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SMALL-MOLECULE CYCLIC MODELS FOR THE SYNTHESIS OF NEW POLYPHOSP--ETC(U)
NOV 79 H R ALLCOCK , T L EVANS , T J FULLER N00014-75-C-0685

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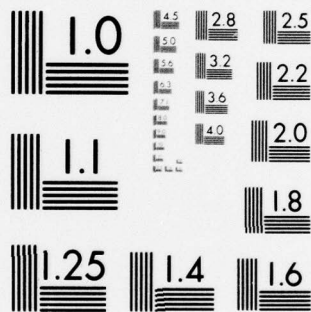
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SMALL-MOLECULE CYCLIC MODELS FOR THE SYNTHESIS OF
NEW POLYPHOSPHAZENES: SIDE GROUP CONSTRUCTION VIA
LITHIOPHENOXY DERIVATIVES

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Small-Molecule Cyclic Models for the Synthesis of New Polyphosphazenes:
Side Group Construction Via Lithiophenoxy Derivatives

H. R. ALLCOCK,* T. L. EVANS, and T. J. FULLER

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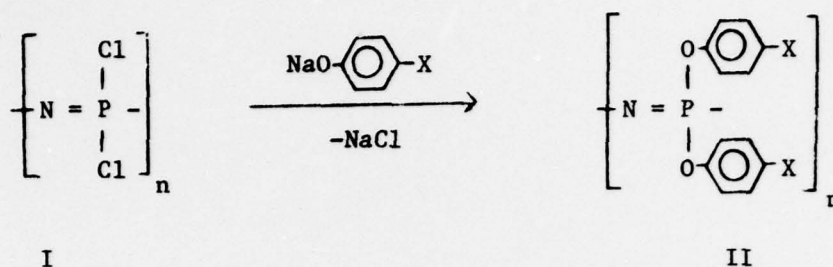
Hexa(p-lithiophenoxy)cyclotriphosphazene, $[\text{NP}(\text{OC}_6\text{H}_4\text{Li-p})_2]_3$ (IV) has been synthesized as an intermediate for the covalent attachment of metallo-, phosphino, carboxylato, alkyl, or tertiary alcohol units to the side group structure. These reactions are models for the preparation of the corresponding phosphazene high polymers. Intermediate IV was prepared by the metal-halogen exchange reaction between $[\text{NP}(\text{OC}_6\text{H}_4\text{Br-p})_2]_3$ (III) or $[\text{NP}(\text{OC}_6\text{H}_4\text{I-p})_2]_3$ and *n*-butyllithium in tetrahydrofuran at -40°C to -60°C . The subsequent interaction of IV with deuterium oxide, diphenylchlorophosphine, carbon dioxide, butyl bromide, benzophenone, triphenyltin chloride, or triphenylphosphinegold (I) chloride yielded the para-substituted derivatives, $[\text{NP}(\text{OC}_6\text{H}_4\text{D})_2]_3$ (VII), $[\text{NP}(\text{OC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2)_2]_3$ (VIII), $[\text{NP}(\text{OC}_6\text{H}_4\text{COOH})_2]_3$ (IX), $[\text{NP}(\text{OC}_6\text{H}_4\text{C}_4\text{H}_9)_2]_3$ (X), $[\text{NP}(\text{OC}_6\text{H}_4\text{C}(\text{OH})(\text{C}_6\text{H}_5)_2)_2]_3$ (XI), $[\text{NP}(\text{OC}_6\text{H}_4\text{Sn}(\text{C}_6\text{H}_5)_3)_2]_3$ (XII), and $[\text{NP}(\text{OC}_6\text{H}_4\text{AuP}(\text{C}_6\text{H}_5)_3)_2]_3$ (XIII), respectively. Compounds VII-XIII cannot be obtained readily by other synthetic routes. For example, the reaction of III with $\text{NaP}(\text{C}_6\text{H}_5)_2$ is a less efficient route to the preparation of VIII. Compound VIII is a model coordination carrier species for transition metal catalysts. The possible extension of these reactions to linear phosphazene high polymers is discussed.

Introduction

Considerable interest exists in the synthesis of new macromolecules that can function as carrier molecules for transition metal catalysts, chemotherapeutic agents, or polyelectrolyte functions. Relatively few conventional organic polymers can be used in this way. However, one group of inorganic backbone polymers, the poly(organophosphazenes), can be modified structurally to a more subtle degree than most conventional macromolecules. Many high molecular weight linear polyphosphazenes are already known,¹⁻³ but few of these possess substituent groups that permit the binding of metals or biologically active organic residues, and none has been prepared that bears carboxylic acid units.

In this paper we explore the prospect that side group modification reactions might be used to introduce the desired functionality into a preformed organophosphazene. Because the reactions of high polymers are nearly always more complex than those of the related small molecules, it was necessary to explore first the side group modification reactions of small-molecule cyclic organophosphazenes. These species are models for the linear high polymers.⁴ Aryloxy-cyclophosphazenes were chosen for this purpose because of the ease of attachment of aryloxy groups to a phosphazene skeleton⁵ and the known stability of aryloxy-cyclo- and polyphosphazenes.

The most obvious route to the synthesis of functionalized organophosphazenes is one that involves the reaction of a halogenophosphazene with a difunctional reagent, as shown in the conversion of I to II.



