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A hexaferrocenyl cluster based on a cyclotriphosphazene core: synthesis and electrochemistry

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Abstract

Sixfold substitution reaction of hexachlorocyclotriphosphazene with 4-ferrocenylphenol gave a covalent hexaferrocenyl cluster in which all six ferrocene units were electrochemically equivalent. On the other hand, reaction of hexachlorocyclotriphosphazene with ferrocene methanol produced ferrocene aldehyde in high yield.

Keywords: Ferrocene; Cyclotriphosphazene; Synthesis; Electrochemistry

1. Introduction

Electroactive compounds containing multiple but identical redox units are of much current interest because of their potential use as electrode modifiers, multielectron redox catalysts and electron reservoirs or batteries [1,2]. A wide variety of redox-active dendrimers have been studied towards these ends [3–6] among which, ferrocene dendrimers are the most studied variety [2,7–13]. This is primarily due to the fact that ferrocene and its derivatives are easy to functionalize and show stable reversible redox properties [14]. In continuation of our interest in dendritic multiferrocenyl compounds [15,16], we now describe the synthesis and electrochemistry of a covalent hexaferrocenyl cluster based on a cyclotriphosphazene core.

Cyclotriphosphazene is a redox passive hexavalent scaffold that can be easily perfunctionalized via substitution reactions on the corresponding hexachloride $N_3P_3Cl_6$ with heteroatomic nucleophiles [17–22]. There are a few reports on cyclotriphosphazene derivatives that are partially substituted with metal/organometallic residues [22–26]. In such cases, it has been shown that the cyclophosphazene ring does not interfere with the redox property of the metal/organometallic substituents. However, there are no reports on cyclotriphosphazenes that are persubstituted with redox-active units, which provided the major impetus behind this study.

2. Experimental

2.1. Materials

4-Ferrocenylphenol (**2**) was prepared via reaction of diazotized 4-amino phenol with ferrocene according to a literature procedure [27]. Sodium hydride (60% dispersion in mineral oil) and hexachlorocyclotriphosphazene (**1**) were commercial materials and used as received. Tetrahydrofuran was dried over sodium-benzophenone ketyl. All reactions were carried out under an atmosphere of dry nitrogen. Column chromatography was carried out over neutral alumina (SRL, 60–120 mesh). Petroleum ether refers to the fraction boiling at 60–80 °C range.

2.2. Preparation of $[4\text{-}(C_5H_5FeC_5H_4)C_6H_4O]_6N_3P_3$ (3)

To a suspension of sodium hydride (60% dispersion in mineral oil, 0.021 g, 0.53 mmol) in THF (3 cm^3) was added dropwise a solution of 4-ferrocenylphenol (**2**) (0.1 g, 0.36 mmol) in THF (2 cm^3) at 0 °C. The reaction was

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brought to room temperature (r.t.) and stirred for 30 min. Then a solution of hexachlorocyclotriphosphazene (**1**) (0.01 g, 0.029 mmol) in THF (2 cm^3) was added to the above solution and the whole heated under reflux for 3 h. After being cooled to r.t., all volatiles were removed under reduced pressure and the orange residue chromatographed over neutral alumina using petroleum ether–dichloromethane (1:1) as the eluent to give **3** as a yellow solid. The yield was 0.035 g (65%). Melting point (m.p.) 206–209 °C (dichloromethane–hexane). IR (KBr): 3089 (w), 1519 (s), 1454 (m), 1265 (m), 1203 (s), 1184 (s), 1160 (s), 954 (s), 887 (m) cm^{-1}. MS (MALDI-TOF): m/z 1798 (M+1). ^1H NMR ($CDCl_3$, 300 MHz): δ 4.09 (br s, 30 H), 4.45 (br s, 12 H), 4.68 (br s, 12 H), 6.79 (br s, 12 H), 7.16 (br s, 12 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 67.5, 70.4, 71.1, 121.0, 127.2, 136.0, 149.0. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 27.0 (s). *Anal*. Calc. for $C_{96}H_{78}Fe_6N_3O_6P_3$: C, 64.14; H, 4.34; N, 2.33. Found: C, 64.01; H, 4.67; N, 2.44%.

