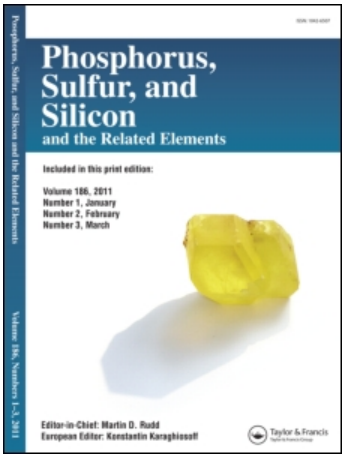

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REACTIONS OF FERROCENYL AMINES AND ALCOHOLS WITH HEXACHLOROCYCLOTRIPHOSPHAZENE

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The reactions of ferrocenyl methanol, ferrocenyl 2-propanol and N-methyl-2-ferrocenylmethylamine with chlorocyclophosphazenes have been examined. The pentachlorocyclotriphosphazene derivative of ferrocenylmethanol undergoes rapid decomposition via a phosphazene-phosphazane rearrangement, however when the alcohol function is β to the cyclopentadienyl ring modest yields of $N_3P_3Cl_5OCHMeCH_2C_5H_4FeCp$ may be obtained. By way of contrast N-methyl-2-ferrocenylmethylamine gives a broad range of stable derivatives, $N_3P_3Cl_{6-n}[NMeCH_2C_5H_4FeCp]_n$(n=1-3). The substitution process follows a predominantly trans non-geminal pathway. The corresponding reaction with the butylmethacrylate derivative, $N_3P_3Cl_5O(CH_2)_4OC(O)CMe{=}CH_2$ leads to the unexpected geminal product, 2,2′-$N_3P_3Cl_4[O(CH_2)_4OC(O)CMe{=}CH_2]NMeCH_2C_5H_4FeCp$. Polymers containing the 2-ferrocenylmethylamine function have been obtained by reactions of poly(dichlorophosphazene) with the ferrocenylamine and by radical addition polymerization of the aforementioned mixed ferrocenylamino butylmethacrylphosphazene. The new materials have been characterized by standard methologies including ^{31}P NMR spectroscopy, cyclic voltametry and gel permeation chromatography.

Keywords: cyclophosphazenes, polyphosphazenes, ferrocene derivatives, redox active phosphazenes, electrochemistry

INTRODUCTION

Over the years, chemists have prepared hundreds of cyclo- and polyphosphazenes derivatives. These reactions have either been direct substitution processes involving halo phosphazenes or

synthetic transformations of exocyclic groups attached to the phosphazene moiety.[1-5] In spite of the extraordinary number and diversity of these substituents, very few are, or have been exploited as, redox active units. Earlier work involved organic substituents which could be reduced to radical anions and examined by ESR spectroscopy.[6,7] More recently, organometallic substituents have been considered.[8] Certain of these have received detailed electrochemical characterization. The behavior of ferrocene units directly bonded to a phosphazene unit[9,10] or bound to the phosphazene through a saturated carbon center[11] has been the focus of substantive electrochemical studies. The addition of dicolbalt octacarbonyl to phenylacetylene units on fluorocyclophosphazenes gives organocolbalt cluster sutstituents which have been examined by electrochemical techniques as well as ESR studies on the one electron reduction product.[12] In most, if not all, of these investigations the explicit or implicit goal was explore interactions of the phosphazene center with exocyclic unpaired spin density. In this study we have chosen to electronically isolate the redox center from the phosphazene with the goal of developing electron transfer materials utilizing numerous redox centers operating at the same or similar potentials. The well characterized electrochemically and chemically reversible one electron oxidation of ferrocene makes it an excellent choice as the redox center. The extensive organic chemistry of ferrocene provides a variety of substituents with functional groups which allow for connecting the redox center to the phosphazene through electronically insulating units.

RESULTS AND DISCUSSION

Initial investigations focused on ferrocene derivatives with alcohols as substituents. The borohydride reduction of ferrocenylaldehyde leads to ferrocenyl methanol. The sodium salt of the alcohol reacts with $N_3P_3Cl_6$ (1) but the ^{31}P NMR spectrum shows the presence of an oxyphosphazene. We have previously demonstrated the phosphazene-phosphazane rearrangement occurs readily in cases where a developing carbocation α to the phosphorus-oxygen bond can be stabilized.[13] In the present circumstance the well known stabilization of a carbocation by interaction with the cyclopentadiene

unit in ferrocene[14] is apparently the driving force for the oxyphosphazane formation. We have tested this hypothesis by

