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# A ferrocene dendrimer based on a cyclotriphosphazene core

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**Abstract**—A ferrocene dendrimer based on a cyclotriphosphazene core was prepared via a sixfold substitution reaction of $N_3P_3Cl_6$ with a diferrocenyl benzyl alcohol dendron. All twelve ferrocene units in the dendrimer were found to be electrochemically equivalent.


Electroactive materials containing multiple but electrochemically equivalent redox units are of much current interest. These materials can transfer multiple numbers of electrons under the same applied potential and hence, are potentially useful as electrode modifiers, multielectron redox catalysts and electron reservoirs or batteries.[1] A wide variety of dendrimers that are peripherally functionalized with redox-active units have been studied towards these ends.[2] In view of the fact that ferrocene and its derivatives show stable reversible redox properties and are easy to prepare, ferrocene containing dendrimers are the most studied class of redox-active dendrimers.[1b,3] In continuation of our studies on dendritic multiferrocenyl compounds,[4] we now describe the synthesis of a representative member of a new class of ferrocene dendrimers that are built on a cyclotriphosphazene core. A few phosphorus centered ferrocene dendrimers were recently reported by Majoral et al.[3f,g] but, to the best of our knowledge, those having a cyclotriphosphazene core were not known.[5]

Most of the dendrimer cores used until now are based on either tri- or tetravalent scaffolds. A hexavalent core[6] has obvious advantages because it can accommodate a greater number of dendrons and hence, more functional groups for a given dendrimer generation. Cyclotriphosphazene is a thermally and chemically stable hexavalent scaffold which can be easily perfunctionalized via substitution reactions on the corresponding hexachloride $N_3P_3Cl_6$, especially with heteroatomic nucleophiles.[7] Cyclotriphosphazenes are also electrochemically inert. It is known that in substituted cyclotriphosphazenes where the substituents themselves are redox-active, the inorganic ring does not interfere with the electrochemical properties of the substituents.[8] These features make cyclotriphosphazene an ideal scaffold for the construction of electroactive dendrimers having multiple (6n) redox-active units at the periphery.

In a convergent approach, a sixfold substitution reaction of $N_3P_3Cl_6$ with a Fréchet-type diferrocenyl dendron **6** was envisaged for dendrimer synthesis (Scheme 1). Towards this end, *p*-amino phenol **1** was first diazotized in the conventional way ($NaNO_2$, aq. $H_2SO_4$, 0°C) and the diazonium salt solution treated with ferrocenium hydrogen sulfate ($Cp_2Fe$/conc. $H_2SO_4$) at 0°C followed by reduction with aqueous ascorbic acid to produce the known *p*-ferrocenyl phenol **2** in 60% yield.[9] The latter was monoalkylated with excess 1,4-dibromobutane ($K_2CO_3$, acetone, reflux) to give the bromide **3** (70%) which was then used in a twofold alkylation reaction of methyl 3,5-dihydroxybenzoate **4** ($K_2CO_3$, cat. 18-c-6, acetone, reflux) to produce **5** in 85% yield.[10] $LiAlH_4$ reduction of **5** then led to the desired diferrocenyl benzyl alcohol dendron **6** in 80% yield. In an alternative approach to **6**, a selective dialkylation of 3,5-dihydroxybenzyl alcohol with **3** via its phenolic groups was also explored but this led to incomplete conversion even after prolonged reflux in acetone. A sixfold substitution of $N_3P_3Cl_6$ with excess **6** (10 equiv.) in refluxing THF using NaH as the base[11] then gave rise to the dodecaferrocenyl dendrimer **7** in 26% yield after purification by preparative thin layer chromatography over neutral alumina (light petroleum/$CH_2Cl_2$/MeOH 45/50/5).

