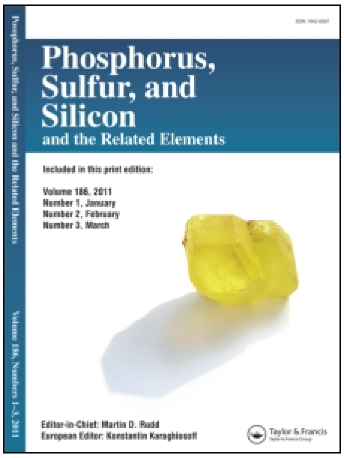

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Organostannoxanes and Cyclophosphazenes as Scaffolds for Multi-Ferrocene Assemblies

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The reactions of *n*-butylstannonic acid and di *n*-butyltinoxide with ferrocene monocarboxylic acid have been studied. In the former reaction a hexameric compound, $[n\text{-BuSn(O)OC(O)C}_5\text{H}_4\text{FeC}_5\text{H}_5]_6$ has been isolated in a quantitative yield. In the latter reaction a tetrameric compound $[\{n\text{-Bu}_2\text{SnO}_2\text{C(C}_5\text{H}_4\text{FeC}_5\text{H}_5)\}_2\text{O}]_2$ has been isolated. In contrast to the drum like structure of the former compound, the latter has a ladder like arrangement. Both $[n\text{-BuSn(O)OC(O)C}_5\text{H}_4\text{FeC}_5\text{H}_5]_6$ and $[\{n\text{-Bu}_2\text{SnO}_2\text{C(C}_5\text{H}_4\text{FeC}_5\text{H}_5)\}_2\text{O}]_2$ are electrochemically robust and show a single oxidation peak in the cyclic voltammetric experiment corresponding to the simultaneous oxidation of six and four ferrocene substituents respectively. The hydrazine substituted cyclophosphazenes, $\text{N}_3\text{P}_3[\text{N(Me)NH}_2]_6$, *gem*-$\text{N}_3\text{P}_3\text{Ph}_2[\text{N(Me)NH}_2]_4$, and *gem*-$\text{N}_3\text{P}_3(\text{O}_2\text{C}_{12}\text{H}_8)_2[\text{N(Me)NH}_2]_2$, are readily condensed with ferrocene carboxaldehyde, $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CHO}$, to afford the corresponding cyclophosphazenes linked to the ferrocenyl moiety through the hydrazone linkage, $\text{N}_3\text{P}_3[\text{N(Me)N=CHC}_5\text{H}_4\text{FeC}_5\text{H}_5]_6$, *gem*-$\text{N}_3\text{P}_3\text{Ph}_2[\text{N(Me)N=CHC}_5\text{H}_4\text{FeC}_5\text{H}_5]_4$, and *gem*-$\text{N}_3\text{P}_3(\text{O}_2\text{C}_{12}\text{H}_8)_2[\text{N(Me)N=CHC}_5\text{H}_4\text{FeC}_5\text{H}_5]_2$.

These cyclophosphazene linked multi-ferrocene derivatives are also thermally as well as electrochemically robust similar to the stannoxane linked derivatives. All of these compounds have been characterized by multinuclear NMR(^{1}H, ^{13}C, ^{31}P, ^{119}Sn), mass spectroscopy, and X-ray crystallography.

Keywords: stannoxanes; cyclophosphazenes; ferrocene; cyclic voltammetry; multi-metallocene; ladder; drum

INTRODUCTION

Multi-metallocenyl compounds in general and multi-ferrocenyl compounds in particular are attracting a considerable amount of interest in recent years.[1] This is because of the following reasons. (1) The preparation of these compounds is not trivial and therefore has been of interest from a synthetic point of view.(2)These multi-metallocene compounds are expected to function as multi-electron reservoirs with several possible electrochemical applications such as redox-active materials for modification of electrodes, bio sensors, new optical and magnetic materials etc. Several synthetic methodologies are known for the preparation of multi-ferrocene assemblies in polymeric, oligomeric, cyclic or dendrimeric forms. The most successful strategy for the preparation of polymeric compounds involves the methodology of Manners and coworkers.[2-3] A ring opening of strained ferrocenophanes is readily accomplished by thermal or ionic methods to afford a family of polymeric ferrocenes containing several heteroatoms in the backbone such as silicon, phosphorus etc. For the preparation of the compounds contaning ferrocenyl units linked in a cyclic manner two distinct synthetic strategies are known. Astruc and coworkers have developed an elegant synthetic methodolgy which involves the synthesis of molecular trees where a $[Fe(C_5Me_5)]$ unit serves as the core and suitable alkylation reactions lead to the grafting of the branches.[4-5] Alternative core structures have also been successfully utilized by these researchers.[6] Jutzi and coworkers have utilized the hydrosilylation reaction on decaallylferrocene to construct dendrimer-like multi-ferrocene compounds.[7] The hydrosilylation methodology has also been used by Astruc to prepare convenient synthons for the final assembly of ferrocenyl dendrimers via a convergent strategy.[8] Very recently mixed ferrocene-cobaltocenium dendrimers have been synthesized.[9] This involves the reaction of $[(C_5H_4COCl)Co(C_5H_5)]^+[PF_6]^-$ and $[(C_5H_4COCl)Fe(C_5H_5)]$ with the terminal $-NH_2$ groups of poly(propyleneimine) dendrimers. We have recently reported a hexa-ferrocene assembly supported on a stannoxane core.[10]