2.3. Ferrocene aldehyde (5)

A mixture of ferrocene methanol (**4**) (0.070 g, 0.32 mmol), hexachlorocyclotriphosphazene (**1**) (0.011 g, 0.032 mmol) and pyridine (0.025 g, 0.32 mmol) in THF (5 cm^3) was heated under reflux for 5 h. All volatiles were then removed under reduced pressure and the residue diluted with water (5 cm^3) and extracted with dichloromethane (3 × 5 cm^3). The organic layer was separated, washed with 10% HCl solution and dried over anhydrous Na_2SO_4. Removal of solvent followed by column chromatography over silica gel using 10% ethyl acetate in petroleum ether gave **5** which was identical in all respect (m.p., IR, NMR) with an authentic sample of ferrocene aldehyde. The yield was 0.050 g (77%).

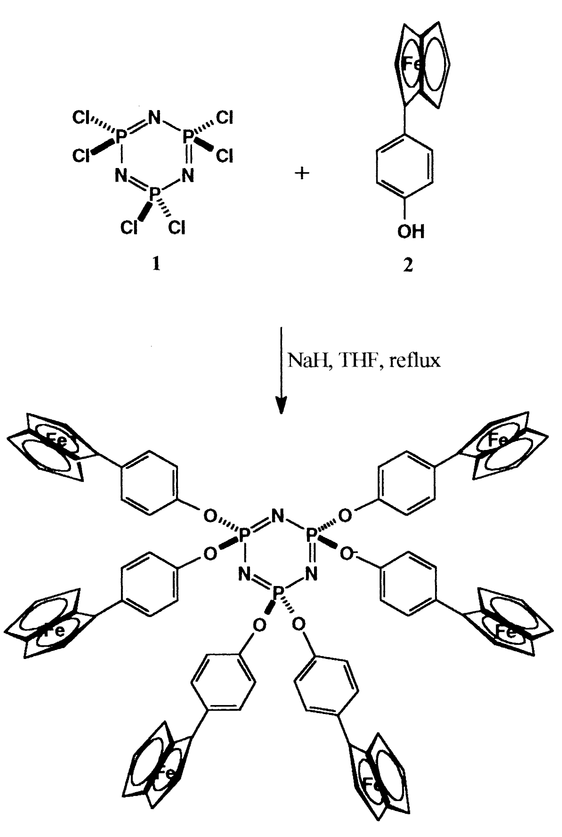
2.4. Physical measurements

M.p. are uncorrected. Microanalysis (C, H, N) was performed using a Perkin–Elmer 240C elemental analyzer. IR spectra were obtained on a Shimadzu FTIR-8300 instrument with samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV 240 spectrophotometer. NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 300 (300 MHz) or on a Bruker ARX-500 (500 MHz) instrument. Operating frequencies were 300 MHz (^1H), 202 MHz (^{31}P) and 75 MHz (^{13}C). Chemical shifts are reported downfield from tetramethylsilane (for ^1H and ^{13}C NMR spectra) or 85% H_3PO_4 (for ^{31}P NMR spectra). Electrochemical measurements were made using a CH Instruments 600A electrochemical analyzer. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three electrode configuration. All electrochemical data were collected at 298 K and are unconnected for junction potentials.

3. Results and discussion

3.1. Synthesis and characterization

Sixfold substitution reactions of hexachlorocyclotriphosphazene (**1**) with phenols have been reported in the literature [28–30]. Similar substitution reaction of **1** with excess 4-ferrocenylphenol (**2**) [27,31] in presence of NaH in refluxing THF smoothly produced the hexaferrocenyl cluster **3** in 65% yield (Scheme 1). No partially substituted cyclotriphosphazene products were obtained in this reaction. The use of Et_3N as a base in the above reaction led to little conversion even after prolonged heating. The product **3** was characterized by IR, ^1H, ^{13}C and ^{31}P NMR spectra and elemental analysis. The IR spectrum of **3** showed typically strong PN stretching bands at 1198 and 1223 cm^{-1} whereas the ν(O–H) streching band of 4-ferrocenylphenol at 3500 cm^{-1} was absent. The ^1H NMR spectrum of **3** showed small but significant deviations from the spectrum reported for 4-ferrocenylphenol (**2**) [31]. While the unsubstituted Cp-ring protons in **2** and **3** appeared at the same chemical



3 (65%)

Scheme 1.

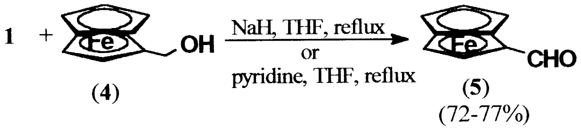
shift value, the substituted Cp-ring protons in **3** were shifted downfield by approximately 0.2 ppm. Again, the phenolic *ortho*-protons in **2** and **3** appeared at the same chemical shift value whereas the aromatic protons *ortho* to the ferrocene group in **3** were shielded by approximately 0.2 ppm. Notably, all the peaks in the ^{1}H NMR spectrum of **3** were broadened, probably due to restricted rotation among its geminally substituted ferrocenylphenol units. Finally, the persubstituted nature of the cyclotriphosphazene ring was confirmed from the ^{31}P NMR spectrum, which showed only a singlet at 27.0 ppm (H_3PO_4 standard).