*Keywords*: dendrimer; cyclotriphosphazene; ferrocene; electroactive.
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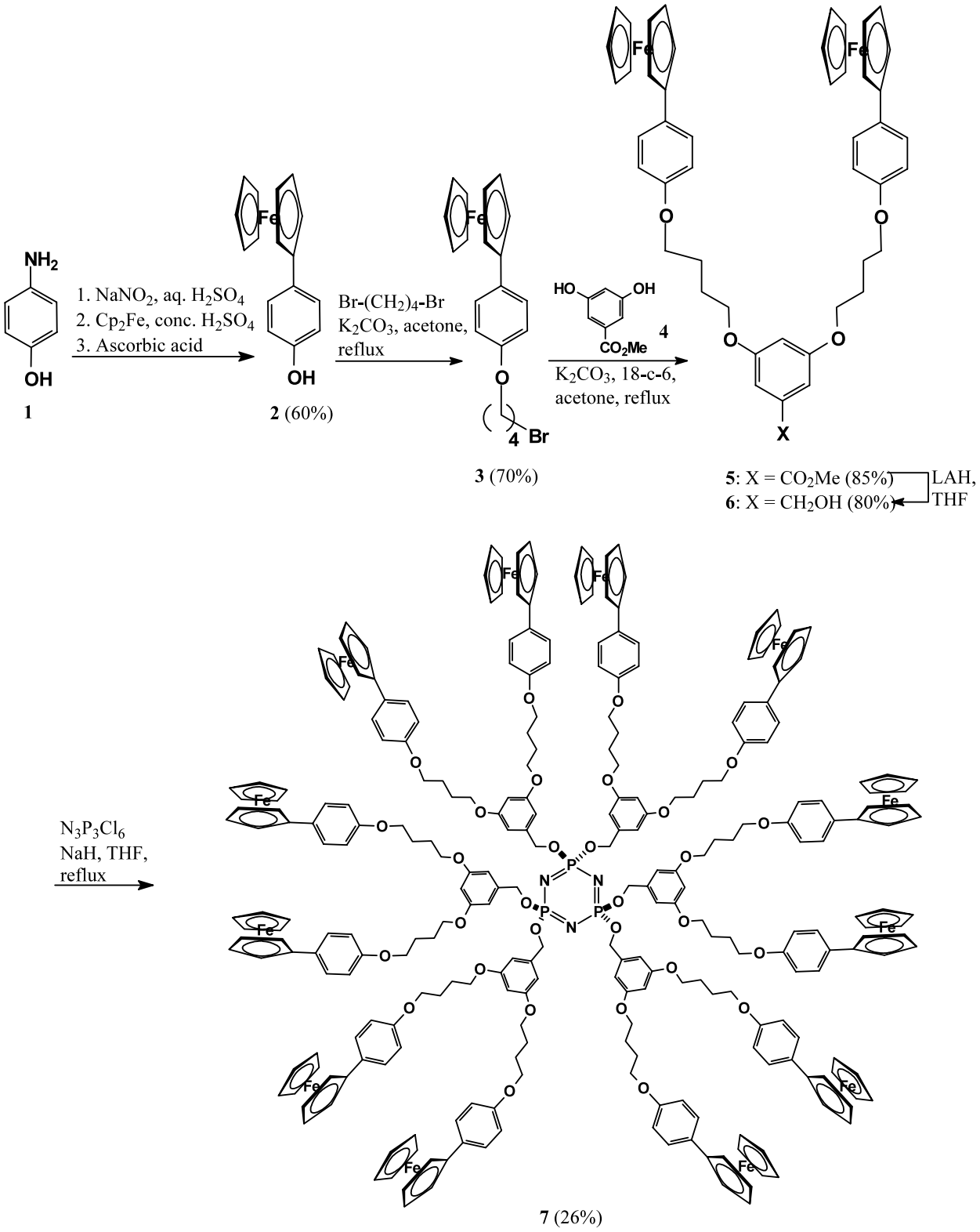


**Scheme 1.**

The low yield of the dendrimer is perhaps due to incomplete substitution of the cyclotriphosphazene ring caused by the bulky nature of the dendrons. Several partially coupled products (as shown by $^{31}P$ NMR) were isolated from the crude reaction mixture. The dendrimer was characterized by its IR, $^{1}H$, $^{13}C$ and $^{31}P$ NMR and MALDI-TOF mass spectra.[10] Its IR spectrum showed typically strong PN stretching bands at 1196 and 1221 $cm^{-1}$. The $^{1}H$ and $^{13}C$ NMR spectra did not differ significantly from those of the dendron **6**, except that the benzylic protons in the $^{1}H$ NMR spectrum of **7** were shifted downfield by ca. 0.2 ppm.