(n = 3, 4, or $\approx 15,000$)

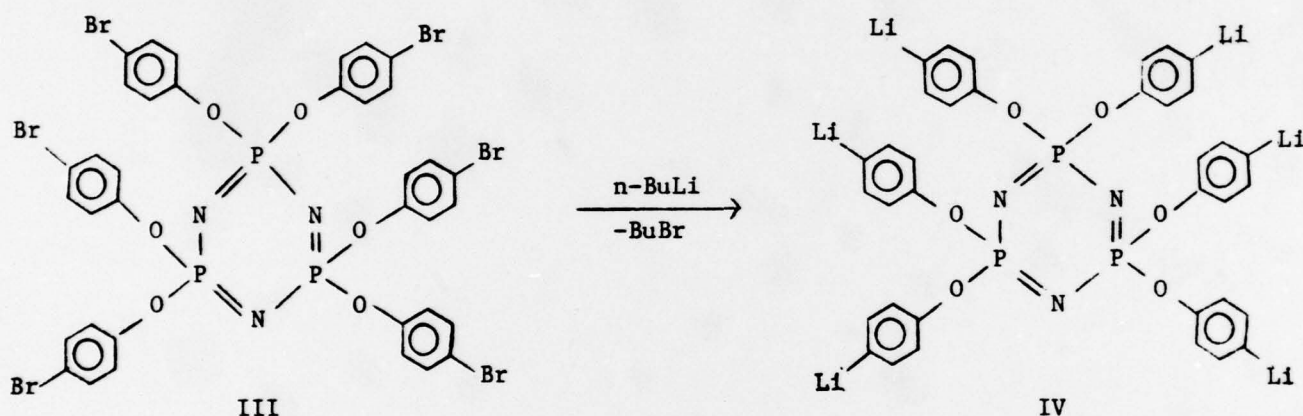
However, if the functional group, X, is itself a reactive unit such as OH, COOH, NHR, etc., it will react with the P-Cl bonds of another molecule to generate a crosslinked structure.⁶ This is an unacceptable possibility, especially in a high polymeric system.⁷

Thus, the approach taken in this present work has been to prepare species of type II in which the group X is unreactive during the conversion of I to II but is, nevertheless, capable of reaction with an active reagent in a later phase of the synthetic sequence. This can be accomplished when X is bromine or iodine. In this paper we describe the replacement of bromine in III by lithium⁸ with the use of *n*-butyllithium at low temperatures. We also discuss the subsequent utilization of the lithio-derivative as a reactive intermediate for the introduction of a diverse range of substituents.⁹

Four questions were of interest. First, can the metal-halogen exchange be carried out with species of type III without cleavage of the phosphorus nitrogen skeleton and, if so, what are the most effective reaction conditions? Second, how reactive are lithioaryloxyphosphazenes to different electrophiles? Third, what are the properties of the products formed by the interaction of the lithio-derivative with electrophiles? And, fourth, what are the prospects that these interactions can be extended to the synthesis of the analogous high molecular weight polymers?

Results and Discussion

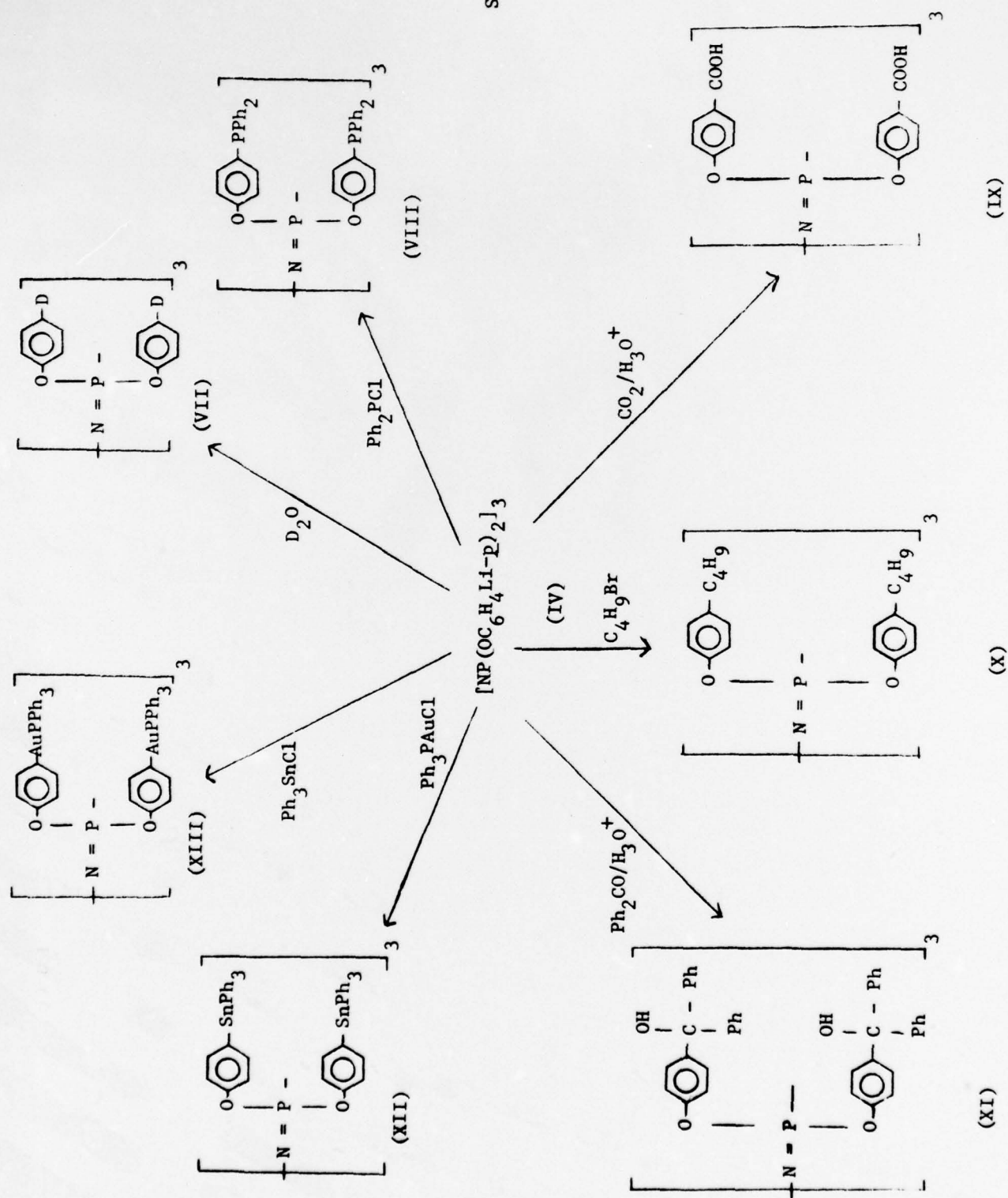
Synthesis and Reactions of $[\text{NP}(\text{OC}_6\text{H}_4\text{Li-p})_2]_3$ (IV) (General Aspects). Hexa-(p-lithiophenoxy)cyclotriphosphazene (IV) was prepared by the treatment of hexa-(p-bromophenoxy)cyclotriphosphazene (III) with a 1-molar excess of *n*-butyllithium at -60°C . Species IV was then allowed to react with a variety of reagents, as shown in Scheme 1.



