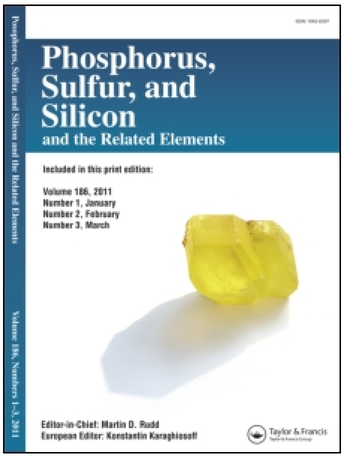

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Reactions of Organometallic Reagents with Halogenophosphazene Cyclic Trimers, Tetramers, and High Polymers

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To cite this Article Allcock, H. R.(1983) 'Reactions of Organometallic Reagents with Halogenophosphazene Cyclic Trimers, Tetramers, and High Polymers', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 267 — 270
To link to this Article: DOI: 10.1080/03086648308076017
URL: http://dx.doi.org/10.1080/03086648308076017

Phosphorus and Sulfur, 1983, Vol. 18 pp. 267-270
0308-664X/83/1801-0267/$18.50/0

Printed in the United States of America

REACTIONS OF ORGANOMETALLIC REAGENTS WITH HALOGENOPHOSPHAZENE CYCLIC TRIMERS, TETRAMERS, AND HIGH POLYMERS

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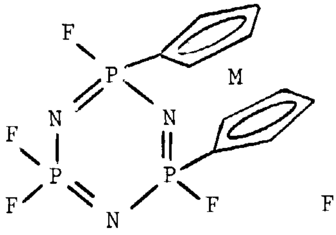
Abstract Three main mechanistic pathways are now evident when Grignard, organolithium, organocopper, or transition metal anions are used as reagents for reactions with halogenophosphazenes-substitution, metal-halogen exchange, and skeletal cleavage. Use of these reaction pathways allows the synthesis of species such as I-X. A general mechanistic theory of these reactions is presented, together with an application of these mechanisms to macromolecular synthesis.

Since the work of Rosset in 1925 and Bode in 1942,[1,2] the reactions of organometallic reagents with halogenophosphazenes have generated deep interest[3-7] coupled with controversy. Seemingly similar reactions give rise to quite different types of products. We have attempted to develop a general mechanistic understanding of these complex interactions and to explain many of the earlier anomalies. Moreover, our ability to understand these processes has facilitated the syntheses of several new classes of phosphazenes, including those that contain transition metal organometallic units. Some of the results may be applicable to phosphorus halide chemistry in general. All the conclusions are relevant to the synthesis of phosphazene high polymers.

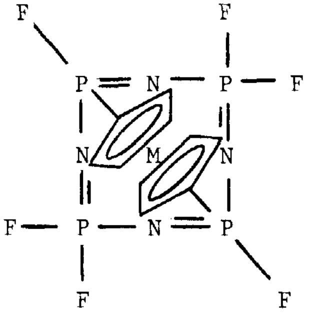
In the present work we have attempted to compare the interactions of fluoro- and chlorophosphazenes with Grignard, organolithium, and organocopper reagents, as well as a number of transition metal organometallic anions. Typical reagents used in these studies include: RMgX where R = CH_3, C_2H_5, $\underline{n}$-C_3H_7, $\underline{n}$-C_4H_9, $\underline{i}$-C_3H_7, $\underline{t}$-C_4H_9, C_6H_5; RMgX/$[Bu_3PCuI]_4$ where R = CH_3, C_2H_5, $\underline{n}$-C_3H_7, $\underline{n}$-C_4H_9, $\underline{i}$-C_4H_9, $\underline{t}$-C_4H_9, allyl; RLi where R = CH_3, $\underline{n}$-C_4H_9, C_6H_5, $C_2B_{10}H_{10}C_6H_5$, $C_2B_{10}H_{10}CH_3$, $CH_2C_2B_{10}H_{10}CH_3$, $C_5H_4FeC_5H_5$, $C_5H_4RuC_5H_5$; LiRLi where R = $(C_5H_4)_2Fe$, $(C_5H_4)_2Ru$; RMK where RM = $Fe(CO)_2C_5H_5$, $Ru(CO)_2C_5H_5$; RM_2Na_2 where RM_2 = $Fe_2(CO)_8$.

