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Abstract

Thermal, electrochemical and transition metal mediated reactions of phosphaacetylene monomers were conducted in attempts to form novel polyphosphaacetylenes as a new class of potentially electrically conducting polymers. Molecular modeling was used to simulate the molecular conformations of optimized, isolated oligomers to identify the proper monomeric repeat units for highly conjugated molecules. Electrodeposition of suitable monomers led to low molecular weight oligomers. Thermal polymerization of phosphaacetylene monomers bearing aromatic substituents led to the formation of polyhedral cage oligomers. Under metathesis polymerization conditions the phosphaacetylene monomers form unique complexes via an unprecedented sequence of intermediates which suggest that metathesis to linear oligomers is achievable. Conductivity measurements on electrodeposited oligomers indicate modest electrical conductivity.
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Introduction

This project was designed to develop a new class of conducting polymer with improved processability over conventional organic conductors for uses as electronic component protective coatings, cable shielding, rechargeable batteries, semiconductors, etc.

A recent report "Electrically-Conducting Synthetic Materials Remain Preserve of Small and Mid-Sized Firms," identified intrinsically conducting polymers as an important class of materials whose utility is limited in large part by their lack of mechanical stability and inconsistency in conductivity. Typical soluble organic conductors have low to modest intrinsic conductivities ($\sigma \approx 10^{-5} - 10^{-3}$ S/cm) unless oxidative or reductive doping is used, a process which is difficult to control in large scale processes. Those materials which do display metal-like electrical conductivities suffer from processing limitations due to their highly conjugated and rigid molecular structures; when solubilities are enhanced by incorporation of solubilizing groups conjugation, and therefore conductivity, is diminished. Furthermore, the potential applications of intrinsically conducting, formable polymers include markets in which the United States is already losing ground, being dominated by European and Japanese research and development efforts.

Through oligomerization of phosphorus-containing alkyne analogues, called phosphaacetylenes, we have attempted to generate hybrid organophosphorus materials analogous to polyacetylenes; ideally the polyphosphaacetylenes would have a [P=C(R)] repeat unit containing a longer double bond length than polyacetylene and only a single solubilizing substituent (R) per repeat unit. Our approach has involved 1) the molecular modeling of isolated linear oligophosphaacetylenes, 2) the optimized synthesis and characterization of phosphaacetylene monomers and their thermal and electrochemical oligomerizations, 3) conductivity determinations of electrodeposited oligophosphaacetylene films and 4) the synthesis, characterization and reactivity of low valent transition metal metathesis catalysts with phosphaacetylene monomers.

We have pursued characterization of thermally and electrochemically oligomerized materials from the phosphaacetylenes, the first such studies to date. Our efforts to conduct metathesis polymerization with phosphaacetylenes have led to the formation of discreet organometallic intermediates with unique molecular geometries and connectivities; the elucidation of an unprecedented reaction pathway provides insight into the possibilities of
generating high molecular weight linear polymers with a hybrid organophosphorus backbone.

Results

Results from this project were very informative as to the possibility of preparing linear oligomers based on the phosphaalkene repeat unit \([P=C(R)]\). The participants on the project have made significant contributions to the understanding of the polymerization behavior of phosphaacylenes through thermal and electrochemical means, the conformational assessment of potentially conducting model compounds for electrical conductivity, and the behavior of phosphaacylene monomers with high oxidation state molybdenum and tungsten alkylidenes as potential metathesis catalysts for phosphaacylene oligomerization. The remainder of the report is a summary, including a list of publications and presentations, describing the research areas impacted by this LDRD: "Electrodeposition of Phosphaacylenes," "Novel Reaction Pathways in the Reaction of \(t\)-BuC≡P with High Oxidation State Metal Alkylidenes," and "Thermal Oligomerization of Phenylphosphaethyne."

1. Electrodeposition of Phosphaacylenes

Phosphaalkyne monomers \(P=C-t\)-Bu and \(P=C-CH(Et)_2\) were prepared by the base-catalyzed elimination of hexamethyldisiloxane from their respective phosphaalkene precursors TMSP=C(OTMS)(t-Bu) and (TMS)P=C(OTMS)(CH(Et)_2). The purity of the resulting monomers was verified by multinuclear NMR and IR spectroscopies. The electrochemical behavior of the phosphaalkyne monomers was probed by cyclic voltammetry. \(P=C-t\)-Bu displays a slight tendency toward oxidative electrodeposition at +0.8V (vs. SCE reference) in acetonitrile. Attempts to determine the electrochemistry of the deposited film in acetonitrile showed a reversible redox couple, though these results are not reproducible, presumably due to the instability of the oligomers formed at the electrode surface.

