AD-A061 690   PENNSYLVANIA STATE UNIV UNIVERSITY PARK DEPT OF CHEMISTRY F/G 7/3
THE PREPARATION OF (NP(P-OC6H4LI)2)3 BY METAL -HALOGEN EXCHANGE--ETC(U)
NOV 78 T L EVANS, T J FULLER, H R ALLCOCK   N00014-75-C-0685

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LEVEL

(12)

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER (14) TR-5
2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle) (6) THE PREPARATION OF $[NP(p\text{-}OC_6H_4Li)_2]_3$ BY METAL-HALOGEN EXCHANGE, AND ITS REACTIONS WITH ELECTROPHILES.

5. TYPE OF REPORT & PERIOD COVERED (9) Interim Technical Report.
6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s) (10) T. L. Evans, T. J. Fuller, and H. R. Allcock
8. CONTRACT OR GRANT NUMBER(s) (15) N00014-75-C-0685

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Department of Chemistry, The Pennsylvania State University, University Park, Pa. 16802

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
NR 356-577

11. CONTROLLING OFFICE NAME AND ADDRESS
Department of the Navy
Office of Naval Research, Arlington, Va. 22217

(11) 13

12. REPORT DATE November 13, 1978
13. NUMBER OF PAGES 3

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

(12) 5p.

15. SECURITY CLASS. (of this report) Unclassified
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Distribution unlimited; approved for publication

DDC
NOV 30 1978
F

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Accepted for publication in the Journal of the American Chemical Society

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Parabromophenoxyphosphazenes, cyclic phosphazene, hexa(p-bromophenoxy)-cyclotriphosphazene, hexalithio, reactions of hexalithio with electrophiles, metal complexes.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The first example of a successful metal-halogen exchange reaction between n-butyllithium and a hexa(p-halogenophenoxy)cyclotriphosphazene is described. The hexalithio derivative was allowed to react with electrophiles to yield carboxylic acid, stannane, and phosphine-derivatives.

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S/N 0102-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

78 11 27 051

400 343

Office of Naval Research

Contract No. N00014-75-C-0685

Project No. NR 356-577

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by

T. L. Evans, T. J. Fuller, and H. R. Allcock

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Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

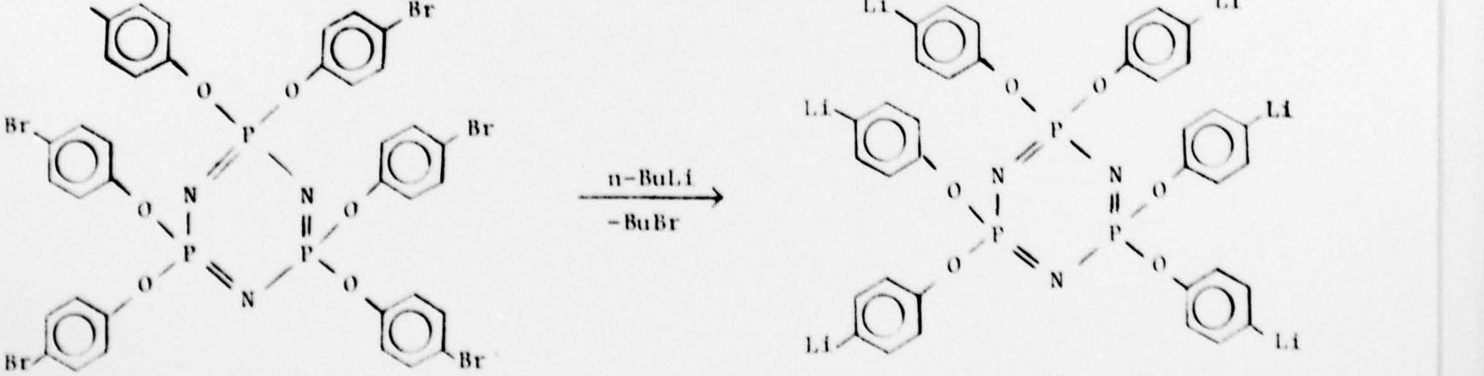
November 13, 1978

The Preparation of $[NP(p\text{-}OC_6H_4Li)_2]_3$ by Metal-Halogen Exchange, and Its Reactions with Electrophiles

Sir:

The reactions of cyclic and polymeric *halo*phosphazenes with organolithium reagents have been studied extensively,[1,2,3] but the reactions of organometallic reagents with cyclic and polymeric *organo*-functional phosphazenes have not been explored in detail. Of particular interest to us were reactions that could yield carbanionic species bound directly to phosphazene cyclic and polymeric compounds. Such reactive intermediates could be used to synthesize a wide range of new cyclic and high polymeric phosphazenes not accessible by other synthetic routes, including those that might form unusual ligands for transition metals.

We have found that hexa(*p*-bromophenoxy)cyclotriphosphazene, (I), undergoes a high yield metal-halogen exchange reaction with *n*-butyllithium to yield the hexalithio derivative, (II). The reaction conditions employed involved a rapid addition of *n*-butyllithium (1.6 M in hexane) in a 15% excess to a tetrahydrofuran solution of (I) at -40°C.



I

II

The presence of (II) was confirmed by its reactions at -40°C with electrophiles, such as deuterium oxide, carbon dioxide, chlorodiphenylphosphine and triphenyltin chloride to yield the following derivatives: $[NP((\underline{p}\text{-}OC_6H_4D)_2]_3$, (III); $[NP(\underline{p}\text{-}OC_6H_4COOH)_2]_3$, (IV); $[NP(\underline{p}\text{-}OC_6H_4P(C_6H_5)_2)_2]_3$, (V); and $[NP(\underline{p}\text{-}OC_6H_4Sn(C_6H_5)_3)_2]_3$, (VI). All of these compounds were identified by ^{31}P nmr spectra, infrared spectra, and chemical analysis. The position of lithium incorporation on the aromatic ring was confirmed by the ^{13}C nmr spectrum of compound (III) which revealed both the presence of a triplet structure and a decrease in the resonance signal for the carbon at the para position of the aromatic unit when compared with the ^{13}C nmr spectrum of $[NP(OC_6H_5)_2]_3$.[4] The absence of significant skeletal cleavage during metallation is a considerable advantage for the use of such processes in phosphazene high polymer syntheses.

The binding of metal complexes to phosphazene compounds is of structural, catalytic, and potential biomedical importance.[5,6] This reaction system possesses a capacity for the binding of metals both through reactions of (II) with metal halides, as demonstrated by the synthesis of compound (VI), and through the reactions of compound (V) with metal complexes. In order to illustrate this second reaction pathway, (V) was allowed to react with $H_2Os_3(CO)_{10}$, (VII), a compound which has been demonstrated previously to react with tertiary phosphines to yield mono-substituted phosphine osmium cluster compounds, $H_2Os_3(CO)_{10}(PR_3)$.[7] The high reactivity of this osmium cluster (VII) was ascribed to a metal-metal double bond.[8] When compound (V) was allowed to react with a deficiency of (VII) at 25°C in methylene chloride solvent, the expected color change from violet to yellow was observed. Furthermore, infrared spectral comparisons of the carbonyl stretching regions for the osmium complex derived from triphenylphosphine and that derived from (V) confirmed the existence of metal binding through the phosphine residues of (V) rather than through the skeletal nitrogen atoms.

Experiments are now underway in our laboratory to extend these small molecule cyclic model reactions to high polymeric phosphazenes.

Acknowledgment. This work was supported by grants from the Office of Naval Research and the Army Research Office.

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T. L. Evans, T. J. Fuller, and H. R. Allcock*
Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

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