The reactions induced by these reagents include halogen replacement (substitution), metal-halogen exchange, and P-N skeletal bond cleavage. In some cases, all three reactions can be detected in the same system. Each of these reaction types will be considered in turn.

Substitution Reactions Substitution appears to predominate when (NPF$_2$)$_3$ or (NPF$_2$)$_4$ react with phenyllithium, lithioferrocene,[8] lithioruthenocene,[8] dilithioferrocene,[8] dilithioruthenocene,[8] or transition metal anions.[9,10] Some new derivatives prepared by this method are depicted in I-III.



I



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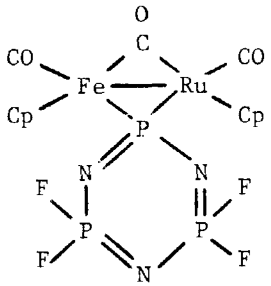
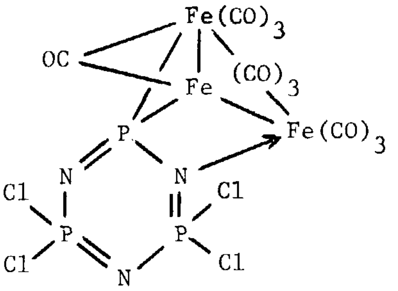
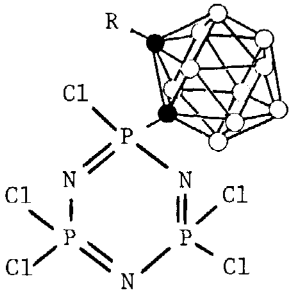