The treatment of IV with deuterium oxide yielded $[\text{NP}(\text{OC}_6\text{H}_4\text{D-p})_2]_3$ (VII). This compound was identified by mass spectrometry, by elemental microanalysis, and by ^{13}C NMR analysis (see Experimental section). The formation of VII was considered to be good evidence for the existence of IV as a reactive intermediate.

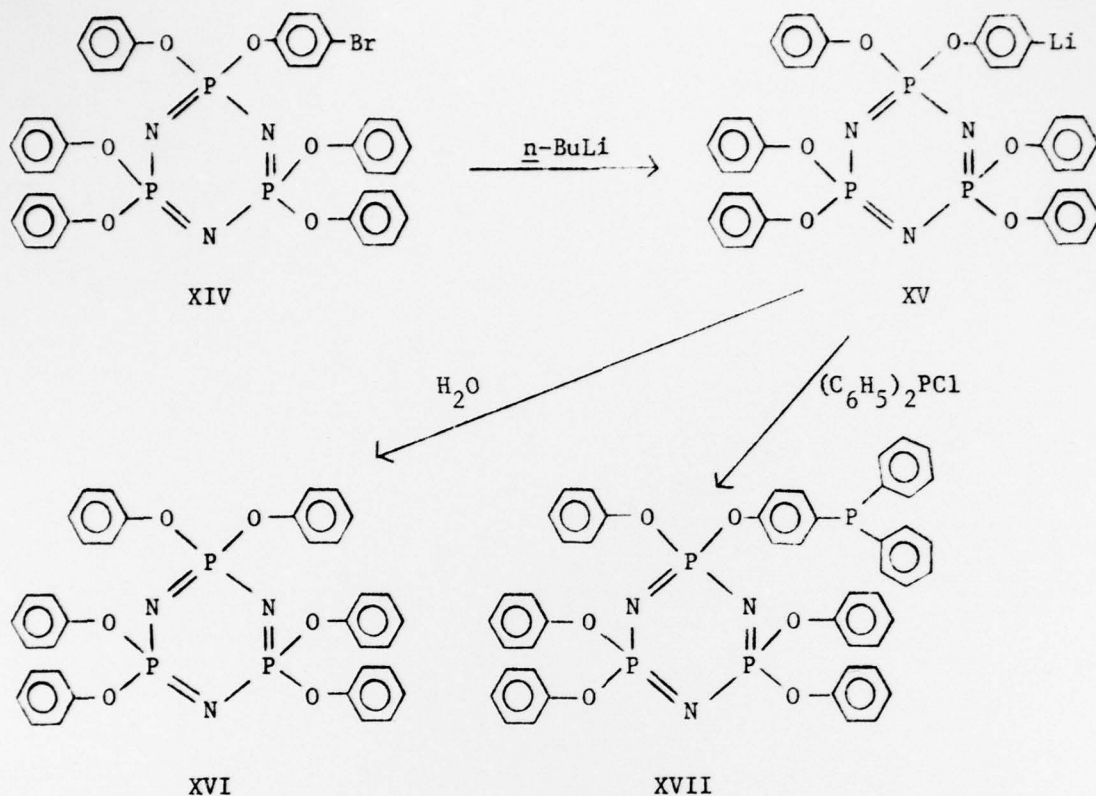
The reaction of IV with the electrophiles, diphenylchlorophosphine, carbon dioxide (followed by acidification), *n*-butyl bromide, benzophenone, triphenylphosphinegold chloride, or triphenyltin chloride, yielded the para-substituted derivatives $[\text{NP}(\text{OC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2)_2]_3$ (VIII), $[\text{NP}(\text{OC}_6\text{H}_4\text{COOH})_2]_3$ (IX), $[\text{NP}(\text{OC}_6\text{H}_4\text{C}_4\text{H}_9)_2]_3$ (X), $[\text{NP}(\text{OC}_6\text{H}_4\text{C}(\text{OH})(\text{C}_6\text{H}_5)_2)_2]_3$ (XI), $[\text{NP}(\text{OC}_6\text{H}_4\text{AuP}(\text{C}_6\text{H}_5)_3)_2]_3$ (XII), or $[\text{NP}(\text{OC}_6\text{H}_4\text{Sn}(\text{C}_6\text{H}_5)_3)_2]_3$ (XIII) (see Scheme 1). Compounds VIII-XIII were isolated in yields that were more than 20%. The formation of VIII took place in 70% yield

Scheme 1



(relative to III). The characterization of these products is described in the Experimental section. Compound VIII is of particular importance because of its ability to function as a phosphine-type ligand for transition metals. Species XIII is a prototype for compounds that may be of value in medicine or as vehicles for the deposition of gold on electrode surfaces.

