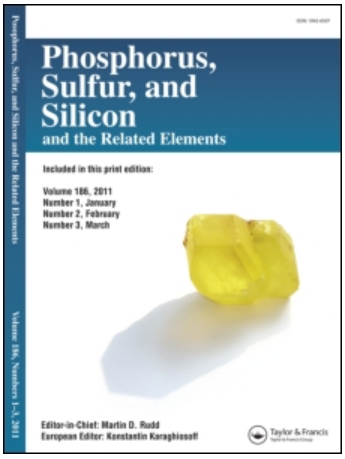

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Synthesis, Structure, and Complex Formation of Phosphazenes with Pyridine Side Groups

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SYNTHESIS, STRUCTURE, AND COMPLEX FORMATION OF PHOSPHAZENES WITH PYRIDINE SIDE GROUPS

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Abstract Aminoalkylpyridine-substituted cyclo- and polyphosphazenes were synthesized as a new type of N-donor ligands for transition metal complexes.

INTRODUCTION

Polymers that form metal complexes through N-donor side groups find a growing interest due to the wide range of possible applications for those materials.[1,2]

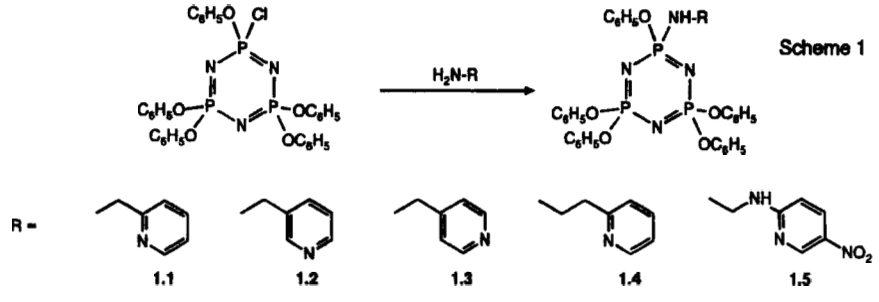
Organic polymers, for example, the poly(vinylpyridine) are well investigated. Polyphosphazenes with pendent pyridine side groups which should offer wider opportunities for property modification have not been synthesized previously, mainly because halogenated phosphazenes are known to form adducts or to decompose in the presence of pyridine.[3,4]

We describe here a synthetic route to pyridine-substituted cyclo- and polyphosphazenes as a new class of N-donor ligands.

RESULTS AND DISCUSSION

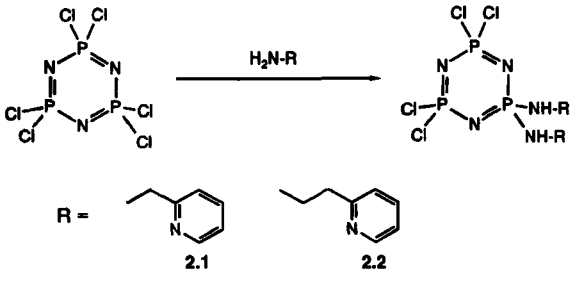
The phosphazene PN-system can be protected against pyridine induced adduct formation or degradation by the presence of electron withdrawing cosubstitutents.

1.1-1.5 were obtained from reactions of monochloropentaphenoxycyclotriphosphazene, $N_3P_3(OC_6H_5)_5Cl$, with aminoalkylpyridine derivatives (Scheme 1).

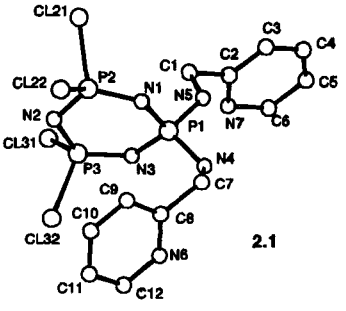


Scheme 1

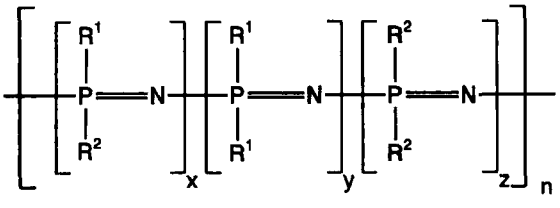
Depending on the reaction conditions, the geminal disubstituted cyclotriphosphazenes **2.1** and **2.2** are accessible directly from hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, and the functionalized pyridine (Scheme 2).



Scheme 2



The mixed-substituent copolymers **3.1-3.3**, **3.5-3.7**, and **3.9-3.11** were obtained in a two-step reaction of poly(dichlorophosphazene), $[NPCl_2]_n$, with sodium trifluorethoxide or -phenoxide and the aminoalkylpyridine. Partial chain cleavage occurs when $[NPCl_2]_n$ is exposed directly to the pyridine to yield the lower molecular weight homopolymers **3.4**, **3.8**, **3.12**.



	3.1	3.2	3.3	3.4
R^1 OC_6H_5	75 %	50 %	25 %	0.0 %
R^2 NH-(2-pyridyl)	25 %	50 %	75 %	100 %
	3.5	**3.6**	**3.7**	**3.8**
R^2 NH-(3-pyridyl)	25 %	50 %	75 %	100 %
	3.9	**3.10**	**3.11**	**3.12**
R^1 OCH_2CF_3	75 %	50 %	25 %	0.0 %
R^2 NH-(CH2)2-(2-pyridyl)	25 %	50 %	75 %	100 %

1.1-1.3 react with transition metal salts to form complexes of the general type $[N_3P_3(OC_6H_5)_5(NHCH_2C_5H_4N)]_{1 \text{ or } 2} * MX_2$ with M=Cu, Ni, Co, Pd and X=Cl, NO_3.

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