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NEW ORGANOFUNCTIONAL CYCLOPHOSPHAZENE DERIVATIVES

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Abstract The rational design, synthesis and polymerization of the methacrylphosphazenes $N_3P_3Cl_5O(CHR)_x(CHR')_yOC(O)CMe=CH_2$ (x=y=1,2, R=R'=H; x=1, R=Me, y=1, R'=H; x=1, R=H, y=1, R'=Me) is reported. Another new type of alkenyloxy derivative is prepared from 5-nonbornene-2-methoxide and $N_3P_3Cl_5$. The preparation of spirocyclic derivatives with methacrylate or protected hydroxyl groups is reported. Various functionalized ferrocene derivatives of the cyclophosphazenes have been prepared with particular attention being paid to the synthesis and electrochemical characterization of the $N_3P_3Cl_{6-n}(NMeCH_2C_5H_4FeC_5H_5)_n$(n=1,2,3,4) series.

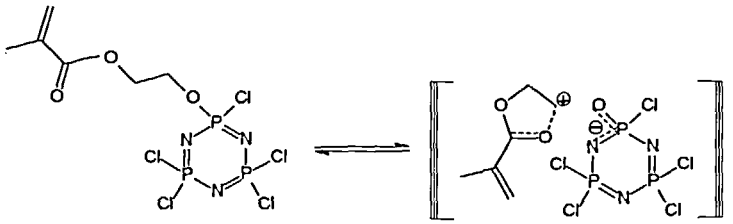
Key Words: cyclophosphazenes, organofunctional phosphazenes, exocyclic group polymerization, redox active phosphazenes

INTRODUCTION

The range of accessible synthetic transformations of polymeric and cyclic phosphazenes is significantly enhanced by the incorporation of substituents which can undergo further reactions. This expanded range of reactivity is directed towards property modification of poly(phosphazenes)[1], the formation of polymerizable cyclophosphazene monomers[2] or providing substituents suitable for classical step polymerization[3]. In this paper, we report a series of new cyclophophazenes with organofunctional substituents which can serve as sites for addition polymerization, step polymerization or redox behavior.

RESULTS AND DISCUSSION

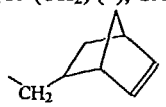
Previous work in our research group has focused on the synthesis of carbon chain polymers with cyclophosphazenes as substituents.[2] The polymerization and copolymerization of $N_3P_3Cl_5OCH_2CH_2OC(O)CMe=CH_2$ (**1**) was explored as an entry to the important acrylate polymer series.[4] While polymerization proceeded as expected, a phosphazene/phosphazane rearrangement was slowly occurring in the monomer. We have reported detailed study of the mechanism of this rearrangement.[5] The process proceeds through a transition state in which the developing carbocation is stabilized by interaction with the carbonyl group of the methacrylate. This model allows for the rational design of stable methacrylate monomers since an extension



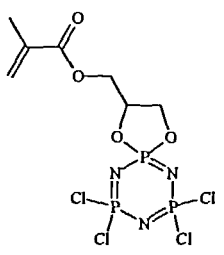
of the alkane chain length of the ester will produce species which are not prone to rearrangement due to the requirement of forming highly strained dioxo rings in the transition state. This proposal was verified by the synthesis of **2-5**. Very slow rearrangement occur for **2-4** and none

$$N_3P_3Cl_6 \quad + \quad ROH \quad \longrightarrow \quad N_3P_3Cl_5OR$$

R = R'OC(O)C(CH_3)=CH_2; R' = $(CH_2)_n$ [n = 2 (**1**), 3 (**2**), 4 (**5**)]
$CH_2CH(CH_2)$ (**3**), $CH(CH_3)CH_2$ (**4**)