Preparation and Reactions of $N_3P_3(OC_6H_5Li-p)(OC_6H_5)_5$ (XV). Although compound IV is a valuable intermediate for the synthesis of new phosphazene trimers, it is not an ideal model for carrier polymers. A carrier polymer system is usually more useful if the "active" side group units are dispersed at separated sites along the chain. In this way, one type of substituent determines the solubility and other physical properties of the macromolecule, while the "active" substituent is responsible for the chemical behavior. Thus, a more appropriate model for a carrier polymer is provided by a cyclotriphosphazene that contains one "active" substituent and five "inactive" side groups. Compound XV is an intermediate that allows the synthesis of such species. Intermediate XV was prepared in high yield by the interaction of XIV with *n*-butyllithium at $-60^\circ C$. Treatment of XV with water gave $[NP(OC_6H_5)_2]_3$ (XVI) in high yield and provided firm evidence for the efficiency of the metal-halogen exchange process in this system. The reaction of XV with diphenylchlorophosphine gave compound XVII.



Details of the Lithiation Reaction. Information was needed on three aspects of the lithiation process: (a) the stability of species such as IV at the relatively high reaction temperatures (0°C) needed for the coupling reactions with some electrophiles, (b) the efficiency of formation of lithio derivatives such as IV at different temperatures, and (c) the influence of the type of halogen (X in II) on the ease of metal-halogen exchange.

Intermediate IV was not stable for long periods of time when warmed to 0°C . For example, when IV was prepared at -60°C and the reaction mixture was then allowed to warm to 0°C during 0.75 h before treatment with diphenylchlorophosphine, compound VIII was formed in only a $\approx 5\%$ yield. By contrast, treatment of IV with diphenylchlorophosphine at -60°C followed by a warming of the system to 25°C gave VIII in 70% yield. The reaction of diphenylchlorophosphine with IV at -50 to -60°C appeared to be very rapid, and this is compatible with the observation that the interaction of diphenylchlorophosphine with phenyllithium is almost instantaneous (as deduced from ^{31}P NMR changes).

Intermediate IV could not be prepared by the interaction of III with *n*-butyllithium at 25°C. Even rapid treatment of the reaction mixture with diphenylchlorophosphine failed to yield VIII.

The metal-halogen exchange reaction at -60°C in THF was less efficient when $[\text{NP}(\text{OC}_6\text{H}_4\text{Cl-p})_2]_3$ was employed in place of $[\text{NP}(\text{OC}_6\text{H}_4\text{Br-p})_2]_3$ and only low yields of VIII could be detected after treatment with diphenylchlorophosphine. This result is consistent with the known fact that chlorobenzene does not readily undergo a metal-halogen exchange reaction.⁸ However, $[\text{NP}(\text{OC}_6\text{H}_4\text{I-p})_2]_3$ underwent lithiation readily at -60°C in a manner reminiscent of the behavior of III.

Alternative Route to VIII. A possible alternative synthetic route to VIII or XVII is via the reaction of sodium diphenylphosphide, $\text{NaP}(\text{C}_6\text{H}_5)_2$, with III or XIV. In fact, it was shown by means of a ^{31}P NMR study that the interaction of sodium diphenylphosphide with III at 25°C resulted in only 30% replacement of the bromine atoms by diphenylphosphorus units after 20 h reaction. Hence, this reaction route is less efficient than the one involving metal-halogen exchange.

Relationship to High Polymeric Analogues. Chemical reactions that involve macromolecular reagents are generally more complex than those between small molecules. This is because low yield intermolecular coupling reactions or skeletal cleavage processes have a catastrophic effect on macromolecular systems. It is for this reason that the small molecule model reactions discussed in this paper have been examined. This model-compound work suggests that for high polymers of type $[\text{NP}(\text{OC}_6\text{H}_4\text{Br})_2]_n$, $[\text{NP}(\text{OC}_6\text{H}_4\text{I})_2]_n$, $[\text{NP}(\text{OC}_6\text{H}_5)_x(\text{OC}_6\text{H}_4\text{Br})_y]_n$, or $[\text{NP}(\text{OC}_6\text{H}_5)_x(\text{OC}_6\text{H}_4\text{I})_y]_n$, the metal halogen exchange reaction with *n*-butyllithium should take place efficiently at -40°C to -60°C with only minimal

interference from chain cleavage or inter-chain coupling processes.¹⁰⁻¹² Moreover, this reaction route appears to be promising for the attachment of phosphine, carboxylic acid, alcohol, or transition metal catalyst units to the macromolecular species. This prospect will be examined in a later paper.

Experimental

Equipment and Materials. ³¹P NMR spectra were obtained in the Fourier transform mode at 40.4 MHz with a JEOL PS-100 FT spectrometer. The spectra were processed with the use of a Nicolet 1080 computer. ¹H NMR and ¹³C NMR spectra were obtained with the same spectrometer operated at 100 MHz and 95 MHz, respectively. Infrared spectra were recorded with the use of a Perkin-Elmer Model P.E. 580 high resolution infrared spectrophotometer, and ion impact mass spectra were obtained with the use of a type A.E.S./M.S. 902 mass spectrometer (Associated Electrical Instruments, Ltd.).

All reactions were carried out under an inert atmosphere of dry nitrogen (Matheson). Tetrahydrofuran (THF) (Fisher) was distilled under nitrogen from sodium benzophenone ketyl immediately before each reaction. n-Butyllithium was used as received (Foote Mineral - 1.6 M solution in hexane). Hexachlorocyclotriphosphazene, (NPCl₂)₃ (Ethyl Corp.), was purified by methods described previously.¹⁰⁻¹² p-Bromophenol, p-iodophenol, p-chlorophenol (Aldrich), n-butylbromide (Aldrich), sodium hydride (Alfa), diphenylchlorophosphine (Orgmet), deuterium oxide (Bio-Rad), triphenylphosphinegold (I) chloride (Strem), and triphenyltin chloride (Strem) were used as received.

Elemental microanalyses were obtained by Galbraith Laboratories, Knoxville, Tennessee.