\(P=C-CH(Et)_2\) shows electrodeposition behavior, with a reductive wave at -0.2V in DMF. This film is soluble in DMF, as attempts to continue monitoring the current flow by cyclic voltammetry after standing in DMF indicated that fresh film was being generated at the electrode surface as opposed to growing on a pre-existing polymer film. Replacement of the platinum working electrode in acetonitrile showed no electrochemistry, confirming the dissolution of the film into DMF. A solvent dependence on film growth of \(P=C-\)
CI(Et)$_2$ was observed, as electrodeposition appeared to occur at +0.2 V. Immersion of the coated electrode into an acetonitrile solution resulted in an irreversible reductive electron transfer at -1.75V.

2. Novel Reaction Pathways in the Reaction of t-BuC≡P with High Oxidation State Metal Alkylidenes

Addition of t-BuC≡P to an ether solution of metal alkylidene [ArN][OR]$_2$Mo=C(H)(t-Bu) (Ar = 2,6-(i-pr)$_2$C$_6$H$_3$; R = (F$_3$C)$_2$CH$_3$CO) 1a at room temperature leads to the formation of a unique cyclic organometallic complex, [ArN][RO]Mo=C(t-Bu)-P(OR)-C(H)(t-Bu), 4a, in which an expected [2+2] cycloaddition between the metal-carbon double bond and the phosphorus-carbon triple bond of the phosphaacetylene is accompanied by a shift of one alkoxide ligand from the molybdenum to the phosphorus nucleus (Scheme 1).

Investigations into the effect of the alkoxide ligand migratory aptitude from the starting molybdenum alkylidene have been very informative and suggest a more complicated reaction mechanism. Under identical conditions, addition of t-BuC≡P to an ether solution of metal alkylidene [ArN][RO]$_2$Mo=C(H)(CMe$_2$Ph) (Ar = 2,6-(i-pr)$_2$C$_6$H$_3$; R = (F$_3$C)(CH$_3$)$_2$CO), 1b, does not form an analogous metallacyclic complex. Rather, the single isolated product from the reaction is a unique molybdenum alkylidyne complex 3b which contains the [t-BuC] and phosphorus termini of the phosphaacetylene in two separate ligands. This unprecedented result verifies the intramolecular metathesis of the phosphaacetylene and suggests that under appropriate conditions the productive metathesis of phosphaacetylenes to form linear polymers is feasible.

It has also been determined that under the influence of heat the isolated alkylidyne complex [(F$_3$C)Me$_2$CO]$_2$Mo(C-t-Bu)[-N(Ar)-P=C(H)(CMe$_2$Ph)] 3b undergoes an intramolecular rearrangement to generate an analogous metallacyclic complex 4b, analogous to cycloadduct 4a.

Utilizing tungsten-based alkylidenes yielded encouraging results in that one equivalent of the tungsten complex [ArN][OR]$_2$W=C(H)(t-Bu) (Ar = 2,6-(i-pr)$_2$C$_6$H$_3$; R = (F$_3$C)$_2$CH$_3$CO) inserts two equivalents of the phosphaacetylene "monomer"; structural characterization verifies the multiple addition of t-BuC≡P into the tungsten-alkylidene triple bond (Scheme 2).

In order to establish a detailed reaction mechanism, additional research in this area is required in order to identify transition metal catalysts which will generate polyconjugated polyphosphaacetylenes.
3. Thermal Oligomerization of Phenylphosphaethyne

Preparation of PhC≡P by flash vacuum pyrolysis of phosphaalkene precursor ClP=C(SiMe3)Ph was optimized to yield pure monomer devoid of chlorosilane impurities. The monomer undergoes a strongly exothermic oligomerization when allowed to warm in
its pure form; disproportionation of the organophosphorus monomer is evident from the
detection of $P_4$ by $^{31}$P NMR experiments. Dilution of phenylphosphaethyne in organic
solvents slows the rate of oligomerization. Purification of the resulting brown polymer by
precipitation from pentane yields a methylene chloride-soluble powder with an empirical
formula consistent with oligophosphaethyne. $^1$H and $^{13}$C NMR spectroscopy suggest that
the material does not possess $P=C$ unsaturation and is a distribution of low molecular
weight oligomers. The absence of expected stretching bands in the IR along with the lack
of electronic absorptions assignable to $P=C$ double bonding suggests a non-conjugated
material. GPC data verify NMR data that solution polymerization leads to a low molecular
weight material, on the order of four to eight repeat units.

