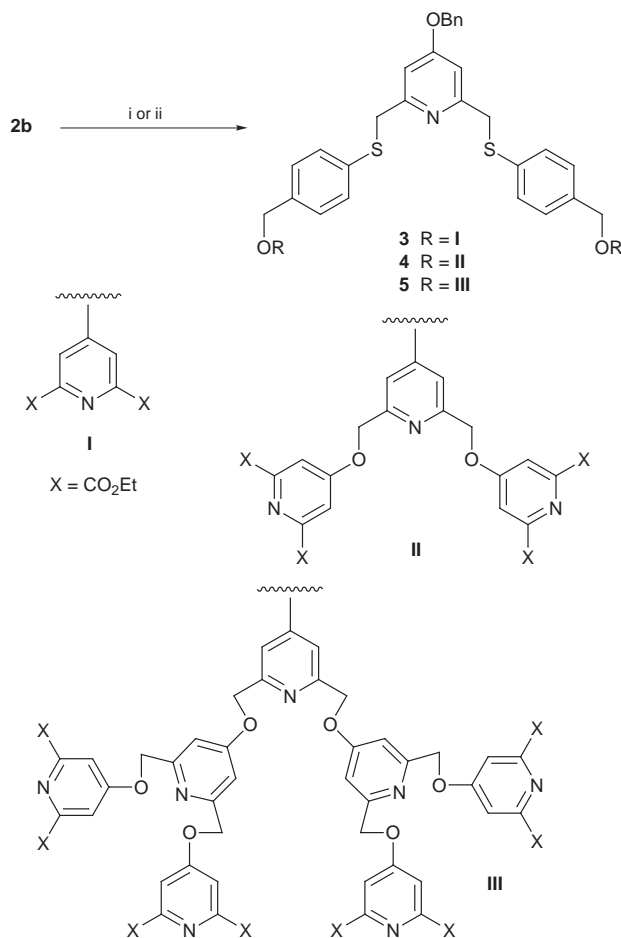
As a preliminary study of the assembly of such dendrimers we report herein the synthesis of the pyridine-based dendrons **3–5** containing the 2,6-di(thiomethyl)pyridine sub-unit, which has been shown to form very stable Pd^{II} complexes.⁸ The complexation of Pd^{II} with **3–5** to give metallodendrons **6–8** is also reported on.

Our approach to the synthesis of the dendrons **3–5** is based on a convergent strategy which implies the preparation of the dendritic fragments **I–III** as 4-hydroxy species⁹ followed by attachment to the metal binding site **2b**. The key building block **2b** (Scheme 1) was prepared by coupling 2,6-bis(chloromethyl)-4-benzyloxy pyridine **1**⁹ with 4-mercaptobenzyl alcohol¹⁰ (DMF, K₂CO₃, 18-crown-6, 70 °C). This reaction occurred with preferential formation of the thioether bond, providing the hydroxymethyl derivative **2a**. Subsequent chlorination (SOCl₂, 50 °C) followed by attachment of the diester **I** to the resulting chloride **2b**, gave **3** in 92% yield after purification by column chromatography (SiO₂, CH₂Cl₂–2% MeOH) (Scheme 2). Similarly, the reactions of **2b** with tetraester **II** and octaester **III** yielded the dendrons **4** and **5** (Scheme 2) in 85 and 51% yield, respectively.

The dendrons obtained were fully characterised by IR and NMR techniques as well as by matrix assisted laser desorption ionization mass spectrometry (MALDI-MS; dithranol 10 mg cm⁻³ acetone matrix). The reaction of the dendritic fragment **3**



Scheme 1 Reagents and conditions: i, K₂CO₃, 18-crown-6, DMF, 70 °C, 24 h; ii, SOCl₂, 50 °C, 4 h.



Scheme 2 Reagents and conditions: i, K₂CO₃, DMF, 70 °C, 24 h; ii, K₂CO₃, DMF, 60 °C, 48 h.

with Pd(PhCN)₂Cl₂ in CH₂Cl₂ at 25 °C (1 : 1 Pd/**3** molar ratio) gave a stable orange microcrystalline Pd^{II} complex **6** in 76% yield (Fig. 1). Direct evidence of a successful complexation at

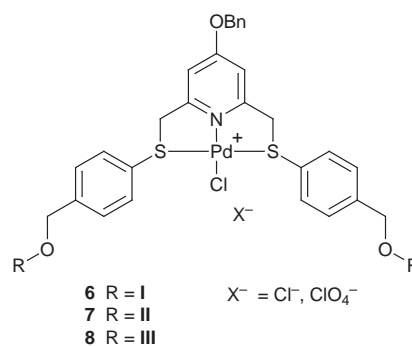


Fig. 1 Schematic representation of metallodendrons **6–8** (dendritic polypyridines of 0, 1, 2 generation).

the 2,6-di(thiomethyl)pyridine site is provided by the significant downfield shifts of the thiomethylene protons (1.2 ppm) and carbons (11.2 ppm) in the ^1H NMR and ^{13}C NMR spectra, respectively. The absence of the 3,5-pyridine protons peak at δ 6.87 further supports the complexation hypothesis. Moreover, the presence of the characteristic molecular peak at m/z 1074 ($[\text{3PdCl}]^+$) in the MALDI-TOF spectrum of **6** clearly indicates the formation of a 1:1 complex between Pd^{II} and **3**.

The complexation of Pd^{II} with the dendron **4** did not proceed smoothly under the same experimental conditions. The ^1H NMR spectrum of a CDCl_3 solution of complex **7**, isolated as its chloride salt, suggests the presence of an undesired product. A possible explanation for its formation is the competition of chloride ion as a nucleophile with other donor centres in the dendritic structure, namely the sulfur and nitrogen atoms of the 2,6-di(thiomethyl)pyridine sub-unit.¹¹ However, **7** was successfully purified by conversion into its yellow ClO_4^- salt, the ^1H NMR spectrum of which exhibits a pattern similar to those observed for **6**, furthermore the MALDI-TOF mass spectrum shows a parent ion at m/z 1792 corresponding to $[\text{4PdCl}]^+$.

Extension of this finding to the reaction of **5** with Pd^{II} allowed us to obtain metallodendron **8**. As in the foregoing spectra, the resonances associated with the 2,6-di(thiomethyl)pyridine fragment are affected by complexation and lie at lower field than those of the uncoordinated domain. In particular, the CH_2S singlet, which is found at δ 4.21 in a uncoordinated ligand, shifts to δ 5.26 (br s) in a coordinated unit. Once again, the MALDI-TOF mass spectrum displaying the characteristic molecular peak at m/z 3225 ($[\text{5PdCl}]^+$) provides convincing evidence for the formulation of product **8**. Analytical data, ^1H , ^{13}C NMR and MALDI-TOF spectra of all species prepared are fully consistent with the proposed structures. In particular, for complex **8** the synthetic approach (1:1 $\text{Pd}/\text{5}$ molar ratio and the ensuing 78% yield) and the presence of one single signal for the carboxylate ethyl protons ($\text{X} = \text{CO}_2\text{Et}$) strongly support the formulation of Fig. 1.

These results indicate that the presence of the 2,6-di(thiomethyl)pyridine sub-unit in dendritic wedges is particularly attractive for developing dendrimers with specifically localised metal centres. The physical properties of the metallodendrons **6–8** are now under extensive investigations. Of particular interest are the selectivity towards other transition metals and the influence of dendrimer framework on the metal-binding process.

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