Synthesis of $[\text{NP}(\text{OC}_6\text{H}_4\text{Br-p})_2]_3$ (III). A sample of p-bromophenol (67.9 g, 0.393 mol) was dissolved in THF (300 mL) and the solution was added dropwise to a stirred suspension of sodium hydride (31.2 g, 1.30 mol) and THF (100 mL) at 0°C. After 1 h, the reaction mixture was filtered (under nitrogen) and the filtrate was transferred to a reaction vessel (1000 mL capacity) equipped with an addition funnel, a water-cooled condenser, and a nitrogen inlet. A solution of $(\text{NPCl}_2)_3$ (10 g, 0.0287 mol) in THF (100 mL) was then added dropwise. Following the complete addition of the solution of $(\text{NPCl}_2)_3$, the reaction mixture was allowed to boil at reflux for 168 h. Isolation of the product was accomplished by removal of the reaction solvent by means of a rotary evaporator and by treatment of the residue with dilute aqueous hydrochloric acid. The solid was collected by filtration and was then washed sequentially with ethanol (100 mL) and with hexane (100 mL). Analytically pure samples of $[\text{NP}(\text{OC}_6\text{H}_4\text{Br-p})_2]_3$ (mp 171-172°C) were obtained by recrystallization from acetone. Micro-analytical data for this compound are summarized in Table III.

Syntheses of $[\text{NP}(\text{OC}_6\text{H}_4\text{Cl-p})_2]_3$ and $[\text{NP}(\text{OC}_6\text{H}_4\text{I-p})_2]_3$. The synthetic procedures used for the syntheses of these compounds were similar to those described for the synthesis of III. The experimental details are summarized in Table I. Analytically pure samples of $[\text{NP}(\text{OC}_6\text{H}_4\text{Cl-p})_2]_3$ (mp 149-150°C) and of $[\text{NP}(\text{OC}_6\text{H}_4\text{I-p})_2]_3$ (mp 182-184°C) were obtained by recrystallization respectively from acetone or from chloroform. Microanalytical data for these compounds are listed in Table III.

Synthesis of $[\text{NP}(\text{OC}_6\text{H}_4\text{D-p})_2]_3$ (VII). A sample of $[\text{NP}(\text{OC}_6\text{H}_4\text{Br-p})_2]_3$ (2.00 g, 0.0171 mol) was dissolved in THF (100 mL) and this solution was then cooled to -50 to -60°C in a Dry Ice-acetone bath. A solution of n-butyllithium

(8.0 ml, 1.3×10^{-2} mol) was then added dropwise. The addition of the *n*-butyllithium resulted in a 10°C exotherm and in the formation of a white precipitate. After the mixture had been maintained for 0.5 h at -40°C, deuterium oxide was added. The mixture was then allowed to warm to 25°C. After 4 h of stirring at 25°C, the reaction mixture was concentrated by means of a rotary evaporator. The resultant oil was recrystallized from acetone to yield $[\text{NP}(\text{OC}_6\text{H}_4\text{D-p})_2]_3$ (VII) (mp 99-101°C). A mass spectrum of this compound was consistent with formula VII (parent ion at $M/e = 699$). The microanalytical data for VII are shown in Table III. The ^{13}C NMR spectrum of VII (with ^1H decoupling) consisted of resonances at 151 ppm (broad singlet); 129.6 ppm (singlet); 125.1 ppm (triplet) and at 121.3 ppm (singlet). These were assigned respectively to the carbon atom bound to oxygen, the carbon atom at the meta-position, the carbon atom at the para-position, and the carbon atom at the ortho-position of the aromatic ring. These assignments were made by comparison with the ^{13}C NMR spectrum (in ^1H decoupled and coupled modes) of the compound, $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$. The ^{13}C NMR spectrum of VII was compatible with a structure in which deuterium was present only at the para-carbon atom of the aromatic ring. This result provides further indirect evidence for the existence of the intermediate, $[\text{NP}(\text{OC}_6\text{H}_4\text{Li-p})_2]_3$ (IV).

Synthesis of $[\text{NP}(\text{OC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{-p})_2]_3$ (VIII). The experimental details used for the preparation of VIII are summarized in Table II. The product was isolated by addition of the reaction mixture to 90% ethanol (500 mL) and by collection of the precipitate by filtration. The solid was then washed several times with ethanol (25 mL portions). The compound, $[\text{NP}(\text{OC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{-p})_2]_3$, was recrystallized at 0°C from a 70:30 THF-acetone mixture. The elemental microanalysis data for VIII are shown in Table III. The ^{31}P NMR spectrum of VIII consisted of two singlets at +8.06 ppm and -7.21 ppm (relative to an external

H_3PO_4 reference). These peaks were assigned to phosphazene and phosphine phosphorus atoms, respectively. The ratio of the integrated peak areas was 1:2 (phosphazene:phosphine).

Attempted Synthesis of VIII at 0°C. A sample of $[\text{NP}(\text{OC}_6\text{H}_4\text{Br-p})_2]_3$, I, (0.50 g, 4.3×10^{-4} mol), was dissolved in THF (100 mL), the solution was cooled to -50°C, and *n*-butyllithium (2.5 mL, 4.0×10^{-3} mol) was then added. The reaction mixture was maintained at -50°C for 1 h and then allowed to warm to 0°C during 0.75 h. When the reaction mixture reached 0°C, diphenylchlorophosphine (2.5 g, 1.7×10^{-2} mol) was added. The reaction mixture was stirred at 0°C for 1 h. Ethanol (300 mL) was added and the mixture was concentrated by means of a rotary evaporator. Precipitation of a product occurred, and this product was collected by filtration. ^{31}P NMR spectroscopic data confirmed that the product was $[\text{NP}(\text{OC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{-p})_2]_3$, VIII (total yield 5%). Thus, these reaction conditions are less favorable for the formation of VIII than are those that involve the formation of IV at -50 to -60°C.