RESULTS AND DISCUSSION

In order to explore alternative methods of multi-ferrocene compounds we have decided to utilize known reactions in organotin chemistry or cyclophosphazene chemistry. Thus it is known, from studies carried out earlier, that the reactions of organostannonic acids with reagents such as carboxylic acids, organophosphates or phosphinic acids afford a variety of cluster types including drums, cubes, ladders etc.[11-14] Utilizing this methodology we have recently reported that the reaction of *n*-butylstannonic acid with ferrocene monocarboxylicacid affords a hexameric cluster $[n\text{-BuSn(O)OC(O)C}_5\text{H}_4\text{FeC}_5\text{H}_5]_6$ **1**:[10]

$$6n\text{-BuSn(O)OH} + 6\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{COOH} \rightarrow$$
$$\underset{\mathbf{1}}{[n\text{-BuSn(O)OC(O)C}_5\text{H}_4\text{FeC}_5\text{H}_5]_6} + 6\text{H}_2\text{O}$$

Compound **1** is formed in a quantitative yield and is thermally very robust(Mp 244 °C). The structure of the compound shows a central hexameric stannoxane core which serves as a structural support for a wheel like arrangement of the hexameric ferrocene assembly. This structure is reminiscent of a hepta ferrocene assembly doubly bridged to each other by silyl bridges.[15] **1** is electrochemically also very robust. It shows a single quasireversible peak with $E_{1/2}$ of 0.73 V(vs. SCE). The observation of a single oxidation peak corresponds to the oxidation of all the six ferrocene units at the same potential. Unlike the electrochemical decomposition observed for $\text{Na}_2[\text{Mo}_6\text{Cl}_8\{\text{O}_2\text{C(C}_5\text{H}_4)\text{Fe(C}_5\text{H}_5)\}_6]$. MeOH, **1** is quite robust electrochemically with the reversibility of its voltammogram unchanged even after several cycles.[16] Encouraged by the electrochemical behavior of **1** we have synthesized another stannoxane frame-work containing ferrocene assembly **2**:

$$2n\text{-Bu}_2\text{SnO} + 2\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{COOH} \rightarrow$$
$$\underset{\mathbf{2}}{1/2[(n\text{-Bu}_2\text{SnO}_2\text{C(C}_5\text{H}_4\text{FeC}_5\text{H}_5))_2\text{O}]_2} + \text{H}_2\text{O}$$

2 is a tetrameric cluster analogous to the previously known compound$[(\text{Me}_2\text{SnO}_2\text{CC}_6\text{H}_4\text{-}o\text{-NH}_2)_2\text{O}]$.[17] Similar to **1** the compound **2** also shows a single oxidation peak in the cyclic voltammetric experiment corresponding to the simultaneous oxidation of all the four ferrocene moieties.

Previous methods of the synthesis of ferrocenyl cyclophosphazenes involved the reaction of the corresponding lithium reagents with the chloro or fluorocyclophosphazenes. Using dilithiated derivatives *ansa*-$N_3P_3F_4(C_5H_4FeC_5H_4)$ has been prepared which can be polymerized by a ring opening of the cyclophosphazene ring. This is believed to be due to the steric strain present in the cyclophosphazene ring due to the *ansa* bridge[18-20]. Other approaches of preparation of ferrocenyl cyclophosphazenes include (1) the reactions of ferrocenyl methanol, ferrocenyl 2-propanol and N-methyl-2-ferrocenylmethylamine with chlorocyclophosphazenes[21] and (2) the reactions of ferrocenol and 1,1′-ferrocene diol with $N_3P_3Cl_6$ and $N_3P_3F_6$.[22]

Our approach for the preparation of ferrocenyl containing cyclophosphazenes is based on a different type of a synthetic strategy. We have chosen to design cyclophosphazenes containing reactive functional groups in the form of terminal $-NH_2$ groups. This was accomplished by the reaction of various chlorocyclophosphazenes with N-methylhydrazine. This reaction proceeds in a regiospecific manner leading to cyclophosphazene derivatives containing multiple reactive NH_2 end groups. These hydrazine substituted cyclophosphazenes,$N_3P_3[N(Me)NH_2]_6$, *gem*-$N_3P_3Ph_2[N(Me)NH_2]_4$and *gem*-$N_3P_3(O_2C_{12}H_8)_2[N(Me)NH_2]_2$ are readily condensed with ferrocene monocarboxaldehyde, $C_5H_5FeC_5H_4CHO$, to afford the corresponding cyclophosphazenes linked to the ferrocenyl moiety through the hydrazone linkage, $N_3P_3[N(Me)N{=}CHC_5H_4FeC_5H_5]_6$, *gem*-$N_3P_3Ph_2[N(Me)N{=}CHC_5H_4FeC_5H_5]_4$, and *gem*-$N_3P_3(O_2C_{12}H_8)_2[N(Me)N{=}CHC_5H_4FeC_5H_5]_2$. The X-ray structures of these ferrocenyl derivatives have been carried out to unambigously prove their structures in the solid-state. The ^{31}P NMR spectra of the hexa substituted derivative shows a single peak confirming the equivalence of all the phosphorus nuclei. Similarly the non-equivalent nature of the phosphorus nuclei in the tetra and bis ferrocenyl derivatives is proved by the A_2X and the AX_2 type of spectra obtained for these compounds. Similar to the multi-ferrocene compounds supported on stannoxane frameworks the cyclophosphazene supported ferrocenyl derivatives also show single reversible oxidation peaks in the cyclic voltammetric experiments. Also all of these compounds are electrochemically stable remaining unchanged through several CV cycles. In view of this we are currently involved in the extension of this concept to polymeric derivatives containing cyclophosphazene as the pendant group as well as where the polymer contains a P-N back bone.

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