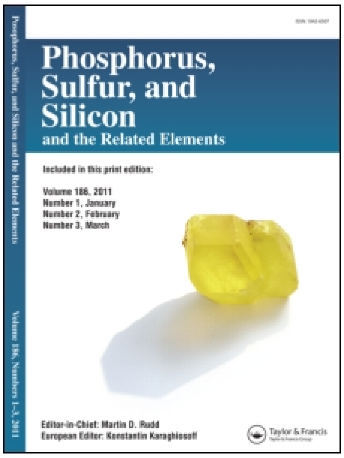

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Gem-Alkylhydroxyalkyltetrachlrocyclotriphospazenes: Synthesis, Structure and Application as Polymer Precursors

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gem-ALKYLHYDROXYALKYLTETRACHLOROCYCLOTRIPHOSPAZENES: SYNTHESIS, STRUCTURE AND APPLICATION AS POLYMER PRECURSORS

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Abstract *gem*-Alkylhydroxyalkyltetrachlorocyclotriphosphazenes $(NPCl_2)_2NPR^1C(OH)R^2R^3$ have been synthesized in high yields starting from $(NPCl_2)_3$. The application of these compounds as polymer precursors is discussed.

INTRODUCTION

Organic polymers bearing pendant chlorocyclophosphazene units gained considerable interest in the past few years.[1,2] These polymers exhibit flame retardant properties, combined with a low temperature crosslinking arising from HCl elimination.[3] They are also potential carrier materials for biologically active ligands, as the chlorine atoms of the inorganic moiety are still susceptible towards nucleophilic substitution.[4]

Preparation of these *hybrid organic-inorganic* polymers can be achieved by radical polymerization of vinyl substituted cyclophosphazenes. In order to avoid complications in the polymerization process the olefin has to be separated from the electron withdrawing phosphazene ring by an insulating group.

Suitable precursors are most advantageously prepared *via* chlorine replacement reactions on the readily available $(NPCl_2)_3$ 1. In general chlorine substitution reactions are non-specific, leading to complicated reaction mixtures, necessitating elaborate work-up procedures.

In our group we developed several procedures, leading to a *regio-selective* introduction of organic side groups onto chlorocyclophosphazenes.[5,6] One of the most versatile methods amongst these involves the nucleophilic addition of phosphazenocuprates $[(NPCl_2)_2NPR^1]_2CuMgX.n\text{-}Bu_3P$ (X= Cl, I) to aldehydes and ketones followed by acid hydrolysis, yielding gem-alkylhydroxyalkyl-tetrachlorocyclotriphosphazenes $(NPCl_2)_2NPR^1C(OH)R^2R^3$ **2**.

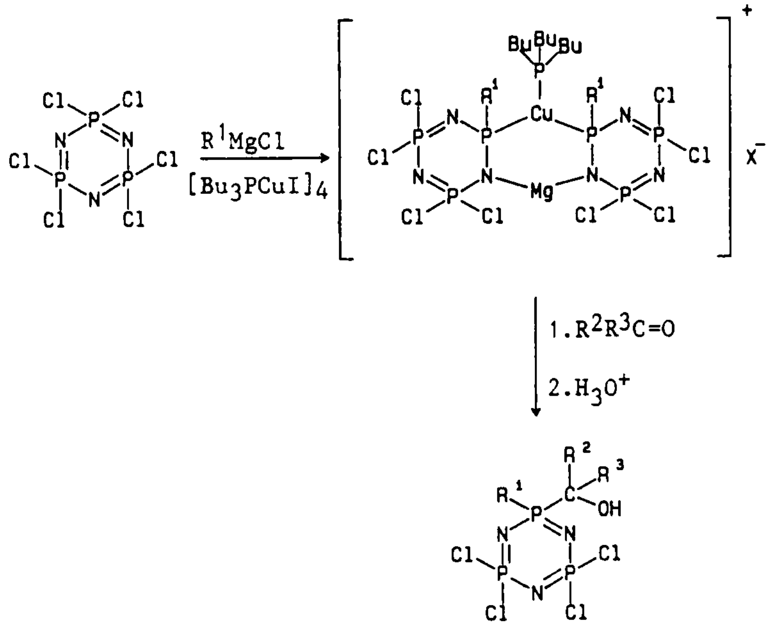
Here we describe the syntheses and structures of compounds **2** together with the application of some of these compounds in the preparation of polymers. In this preparation compounds **2** are used directly or after a subsequent derivatization, *i.e.* an esterification of the OH function by means of (meth)acryloylchloride.

