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PENNSYLVANIA STATE UNIV UNIVERSITY PARK DEPT OF CHEMISTRY F/6 11/9
THE SYNTHESIS AND STRUCTURE OF POLYPHOSPHAZENES.(U)
FEB 82 H R ALLCOCK

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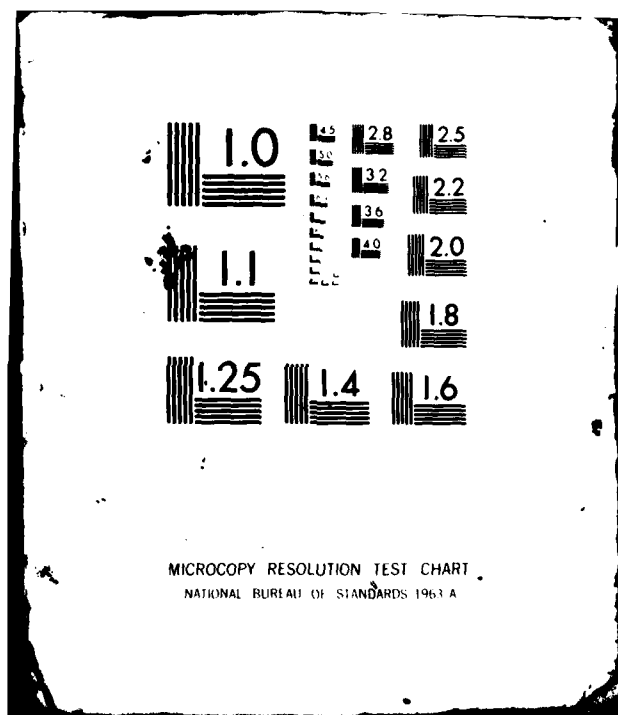
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Polymers, phosphazenes, polyphosphazenes, metallo-phosphazenes, synthesis, structure determination.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) New synthetic methods have been developed for the preparation of polyphosphazenes that contain transition metals as part of the side group structure. Short chain phosphazenes have also been investigated as models for the high polymers.		

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FINAL TECHNICAL REPORT
to the U.S. Army Research Office
on

Grant Number DAAG29-78-G-0190

Completed on November 9, 1981

Harry R. Allcock
Department of Chemistry
The Pennsylvania State University

82 03 03 126

Final Report

The Synthesis and Structure of Polyphosphazenes

September 1, 1978 - November 9, 1981

A. Summary of Research Progress

Our objectives were to synthesize new high polymers based on a backbone of phosphorus-nitrogen repeating units, and to understand the relationship between structure and properties in order to design polymers that may be of practical value. Four areas have been explored. Three of these involve the development of synthetic methods for the preparation of polyphosphazenes that bear transition metals in the side group structure.

We have synthesized the first cyclophosphazenes that bear metals as major components of the side group structure, linked to the skeleton by phosphorus-metal bonds. These species contain units of the type $-N=P(Fe_2Cp_2(CO_3))-$ in which Fe-Fe bonds are also present. The analogous di-ruthenium and iron-ruthenium analogues have also been isolated. These compounds are models for a broad range of high polymers that could have unusual catalytic or electrical properties.

A second method of metal binding is via aryloxyphosphazenes that bear pendent phosphine groups attached to the side groups. These polymers serve as carriers for iron, rhodium, or osmium organometallic species. They function as polymer-bound catalysts.

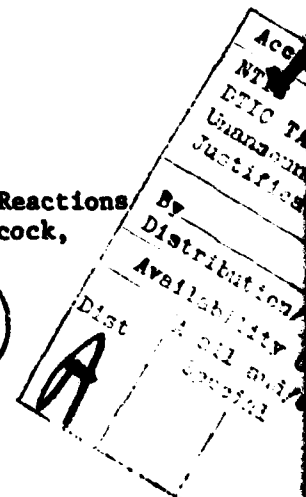
Third, phosphazenes with pendent propynyl groups form π -complexes with cobalt carbonyl species. These complexes are also of interest as catalysts. All three of the metallophosphazenes studies show promise as metallo-polymer surface coatings.

Finally, we have attempted to understand the underlying connection between the properties of phosphazenes and their molecular structure by the synthesis of a number of linear short-chain phosphazenes. These mimic the reactivity of the high polymers and also are amenable to x-ray diffraction studies that are difficult or impossible to carry out with the high polymers.

B. List of Publications

1. Primary Publications

Preparation of $[NP(OC_6H_4Li)_2]_3$ by Metal-Halogen Exchange and its Reactions with Electrophiles. T. L. Evans, T. J. Fuller, and H. R. Allcock, J. Am. Chem. Soc., 1979, 101, 242.



A Spirocyclophosphazene with Iron-Phosphorus Bonds and a P-Fe-Fe Three-Membered Ring. P. P. Greigiger and H. R. Allcock, J. Am. Chem. Soc., 1979, 101, 2492.

Crystalline Transitions and Related Physical Properties of Poly(dichlorophosphazene). H. R. Allcock and R. A. Arcus, Macromolecules, 1979, 12, 1130.

X-Ray Diffraction Analysis of the Structure of Poly(dichlorophosphazene). H. R. Allcock, R. A. Arcus, and E. G. Stroh, Macromolecules, 1980, 13, 919.

Synthesis and Molecular Structure of Two Cyclophosphazenes with Phosphorus-Iron Bonds. H. R. Allcock, P. P. Greigiger, L. J. Wagner, and M. Y. Bernheim, Inorg. Chem., 1981, 20, 716.

2. Book and Review Articles

Contemporary Polymer Chemistry. H. R. Allcock and F. W. Lampe, Prentice-Hall, 1981.

High Polymeric Organophosphazenes - Macromolecules with a Difference. H. R. Allcock, Contemp. Topics Polymer Sci., 1979, 3, 55.

Small Molecule Rings as Models for High Polymeric Chains. H. R. Allcock, Accounts Chem. Res., 1979, 12, 351.

Polymerization of Cyclic Phosphazenes. H. R. Allcock, Polymer, 1980, 21, 673.

Polyphosphazenes and the Inorganic Approach to Polymer Chemistry. H. R. Allcock, Science Progress, 1980, 66, 355.

Controlled Synthesis of Organic-Inorganic Polymers that Possess a Backbone of Phosphorus and Nitrogen Atoms. H. R. Allcock, Makromol. Chem., 1981, Suppl. 4, 3.

Phosphazene Rings and High Polymers Linked to Transition Metals or Biologically Active Organic Species. H. R. Allcock, ACS Symposium Series, 1981, 171, 311.

C. List of Reports Submitted (period covered)

January 1, 1979 - June 30, 1979
July 1, 1979 - December 31, 1979
January 1, 1980 - June 30, 1980
July 1, 1980 - December 31, 1980
January 1, 1981 - June 30, 1981

D. List of Personnel

H. R. Allcock (Principal Investigator)
M. Y. Bernheim (Postdoctoral Crystallographer)
G. H. Riding (Postdoctoral Fellow)
R. A. Arcus (Graduate Fellow) Ph.D. degree awarded.
T. J. Fuller " "
P. P. Greigger " "
T. L. Evans " "
W. T. Ferrar " "
L. J. Wagner " "
P. R. Suszko " "
N. M. Tollefson " "
M. S. Connolly " "
K. D. Lavin " "
J. L. Desorcie " "
R. A. Nissan " "

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