Mass spectrometry was employed to determine the molecular weight of the
oligomers; spectra show a distribution of masses from $m/z$ 40 to 1080 in increments of
phenylphosphaethyne monomer mass (120 amu), corresponding to tetramers through
nonamers (four to nine repeat units) constructed from the PhC=P structural unit.
Additional mass peaks correspond to polyhedra in which there has been some degree of
disproportionation; that is, there has been exchange between the isolobal $P=$ and PhC=
termini of PhC=P which comprise the vertices of the oligomeric cages. These results
constitute an extension of phosphaalkyne oligomerization from the behavior of more
stabilized phosphaalkyne monomers and are apparently characteristic of phosphaalkyne
polymerization chemistry under thermal conditions.
Presentations and Publications


Abstract
Phosphaacetylenes (RC=P) have been intensely studied for their use as either organic synthons or interesting ligands in organometallic reactions. Of particular interest is the similarity in chemical reactivity between phosphaacetylenes and acetylenes that includes participation in cycloaddition reactions, predominantly side-on coordination with metals, and metal catalyzed cyclo-oligomerization to form cage compounds. Many phosphaacetylenes were discovered to undergo uncatalyzed polymerization at room temperature to afford uncharacterized materials. We report the preparation and characterization of phenyl phosphaacetylene oligomers by multinuclear NMR (including isotopic labelling), mass spectrometry, and GPC.


Abstract
Molybdenum alkylidynes 2a, b are formed in the reaction of t-BuC≡P with molybdenum alkylidenes 1a, b. Alkylidynes 2a, b undergo a secondary thermal transformation to form 1-phospha-3-molybdacyclobut-2-enes 3a, b quantitatively; 3c is formed directly from the reaction of t-BuC≡P with 1c. Spectral and structural characterization of complexes 2 and 3 and mechanistic considerations will be discussed.

**Abstract**

Phosphametallacycle 3, [ArN][RO]Mo=C(t-Bu)-P(OR)-C(H)(t-Bu) (Ar = 2,6-(i-Pr)2C6H3, R = CMe(CF3)2), is formed from the cycloaddition of t-butylphosphaalkyne to the high oxidation state molybdenum alkylidene [ArN][RO]2Mo=C(H)(t-Bu), accompanied by an alkoxide metal-to-ligand shift. The 1-phospha-3-molybdacyclobut-2-ene has been characterized by multinuclear NMR spectroscopy, and its molecular structure determined by X-ray crystallographic analysis.


**Abstract**

Novel molybdenum alkylidyne [(F3C)Me2CO]2Mo(C-t-Bu)[N(Ar)-P=C(H)(CMe2Ph)] (Ar = 2,6-(i-Pr)2C6H3) 3b is formed in the reaction of t-butylphosphaalkyne 2 to molybdenum alkylidene 1b. Alkylidyne 3b, which contains a
formal phosphaalkenylamido ligand, rearranges quantitatively at elevated temperature to form the alkoxide-shifted phosphamolybdcyclobutene 4b. Complexes 3b and 4b have been fully characterized by spectroscopic and x-ray crystallographic analysis; cleavage of the P=Ca-Bu triple bond in complex 3b is confirmed.

**Abstract**

Zero-valent tungsten alkylidene 1 reacts with an excess of t-BuC≡P to form cycloadducts formally derived from the insertion of two equivalents of the phosphaalkyne to the tungsten alkylidene double bond. Bicyclic complex 2 has been isolated and characterized by spectral and structural techniques. The observed tungsten alkylidene reactivity will be discussed in light of the reported phosphaalkyne chemistry with high oxidation state molybdenum alkylidenes.

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