Synthesis of $[\text{NP}(\text{OC}_6\text{H}_4\text{COOH-p})_2]_3$ (IX). The synthetic procedures used to prepare IV were as described previously. The experimental details are summarized in Table II. Compound IX was isolated by addition of the concentrated reaction mixture to a dilute solution of aqueous hydrochloric acid. The solid product was then collected by filtration. Analytically pure samples of $[\text{NP}(\text{OC}_6\text{H}_4\text{COOH-p})_2]_3$ (decomposition point, 330°C) were obtained by recrystallization from a 70:30 THF-acetone mixture. Elemental microanalytical data for IX are listed in Table III. The infrared spectrum of IX contained absorbances centered at 3300 cm^{-1} (OH) and at 1750 cm^{-1} (C=O). These absorbances are consistent with the presence of carboxylic acid groups. Compound IX is soluble in basic aqueous media at $\text{pH} > 10$.

Synthesis of $[\text{NP}(\text{OC}_6\text{H}_4\text{C}_6\text{H}_9\text{-P})_2]_3$ (X). Experimental details for the synthesis of (X) are summarized in Table II. Coupling conditions that involved a reaction temperature of 25°C and a reaction time of 92 h were necessary for the synthesis of X. The product was isolated by concentration of the reaction mixture by means of a rotary evaporator, addition of hexane to the residue, separation of the hexane-insoluble material by filtration, and removal of the hexane by means of a rotary evaporator. The resultant oil was purified by means of chromatography on a neutral alumina column with the use of hexane as the eluant. Compound X, isolated in this way, was a colorless oil. It was obtained in a 20% yield. Microanalytical data for X are listed in Table III.

Synthesis of $[\text{NP}(\text{OC}_6\text{H}_4\text{C}(\text{OH})(\text{C}_6\text{H}_5)_2\text{-P})_2]_3$ (XI). The experimental details used for the preparation of XI are summarized in Table II. Compound XI was isolated by the addition of a concentrate of the reaction mixture to a dilute aqueous solution of hydrochloric acid and by collection of the solid by filtration. The adhesive solid was washed several times with water. Recrystallization of XI was accomplished in a 70:30 mixture of THF and ethanol to yield a white solid (decomposition point, 350°C). Microanalytical data for XI are listed in Table III.

Synthesis of $[\text{NP}(\text{OC}_6\text{H}_4\text{Sn}(\text{C}_6\text{H}_5)_3\text{-P})_2]_3$ (XII). The experimental techniques used for the preparation of XII are listed in Table II. The synthesis of XII required a treatment of IV with triphenyltinchloride for 4.5 h at 25°C. Compound XII was isolated by removal of the reaction solvent by means of a rotary evaporator, followed by two recrystallizations from diethyl ether. Microanalytical data for $[\text{NP}(\text{OC}_6\text{H}_4\text{Sn}(\text{C}_6\text{H}_5)_3\text{-P})_2]_3$ (mp 225-228°C) are listed in Table III.

Synthesis of $[\text{NP}(\text{OC}_6\text{H}_4\text{AuP}(\text{C}_6\text{H}_5)_3\text{-P})_2]_3$ (XIII). The experimental details used for the synthesis of XIII are listed in Table II. Compound XIII was isolated in the following way. The reaction mixture was evaporated to dryness by means of a rotary evaporator, diethyl ether was added, and the insoluble materials were removed by filtration. The diethyl ether solution was extracted with a dilute aqueous hydrochloric solution and then several times with water. The diethyl ether solution was concentrated, and n-pentane was then added until a turbid recrystallization mixture was obtained. Compound XIII was collected at 0°C from this solvent system. It was recrystallized from a 70:30 THF-pentane solvent system. After this recrystallization, XIII was no longer soluble in THF. The infrared spectra of XIII obtained before and after this recrystallization were identical. The microanalytical data for this compound are listed in Table III. (These data were obtained for the THF-insoluble modification of XIII). The insolubilization process may perhaps result from the formation of polymeric species that involve intermolecular aggregations between gold atoms.

Attempted Synthesis of VIII via the Use of $[\text{NP}(\text{OC}_6\text{H}_4\text{Cl-P})_2]_3$ and $[\text{NP-OC}_6\text{H}_4\text{I-P})_2]_3$. Either $[\text{NP}(\text{OC}_6\text{H}_4\text{Cl-P})_2]_3$ (2.0 g, 2.22×10^{-3} mol) or $[\text{NP-OC}_6\text{H}_4\text{I-P})_2]_3$ (3.0 g, 2.07×10^{-3} mol) in THF (100 ml) at -60°C was treated with n-butyllithium (9.37 mL, 1.5×10^{-2} mol or 8.75 mL, 1.4×10^{-2} mol). No exotherm was detected with the chloro-derivative but a 15°C exotherm occurred with the iodo-compound. The reaction mixtures were stirred for 1 h at -60°C, and chloro-diphenylphosphine (6.62 g, 3.0×10^{-2} mol or 6.17 g, 2.8×10^{-2} mol) was then added. Both reaction mixtures were allowed to warm to 25°C and were then added to an excess of ethanol. The precipitates were collected by filtration. The ^{31}P NMR spectrum of the product (in THF) from the chloro-derivative showed resonances of +8.0 and -7.21 ppm assigned to phosphazene and phosphine

phosphorus atoms, respectively. However, the ratio of the areas of these two resonances was 1.7:2. This ratio was incompatible with the formation of $[\text{NP}(\text{OC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{-P})_2]_3$ (VIII) for which the expected ratio would be 1:2.

By contrast, the ^{31}P NMR spectrum of the reaction products obtained from the use of $[\text{NP}(\text{OC}_6\text{H}_4\text{I-P})_2]_3$ was consistent with a phosphazene to phosphorus ratio of 1:2. This value was indicative of the formation of $[\text{NP}(\text{OC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{-P})_2]_3$ (VIII). The yield of VIII from the reaction sequence that employed $[\text{NP}(\text{OC}_6\text{H}_4\text{I-P})_2]_3$ was 70%. Therefore, the synthesis of VIII could be accomplished from $[\text{NP}(\text{OC}_6\text{H}_4\text{Br-P})_2]_3$ or $[\text{NP}(\text{OC}_6\text{H}_4\text{I-P})_2]_3$ but not from $[\text{NP}(\text{OC}_6\text{H}_4\text{Cl-P})_2]_3$.