The absorption spectrum of **3** in dichloromethane produced two intense bands in the ultraviolet region (240 and 282 nm) due to benzenoid transitions from the phenolic moiety (Table 1). Additional weak bands were also present in the visible region at 330 (sh) and 450 nm. The latter were due to the cyclopentadienyl π–π* and metal to ligand charge transfer (MLCT) transitions, respectively, arising from the ferrocene ring. The band positions were virtually identical to those of 4-ferrocenylphenol indicating that there are no ground state interactions between the ferrocenylphenolic units in **3**. As expected, **3** did not show any fluorescence properties.

Unexpectedly, reaction of **1** with ferrocene methanol (**4**) under identical reaction conditions (NaH, THF, reflux) led to an oxidation reaction producing ferrocene aldehyde (**5**) in high yield (Scheme 2). The same result was obtained when pyridine was used as the base. The results are all the more surprising since it is known that reaction of **1** with benzyl alcohol (NaH, THF, reflux) produces the persubstituted product in 45% yield [28]. Hence, the above oxidation reaction must be a special case for ferrocene methanol, mechanistic studies on which are currently under way.

3.2. Cyclic voltammetric studies

Cyclic voltammetric studies on **3** (dichloromethane, 0.1 M TBAP, Pt anode) produced a single redox wave with a $E_{1/2}$ value of 0.45 V (vs. SCE, scan rate 50 mV s^{-1}) (Fig. 1 and Table 1) which remained unaltered under different scan rates. The redox wave was somewhat elongated (ΔE_P 130 mV) as is often found in cyclic voltammograms of multi-redox systems when recorded in dichloromethane solutions (**3** was insoluble in acetonitrile or in acetonitrile–dichloromethane mixtures). Nevertheless, appearance of a single redox wave for **3** strongly suggests that the six ferrocene units in the cluster are electrochemically equivalent. However, the cathodic-peak-current (i_{pc}) was found to be greater than the anodic-peak-current (i_{pa}) indicative of cathodic stripping. Perhaps, there is a change in solubility of **3** after oxidation. We believe that, due to its large molecular weight, **3** upon oxidation becomes insoluble in dichloromethane and gets deposited onto the cathode surface giving rise to the stripping phenomenon. It then re-dissolves into solution as it gets reduced during the reverse scan. Similar phenomena have also been reported during CV studies on some large molecular weight ferrocene dendrimers [8,13,15]. Despite this stripping phenomenon, the above study clearly demonstrates that cyclotriphosphazene can indeed be used as a scaffold to construct electroactive materials having multiple but identical (6n) redox units. We are currently engaged in constructing ferrocene dendrimers with higher ferrocene contents based on a cyclotriphosphazene core.



Scheme 2.

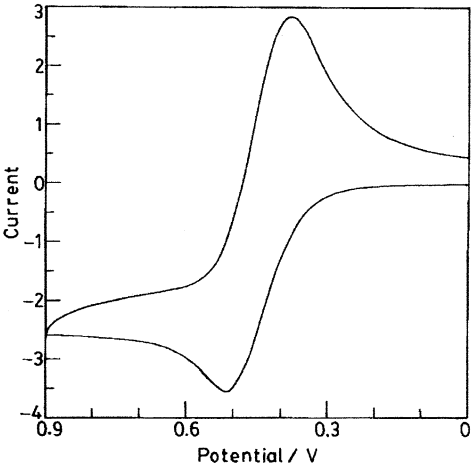


Fig. 1. Cyclic voltammogram of **3** in dichloromethane solution (0.1 M TBAP) at a scan rate of 50 mV s^{-1}.

Table 1
Absorption and cyclic voltammetric data for **3**

Absorption data λ_{max} (nm) (ε, M^{-1} cm^{-1}) [a]	Cyclic voltammetric data $E_{1/2}$ (V) (ΔE_p, mV) [a,b]
240 (58 408), 282 (40 949), 330 (5263), 450 (1283) [c]	0.45 (130)

[a] In dichloromethane.
[b] Reference electrode SCE; scan rate 50 mV s^{-1}.
[c] Shoulder.

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