However, much broadening of peaks, especially in the aliphatic region, was observed in the $^1$H NMR spectrum of **7** probably due to restricted rotation of the attached dendrons. Considerable line broadening was also observed in the $^1$H NMR spectra of the dendron **6** and its precursor **5**. The persubstituted nature of the cyclotriphosphazene core in **7** was confirmed by its $^{31}$P NMR spectrum (202 MHz) which showed only a singlet at 21.5 ppm. Finally, MALDI-TOF mass spectrum of **7** showed a dominant M+1 peak at $m/z$ 4954. The dendrimer was soluble in common organic solvents such as $CHCl_3$, $CH_2Cl_2$ and $CH_3CN$ (sparingly) but was insoluble in alcoholic solvents.

Cyclic voltammetric (CV) studies on **7** were carried out in $CH_2Cl_2$ solutions (Pt anode, 0.1 M $Bu_4N^+ClO_4^-$ as the supporting electrolyte) which produced a single redox wave with an $E_{1/2}$ value of 0.41 V (versus SCE; scan rate 100 mV/s). However, the cathodic-peak-current ($i_{pc}$) was found to be somewhat greater than the anodic-peak-current ($i_{pa}$) indicative of cathodic stripping. Probably, **7** upon oxidation becomes insoluble in dichloromethane and is deposited on to the cathode surface giving rise to the stripping phenomenon. It then redissolves as it is reduced during the reverse scan. Similar phenomena have been reported by others during CV studies on large molecular weight ferrocene dendrimers, especially when carried out in $CH_2Cl_2$ solutions.[3b,h,4a] Unfortunately, **7** was not sufficiently soluble in $CH_3CN$ for CV studies. Nevertheless, the appearance of a single redox wave for **7** strongly suggests that the twelve ferrocene units in the dendrimer are electrochemically equivalent i.e. **7** is capable of transferring 12 electrons under the same applied potential.

In summary, we have demonstrated that cyclotriphosphazene can serve as a hexatopic core for the synthesis of electroactive dendrimers having 6n number of identical redox units. We are currently engaged in preparing higher generation ferrocene dendrimers based on a cyclotriphosphazene core.

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10. All new compounds gave satisfactory IR, $^1$H and $^{13}$C NMR data. Selected data for **5**: $^1$H NMR ($CDCl_3$/TMS, 300 MHz) $\delta$ 1.96 (br s, 8H), 3.89 (s, 3H), 4.04 (s, 10H), 4.21 (s, 8H), 4.52 (br s, 4H), 4.84 (br s, 4H), 6.63–6.78 (m, 5H), 7.17–7.25 (m, 6H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$

26.0, 52.2, 66.1, 67.4, 67.8, 68.6, 69.6, 106.7, 107.8, 114.4, 127.2, 131.2, 131.9, 157.5, 160.0, 166.9. **6**: $^{1}$H NMR ($CDCl_3$/TMS, 300 MHz) $\delta$ 1.90 (br s, 8H), 4.00 (s, 10H), 4.23 (s, 8H), 4.52 (br s, 4H), 4.71 (s, 2H), 4.89 (br s, 4H), 6.60–6.79 (m, 5H), 6.90–7.20 (m, 6H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 25.8, 58.3, 66.2, 67.4, 67.7, 68.6, 69.8, 106.7, 107.7, 114.1, 126.9, 127.4, 131.4, 132.0, 157.1, 160.1. **7**: IR (KBr) 1600, 1520, 1265, 1221, 1196, 1160 $cm^{-1}$; MS (MALDI-TOF) $m/z$ 4954 (M+1); $^{1}$H NMR ($CDCl_3$/TMS, 300 MHz) $\delta$ 1.93 (br s, 48 H), 4.02 (br s, 60H), 4.22 (br s, 48H), 4.53 (br s, 24H), 4.87 (br s, 24H), 4.96 (s, 12H), 6.61–6.80 (m, 30H), 6.95–7.30 (m, 36H); $^{13}$C NMR ($CDCl_3$, 75 MHz) 26.0, 60.6, 66.2, 67.5, 68.0, 68.4, 70.0, 106.5, 107.3, 114.4, 127.0, 128.0, 131.1, 132.0, 157.8, 160.8; $^{31}$P NMR ($CDCl_3/H_3PO_4$, 202 MHz) $\delta$ 21.5 (s).

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