Interaction of $[\text{NP}(\text{OC}_6\text{H}_4\text{Br-P})_2]_3$ with Sodium Diphenylphosphide, $\text{NaP}(\text{C}_6\text{H}_5)_2$.

A sample of $[\text{NP}(\text{OC}_6\text{H}_4\text{Br-P})_2]_3$ (III) (2.0 g, 1.71×10^{-3} mol) was dissolved in THF (100 mL). A dimethoxyethane solution of sodium diphenylphosphide (20 mL, 4×10^{-2} mol) was added to the THF solution of III at 25°C. After 20 h at 25°C, the reaction mixture was deactivated with ethanol, and the solvent was removed by means of a rotary evaporator. A ^{31}P NMR spectrum of the concentrate showed numerous peaks that included resonances at +8.45 ppm and -7.11 ppm (assigned to phosphazene and phosphine phosphorus atoms, respectively). The ratio of the integrated peak areas for these resonances was only 1:0.62 (phosphazene to phosphine), and this indicates that on the average only 30% of the bromine atoms of III were replaced by phosphine units. Therefore, the use of $\text{NaP}(\text{C}_6\text{H}_5)_2$ with III is a much less efficient route for the preparation of $[\text{NP}(\text{OC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{-P})_2]_3$, VIII, than the metal halogen exchange sequence.

Preparation of $[\text{N}_3\text{P}_3\text{Cl}(\text{OC}_6\text{H}_5)_5]$. Phenol (13.5 g, 0.144 mol) was dissolved in tetrahydrofuran (75 mL) and this solution was added to sodium hydride (14 g, as a 50% dispersion in oil) suspended in tetrahydrofuran (75 mL).

When the reaction was complete, additional tetrahydrofuran (200 mL) was added, and the reaction mixture was heated to 50°C. The hot solution was filtered, and the warm filtrate was added dropwise to a solution of $(\text{NPCl}_2)_3$ (10 g, 0.0287 mol) in tetrahydrofuran (100 mL). The reaction mixture was stirred for 12 h at 25°C. The solvent was then removed by means of a rotary evaporator. Toluene (50 mL) was added to the residue, the solution was filtered, and the product was purified by means of a column chromatography (Hi-Flosil, Applied Science). Recrystallization from heptane yielded the compound $[\text{N}_3\text{P}_3\text{Cl}(\text{OC}_6\text{H}_5)_5]$ (mp 68°C). Mass spectrometric measurements ($M/e = 637$ and 635) confirmed the authenticity of the product. A ^{31}P NMR spectrum of the product consisted of an AB_2 pattern ($\nu_{\text{A}} = 22.1$ ppm, $\nu_{\text{B}} = 6.90$ ppm, $J = 83.1$ Hz). The total yield of the compound $[\text{N}_3\text{P}_3\text{Cl}(\text{OC}_6\text{H}_5)_5]$ was 30%.

Preparation of $[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{Br-p})(\text{OC}_6\text{H}_5)_5]$ (XIV). p -Bromophenol (11 g, 0.0636 mol) was dissolved in tetrahydrofuran (150 mL). This solution was added to a suspension of sodium hydride (6 g, as a 50% dispersion in oil) in tetrahydrofuran (100 mL). When the reaction was complete, the reaction mixture was heated to 50°C. The hot solution was filtered, and the filtrate was transferred to a reaction vessel (500 mL capacity). To this solution was added rapidly a sample of $[\text{N}_3\text{P}_3\text{Cl}(\text{OC}_6\text{H}_5)_5]$ (4.03 g, 0.0063 mol) dissolved in tetrahydrofuran (50 mL). The reaction mixture was boiled at reflux for 72 h. The solvent was then removed by means of a rotary evaporator, and water (100 mL) was added to the residue. A saturated aqueous sodium chloride solution (25 mL) was added, and methylene chloride was used to extract the compounds that were not soluble in water. The methylene chloride was dried over solid sodium sulfate, filtered,

and the solvent removed by means of a rotary evaporator. The residue was recrystallized from methanol to yield $[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{Br-p})(\text{OC}_6\text{H}_5)_5]$ (mp 70-72°C). Mass spectrometric data for this compound (parent ion, $M/e = 771$) provided further evidence for its formulation as $[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{Br-p})(\text{OC}_6\text{H}_5)_5]$, XIV, (M.W. 771 for ^{79}Br). The ^{31}P NMR spectrum of the compound consisted of a singlet at +8 ppm. The total yield of the product was 50.1%.

Preparation of Characterization of $[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{Li})(\text{OC}_6\text{H}_5)_5]$ (XV). A sample of $[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{Br-p})(\text{OC}_6\text{H}_5)_5]$ (XIV) (0.66g, 0.00085 mol) was dissolved in tetrahydrofuran (75mL), and the solution was cooled to -50°C. *n*-Butyllithium (3 mL, 0.0048 mol) was then added, and the reaction mixture was stirred at -50°C for 1 h. Water (3 g, 0.17 mol) was added, and the reaction mixture was then allowed to warm to 25°C. The mixture was evaporated to dryness by means of a rotary evaporator, water was added, and the solid was collected by filtration. The precipitate was recrystallized from heptane to yield the compound $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$ (XVI) (mp = 112°C). A sample of $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$, prepared by the reaction of $(\text{NPCl}_2)_3$ with sodium phenoxide had an identical melting point. Mass spectrometric data for this product (parent ion, $M/e = 693$) provided further evidence for its formulation as $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$, XVI, (M.W. = 693). The total yield of the product was 85%.