$$N_3P_3Cl_6 + CpFeC_5H_4CH_2ONa \rightarrow [N_3P_3Cl_5OCH_2C_5H_5FeCp] \downarrow$$
$$N_3P_3Cl_5O^- + CpFeC_5H_4CH_2^+$$

moving the oxygen atom to a β-position relative to the cyclopentadiene ring. Thus lithioferrocene reacts with propylene oxide to give after work up ferrocenyl-2-propanol. The sodium salt of this alcohol when allowed to react with **1** gives moderate yields of the monosubstituted phosphazene, $N_3P_3Cl_5OCHMeCH_2C_5H_4FeCp$. The stability is still somewhat problematic since it is a secondary alcohol derivative and carbo cation stabilization will increase from primary to secondary to tertiary systems.

The difficulties encountered in the oxyanion derivatives, while not insurmountable, lead us to consider ferrocennyl amines as nucleophiles. A convenient synthesis involves the sequential treatment of ferrocennyl aldehyde with methylamine followed by cyanoborohydride reduction to give N-methylferrocennyl-2-methylamine (**2**). The reaction of **2** with **1** under mild conditions leads to a series of ferrocenyl-2-methylamine derivatives which are stable and well behaved. Yields range from good to modest as the degree of substitution increases. The monosubstituted derivative

$$N_3P_3Cl_6 + CpFeC_5H_4CH_2N(Me)H \rightarrow N_3P_3Cl_{6-n}[N(Me)CH_2C_5H_4FeCp]_n \quad n=1\text{-}3$$

exhibits an easily simulated AB_2 ^{31}P NMR spectrum. All three disubstituted (n=2) isomers are obtained. Separation of the geminal and non-geminal isomers can be effected. The geminal species is a minor component with the non-geminal mixture favoring the trans isomer as is typical in the reactions of secondary amines with **1**.[4] The trisubstituted mixture obtained in low yields, can be separated into geminal and trans- non-geminal fractions as identified by ^{31}P NMR spectroscopy. An unexpected result is obtained when the methacrylphosphazene, $N_3P_3Cl_5O(CH_2)_4OC(O)CMe=CH_2$ is allowed to react with **2**. The geminal derivative, 2,2'-$N_3P_3Cl_4[O(CH_2)_4OC(O)CMe=CH_2]N(Me)CH_2C_5H_4FeCp$ (**3**) is formed exclusively. There is a scarcity of information on the

reaction pathways followed in these mixed systems but given the non-geminal preference of both organooxy and secondary amino units the formation of the geminal isomer is surprising. One possibility to consider is hydrogen binding of the incoming amine to the carbonyl of the methacrylate as a driving force to attract **2** to the substituted phosphorus center.

In addition to chemical and NMR spectroscopic characterization, the $N_3P_3Cl_{6-n}[N(Me)CH_2C_5H_4FeCp]_n$ series was studied using electrochemical methods including cyclic and normal pulse voltametry. These data show the systems to exhibit chemically and electrochemically reversible one electron oxidations at each metal center. In cases of multiple substitution on the phosphazene, each ferrocene center is oxidized at the same potential but all centers are oxidized i.e. for the tris derivatives there are three one electron oxidations occuring at indistinguishable potentials. This demonstrates successfull formation of the desired electronically isolated,multiple redox centers on each phosphazene ring.

Polymers of two different types may be obtained which contain aminoferrocenylphosphazene centers. If **3** is allowed to undergo radical initiated olefin copolymerizaiton with methylmethacrylate, carbon chain (polyolefin) polymers with $N_3P_3Cl_5N(Me)CH_2C_5H_4FeCp$ substituents are obtained. The electrochemcial behavior of these systems is similar to the cyclic derivatives noted above. An alternative approach is to carry out ring opening polymerization on **1**, and allow the resulting poly(dichlorophosphazene), $(NPCl_2)_n$, to react with N-methyl-2-ferrocennylmethylamine. The remaining unreacted chlorine atoms are removed by reaction with sodium trifluoroethoxide to give $[NP(N(Me)CH_2C_5H_4FeCp)_x(OCH_2CF_3)_{2-x}]_n$. Carbon paste electrodes containing the ferrocenylphosphazene and glucose oxidaze were constructed. Cyclic voltametric scans using these electrodes in the absence of glucose show a low response but addition of glucose results in a strong electrochemical signal. This result demonstrates the potential for use of these polymers in glucose sensors. The corresponding experiments using the carbon chain polymers with phosphazene substituents noted above were not successful. This comparison indicates the importance of polymer backbone flexibility in the electron transport process.

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