III



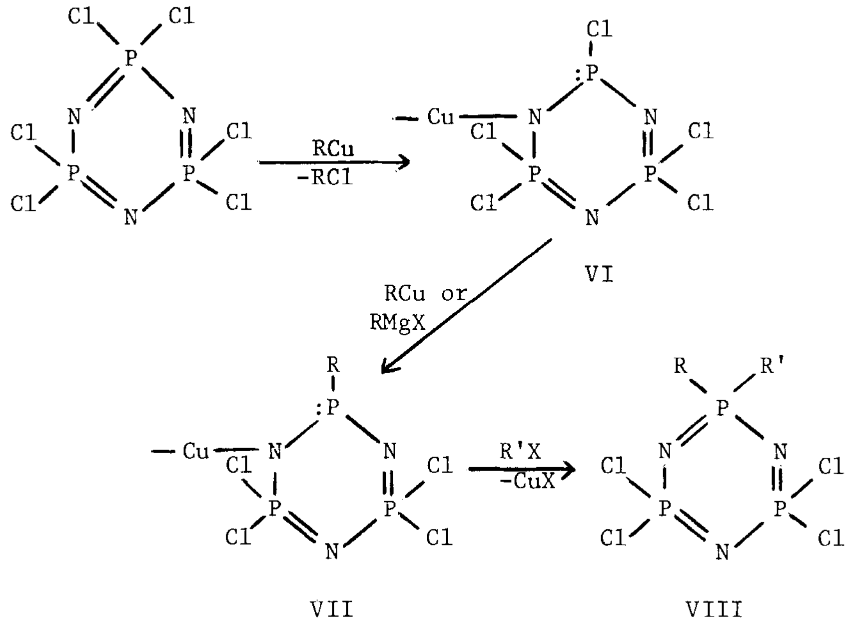
IV



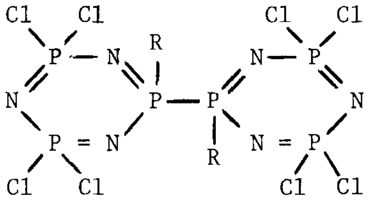
V

In addition, transition metal organometallic dianions, such as Fe$_2$(CO)$_8^{2-}$, react with (NPCl$_2$)$_3$ to yield IV.[11] Substitution without serious side reactions also occurs when (NPCl$_2$)$_3$ reacts with carboranyl-lithium reagents to give, for example, V.[12] Organocopper reagents interact with (NPCl$_2$)$_3$ by a curiously complex pattern that yields products that superficially appear to result from substitution, but which, in reality, are formed by initial metal-halogen exchange followed by substitution.[13]

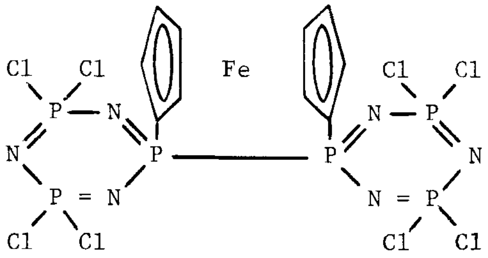
Metal-Halogen Exchange Chlorophosphazenes are especially prone to metal-halogen exchange reactions in the presence of organocopper species or lithiometallocenes. For example, (NPCl$_2$)$_3$ reacts with RMgX[Bu$_3$PCuI]$_4$ to form species VI-VIII.[13,14]



However, the formation of cyclophosphazene dimers of type IX or X provides the most direct evidence for metal-halogen exchange. This process occurs when Grignard reagents or lithiometallocenes react with $(NPCl_2)_3$.[8,15]



IX



X

Skeletal Cleavage The problem of P-N skeletal bond cleavage by organometallic reagents is especially acute for the reactions of the high polymers, $(NPCl_2)_n$ or $(NPF_2)_n$. If 15,000 repeating units are present in each polymer molecule initially, $\simeq$ 25 cleavage reactions per chain would be sufficient to destroy all the useful macromolecular properties. Hence, the ratio of halogen replacement to cleavage must be higher than, say, 600:1 if the substitution is to be employed for the synthesis of alkyl- or arylphosphazene high polymers. Thus, polymers are extremely sensitive probes for cleavage processes that might go unnoticed in the reactions of cyclic trimers or tetramers.

Skeletal cleavage appears to be favored by the presence of P-Cl rather than P-F side group bonds. For example, phenyllithium reacts with $(NPCl_2)_n$ by a slow substitution process and a predominating fast chain cleavage.[4] By the time that 10% of the chlorine atoms have been replaced by phenyl, the molecular weight has fallen from 4×10^6 to 5×10^4. By contrast, with $(NPF_2)_n$, substitution predominates until ≃ 75% of the fluorine atoms have been replaced by phenyl, at which point skeletal cleavage again becomes serious.[7] Presumably, electron-withdrawal by the fluorine atoms lowers the basicity of skeletal nitrogen, thus reducing the ability of that site to coordinate to Li^+. As more and more fluorine atoms are replaced by phenyl, this protective effect is lost. Butyllithium is a far more potent chain cleavage reagent because of the strong electron supply from C_4H_9-P to nitrogen.

The actual pattern of reactions between organometallic reagents and halophosphazenes depends on the type of halogen involved, on the organometallic species, and on other factors such as solvent and reaction temperature.

Acknowledgments It is a pleasure to acknowledge the contributions of my coworkers, G. H. Riding, P. J. Harris, K. D. Lavin, L. J. Wagner, P. R. Suszko, M. S. Connolly, T. L. Evans, J. L. Desorcie, and R. R. Whittle. We thank the U.S. Army Research Office and Office of Naval Research for the support of this work.

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