Preparation of $[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{-p})(\text{OC}_6\text{H}_5)_5]$ (XVII). A sample of $[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{Br-p})(\text{OC}_6\text{H}_5)_5]$ (XIV) (0.66 g, 0.0085 mol) was dissolved in tetrahydrofuran (75 mL) and the solution was cooled to -50°C. *n*-Butyllithium (3 mL, 0.0048 mol) was then added and the reaction mixture was stirred for 1 h at -50°C. Diphenylchlorophosphine (4 g, 0.018 mol) was added, the reaction

mixture was stirred for 1 h, and was then allowed to warm to room temperature. The isolation and purification of $[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{-p})(\text{OC}_6\text{H}_5)_5]$ were complicated by the fact that this product was an oil. However, ^{31}P NMR spectral data for this oil were consistent with its formulation as the compound, $[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\text{-p})(\text{OC}_6\text{H}_5)_5]$, because the integrated peak areas for the phosphazene and pendent phosphine phosphorus atoms were in a ratio of 3:1. Therefore, the metal-halogen exchange process for $[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{Br-p})-(\text{OC}_6\text{H}_5)_5]$ and subsequent treatment with diphenylchlorophosphine were efficient processes.

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Table I

Reaction Conditions for the Synthesis of p-Halophenoxycyclotriphenazenes

Product	Phenol	(g/mol)	NaH (g/mol)	(NPCl ₂) ₃ (g/mol)	Reflux Time	% Yield
[NP(OC ₆ H ₄ Br-P) ₂] ₃	P-BrC ₆ H ₄ OH	(67.9:0.393) in THF (300 mL)	(31.2:1.3) in THF (100 mL)	(10.0:0.029) in THF (100 mL)	7 days	>90%
[NP(OC ₆ H ₄ I-P) ₂] ₃	P-IC ₆ H ₄ OH	(39.2:0.178) in THF (200 mL)	(10.1:0.42) in THF (100 mL)	(5.0:0.014) in THF (100 mL)	4 days	>90%
[NP(OC ₆ H ₄ Cl-P) ₂] ₃	P-ClC ₆ H ₄ OH	(24.0:0.187) in THF (200 mL)	(10.3:0.43) in THF (100 mL)	(5.0:0.014) in THF (100 mL)	4 days	>90%

Table II

Product	[NP(OC ₆ H ₄ Br-P) ₂] ₃ (g/mol) in THF (mL)	n-C ₄ H ₉ Li (ml/mol)	Reaction Time (h)	Electrophile	Electrophile (g/mol)
VII	2.00 (1.71 x 10 ⁻³) in THF (100 mL)	8.0 (1.3 x 10 ⁻²)	0.5	D ₂ O	10(5.56 x 10 ⁻¹)
VIII	2.00(1.7. x 10 ⁻³) in THF (100 mL)	7.2(1.2 x 10 ⁻²)	1.0	ClP(C ₆ H ₅) ₂	5.1(2.3 x 10 ⁻²)
IX	2.00(1.71 x 10 ⁻³) in THF (100 mL)	7.2(1.2 x 10 ⁻²)	1.0	CO ₂ (Dry Ice)	large excess
X	5.00(4.28 x 10 ⁻³) in THF (200 mL)	22(3.5 x 10 ⁻²)	0.5	C ₄ H ₉ Br	31.8(2.3 x 10 ⁻¹)
XI	2.00(1.71 x 10 ⁻³) in THF (100 mL)	7.2(1.2 x 10 ⁻²)	1.0	(C ₆ H ₅) ₂ CO	4.19(2.3 x 10 ⁻²) in THF (25 mL)
XII	2.00(1.71 x 10 ⁻³) in THF (150 mL)	8.0(1.3 x 10 ⁻²)	0.5	(C ₆ H ₅) ₃ SnCl	8.6(2.23 x 10 ⁻²) in THF (50 mL)
XIII	1.50(1.30 x 10 ⁻³) in THF (200 mL)	5.0(8 x 10 ⁻³)	1.0	ClAuP(C ₆ H ₅) ₃	11.03(2.2 x 10 ⁻²) in THF (100 mL)

Table III

Table of Analytical Results

Compound	%C	%H	%N	%P	%O	%X ^b
[NP(OC ₆ H ₄ Cl-P) ₂] ₃	Calc.	2.67	4.67	10.33	10.66	23.67Cl
	Anal.	48.22	2.75	4.79	10.58	23.58Cl
III	37.04	2.06	3.60	7.97	8.23	41.10Br
	37.14	2.06	3.63	8.15	7.81 ^a	41.21Br
[NP(OC ₆ H ₄ I-P) ₂] ₃	29.83	1.66	2.90	6.42	6.62	52.57I
	29.87	1.66	3.07	6.60	6.32	52.48I
IX	52.57	3.13	4.39	9.72	30.10	-
	52.57	3.55	4.41	9.57	29.78	-
XI	76.64	5.04	2.35	5.21	10.76	-
	76.23	5.18	2.33	5.44	10.82 ^a	-
VIII	72.12	4.67	2.34	15.53	5.34	-
	72.20	4.53	2.29	15.37	5.80 ^a	-
XIII	50.20	3.31	1.26	8.11	2.79	34.40Au
	50.13	3.43	1.30	8.21	2.94	34.19Au
XII	62.04	4.09	1.51	3.34	3.45	25.57Sn
	62.06	4.18	1.50	3.29	3.55 ^a	25.43Sn

Table III (continued)

X	Calc.	69.97	7.58	4.08	9.04	9.33	-
	Anal.	69.58	7.99	4.06	8.79	9.58 ^a	-
VII		61.80	5.15	6.01	13.31	13.73	-
		61.76	4.59	5.81	13.01	14.83 ^a	-
[N ₃ P ₃ Cl(OC ₆ H ₅) ₅]		56.21	4.68	6.56	14.52	12.49	5.54Cl
		56.71	4.00	6.56	14.67	12.58	5.42Cl
XIV		56.97	3.76	5.44	12.05	11.43	10.35Br
		56.00	3.86	5.28	11.73	12.55	10.58Br

^a Per cent oxygen determined by difference

^b X = para substituent group in [NP(OC₆H₄X)₂]₃

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