R =  (**6**)

is noted for **5**. The new methacyrlate monomers undergo homopolymerization and copolymerization with methylmethacrylate. While the homopolymerization of **2** proceeds without detectable rearrangement of the monomer, continued heating of the polymers leads to some phosphazene/phosphazane tautomerization. Polymerization of **5** in the presence of 5% of the crosslinking agent CH_2=CMeC(O)O$(CH_2)_4$OC(O)CMe=CH_2 gives a soluble, high molecular weight product. Finally, the chlorine atoms in the **5**/methylmethacrylate copolymer may derivatized with sodium trifluoroethoxide. The reaction of 5-norbornene-2-methanol (endo/exo mixture) with $N_3P_3Cl_6$ produces the novel exocyclic olefin derivative **6** in very high yields. The remaining chlorine atoms do not undergo any further reaction with the norbornene-2-methanol



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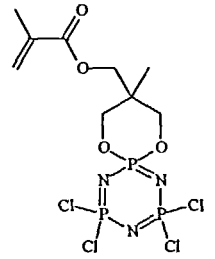

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even under forcing conditions. Exocyclic spirocyclic entities have the advantage of fixing the geometry and providing a more rigid ancor for the organofunctional unit. Both five (**7**) and six (**8**) membered spirocyclic units containing the methylmethacrylate unit have been prepared . The reaction of methylmethacrylate with solketal in the presence of titanium (IV) isopropoxide followed by acidification leads to **7** upon reaction with $N_3P_3Cl_6$. Treatment of tris(hydroxymethyl)ethane with dimethoxypropane followed by coupling with methacrylchloride and subsequent acidic work-up to remove the protecting group gives the diol which upon reaction with $N_3P_3Cl_6$ gives **8**. Homopolymerization and copolymerization with methylmethacrylate of **8** proceeds to give well behaved high molecular weight materials while **7** only gives ologiomers. The chlorine atoms in **8**/methylmethacrylate may be derivatized with sodium trifluoroethoxide. Spirocyclic materials have also been obtained from 1,3-diamino-2-hydroxy propane which has the hydroxyl group protected with a trimethylsiloxy moiey. The ^{31}P NMR of **9** exhibits a ABX pattern rather than the expected A_2X.

$$N_3P_3Cl_6 + NH_2CH_2CH(OSiMe_3)CH_2NH_2 \longrightarrow N_3P_3Cl_{6-2n}[NHCH_2C(OSiMe_3)CH_2NH]_n$$

n=1 (**9**), 2 (**10**)

The origin of the AB behavior at the $\equiv PCl_2$ centers is due to the disposition of H and $OSiMe_3$ centers at the 4 position of the spirocycle. The ^{31}P spectrum of **10** is even more complex due to the fact that stereoisomers based on the arrangements of spirocyclic groups relative to one another occur. Both **9** and **10** represent cyclophosphazenes with protected hydroxyl functions which are structurally constrained to avoid intramolecular reactions. The reaction of $NH_2CH_2CHOSiMe_3$ with $N_3P_3Cl_6$ gives the know spirocycle $N_3P_3Cl_4NHCH_2CH_2O$ demonstrating the viability of the intermolecular reaction possible when substituents are not locked in place.

Techniques for generation of phosphazene monomers and polymers with redox active substituents is also of interest. Our ultimate goal is the synthesis of polymeric materials which have electron transfer properties so we have focused on phosphazenes in which a ferrocene unit is separated from the phosphorus center by a saturated spacer group. The reactions of ferrocenyl methoxide and ferrocenyl 2-propoxide lead to the monosubstituted phosphazene[5]. The reactions of N-methyl-2-ferrocenylmethylamine with $N_3P_3Cl_6$ give rise to a series of stable well behaved ferrocenylamine derivatives.

$$N_3P_3Cl_6 + CpFeC_5H_4CH_2NHMe \rightharpoonup N_3P_3Cl_{6-n}(CpFeC_5H_4CH_2NMe)_n$$
$$n=1\text{-}4$$

The reaction followed a mixed geminal/non-geminal pathway which is solvent dependent. The trans isomer is the dominant non-geminal species. Cyclic voltametry studies show that each of the N-methyl-2-ferrocenylmethlamino derivatives undergoes a single reversible oxidation process indicating the electronic isolation from the phosphazene is sufficient so that all centers oxidize at a similar potential. An analogous poly(phosphazene) derivative containing the ferrocenylmethylamino and trifluoroethoxy derivative has been prepared and characterized.

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