RESULTS AND DISCUSSION

Synthesis and Structure

Compounds **2** are prepared according to Scheme 1. The phosphazenocuprate is formed after an initial metal-halogen exchange reaction, followed by a nucleophilic substitution at phosphorus.[7] Nucleophilic attack of the copper(I) coordinated phosphorus atom to the C=O bond leads to the formation of an alcoholate, which in his turn is hydrolyzed to products **2**.[5]

The reaction proves to be fairly general, only somewhat limited by steric factors. For instance, the reaction of $[(NPCl_2)_2NP\text{-}i\text{-}C_3H_7]_2CuMgX.n\text{-}Bu_3P$ with benzophenone ($R^2= R^3= C_6H_5$) does not result in any product formation.



$R^1 = CH_3$, $i\text{-}C_3H_7$, $t\text{-}C_4H_9$; $R^2 = H$, CH_3; $R^3 = H$, CH_3, C_2H_5, C_6H_5, $C_6H_4\text{-}o\text{-}NO_2$, $C_6H_4\text{-}o\text{-}OCH_3$, cyclic-$C_4H_3O$, $COOC_2H_5$, CH_2Cl, $CH{=}CHCH_3$, $C_6H_4\text{-}p\text{-}CH{=}CH_2$, $\eta^5\text{-}C_5H_4\text{-}Fe\text{-}\eta^5\text{-}C_5H_5$ and $R^2\text{-}R^3 = -(CH_2)_5-$

Scheme 1.

An X-Ray cystal structure determination[8] of the compound with $R^1 = i\text{-}C_3H_7$, $R^2 = H$ and $R^3 = \eta^5\text{-}C_5H_4\text{-}Fe\text{-}\eta^5\text{-}C_5H_5$ shows that both the ferrocenyl part and one of CH_3 groups of the $i\text{-}C_3H_7$ moiety are located over the nearly planar phosphazene ring. As can be expected, the largest P-N bond distances are found adjacent to the organosubstituted phosphorus atom.

Polymerization

When $[(NPCl_2)_2NP\text{-}i\text{-}C_3H_7]_2CuMgX.n\text{-}Bu_3P$ is reacted with *p*-formylstyrene, $(NPCl_2)_2NP\text{-}i\text{-}C_3H_7C(OH)HC_6H_4\text{-}p\text{-}CH{=}CH_2$ **2b** can be isolated in a high yield. Homopolymerization of this compound in the presence of AIBN yields a polymer soluble in THF. When the polymerization is carried out in 1:1 feed ratio with styrene, a linear copolymer is obtained with 25% incorporation of the phosphazene containing monomer.

Esterification of $(NPCl_2)_2NP\text{-}i\text{-}C_3H_7C(OH)HCH_3$ **2c** with methacryloyl- and acrylolylchloride in the presence of $(C_2H_5)_3N$ yields the corresponding methacrylate and acrylate esters in high yields (>70%). These monomers can be converted under radical conditions to linear polymers. Till now the kinetics of the polymerization process are not completely understood. Treatment of **2c** with sodiumphenoxide gives $[NP(OPh)_2]_2NP\text{-}i\text{-}C_3H_7C(OH)HCH_3$ **3** in an almost quantitative yield. Preliminary results prove **3** to be an excellent precursor in polymerization experiments.

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