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## Alkynlphosphazenes: Synthesis, Reactions and Incorporation into Polymers

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## **ALKYNLPHOSPHAZENES: SYNTHESIS, REACTIONS AND INCORPORATION INTO POLYMERS**

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**Abstract** The regio- and stereochemical pathways followed in the reactions of the lithioacetylenes,  $\text{LiC}\equiv\text{CR}$  ( $\text{R}=\text{Ph}$ , Me,  $n\text{-Bu}$ ), with  $\text{N}_3\text{P}_3\text{F}_6$  have been examined by  $^{31}\text{P}$  and  $^{19}\text{F}$  NMR spectroscopy. Mixed propenylphenyl, phenylacetylene derivatives were also prepared. The products formed in these reactions demonstrate substituent control of the reaction pathway. Copolymerization of propenylphenyl alkynylphosphazenes with styrene gives polymers which add dicobalt hexacarbonyl and undergo a one electron, chemical reversible reduction.

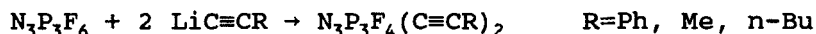
### **INTRODUCTION**

Comparatively few investigations of alkynylphosphazenes have appeared.<sup>1,2</sup> Initial reports of the interactions of lithiophenylacetylene with hexafluorocyclotriphosphazene,  $\text{N}_3\text{P}_3\text{F}_6$ , suggested a geminal pathway is followed.<sup>3</sup> Later work using lithiotrimethylsilyl-acetylene indicated that the non-geminal pathway could also be of importance.<sup>4</sup> Once obtained, the alkynylphosphazene can undergo metal catalyzed cyclooligomerization reactions.<sup>5,6</sup> In this study, we have examined the factors controlling both the regio- and stereoselectivity in alkynyl lithium/ $\text{N}_3\text{P}_3\text{F}_6$  reactions and used these results to design monomers which will allow for incorporation of the alkynylphosphazene into polymeric systems. The availability of these polymers allows for the investigation of the electrochemical activity of dicobalt hexacarbonyl alkynylphosphazene complexes in a polymeric environment.

### **RESULTS AND DISCUSSION**

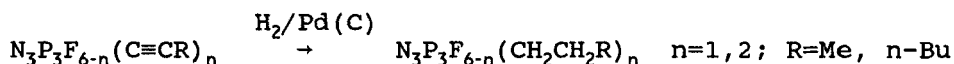
The dependance of the observed substitution pathway on the alkyne substituent ( $\text{R}=\text{Ph}$ , Me,  $n\text{-Bu}$ ) in the reactions of

lithioacetylenes with  $N_3P_3F_6$ , was explored. We have found



that formation of the dicolbalt hexacarbonyl complexes allows for chromatographic separation of the geminal and non-geminal phenylacetylene derivatives. The later makes up about 14% of the isolated yield.

The  $^{31}P$  and  $^{19}F$  NMR spectra of the alkylacetylene derivatives indicate a mixture of all isomers but the relative closeness of the  $\equiv PF_2$  and  $\equiv PF(C\equiv CR)$  chemical shifts is such that extraordinarily complex spectra are obtained. We found that catalytic hydrogenation leads to high yields of the corresponding alkanes. This is a useful process from two perspectives. Firstly, it allows for preparation of n-alkylfluorophosphazenes which, with

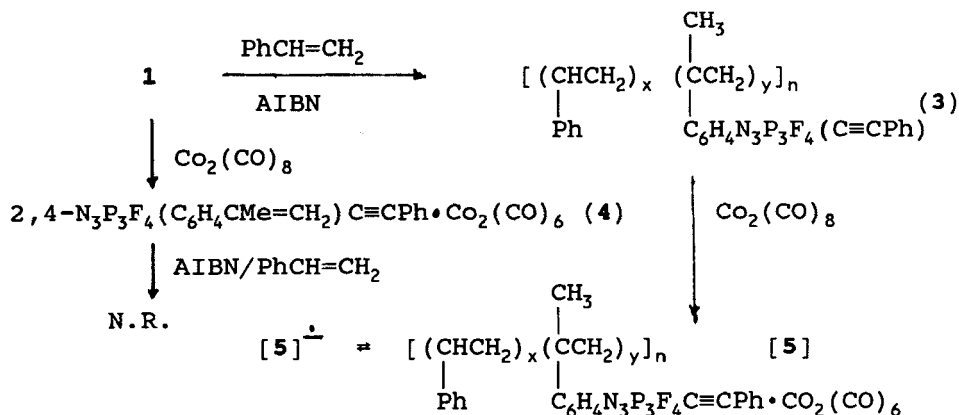


the exception of the methyl derivatives<sup>7</sup>, are only available in low yields.<sup>8</sup> There is a 40-50 ppm downfield shift of the  $^{31}P$  chemical shift on going from a  $\equiv PF(C\equiv CR)$  to a  $\equiv PF(CH_2CH_2R)$  center. The spectra are now largely first order and quantification of the composition of the reaction mixture is possible. In each case, all three bis isomers are present with non-geminal regioselectivity and cis stereoselectivity being observed.

In the absence of steric effects, the geminal pathway is favored in the reactions of carbanionic reagents with cyclophosphazenes.<sup>9</sup> The geminal regioselectivity observed in the lithiophenylacetylene reaction is consistent with this prediction. The crystal structure of  $2,2-N_3P_3F_4(C\equiv CPh)_2$  shows that the two phenyl groups are cofacial<sup>10</sup> thus there is no steric barrier to the geminal disposition of the alkynes. In the alkylacetylenes, the increased steric demand of the alkyl group will favor a non-geminal pathway. The  $^{13}C$  NMR data on the alkynylphosphazenes suggest the possibility of electronic effects also being operative. The product expected when

steric control is predominant is the trans isomer as shown by the stereospecific formation of trans-2,4-N<sub>3</sub>P<sub>3</sub>F<sub>4</sub>(CMe<sub>3</sub>)<sub>2</sub> from N<sub>3</sub>P<sub>3</sub>F<sub>6</sub> and tert-butyl lithium.<sup>8</sup> Cis isomers are only favored in phosphazenes with unsaturated organic groups as substituents. This has been ascribed to association between the electron rich incoming reagent and the polarized substituent on the phosphazene.<sup>9</sup> This model is consistent with the results of this investigation.

We have previously shown that 4-(2-propenyl)phenyl lithium primarily follows a non-geminal path with cis stereoselectivity<sup>11</sup> and that lithiophenylacetylene predominantly follows a geminal path (*vide ante*). The fact that the reaction of the arylpentafluorophosphazene with lithiophenylacetylene follows a non-geminal path (with cis stereoselectivity) and that the phenylalkynyl pentafluorophosphazene gives a geminal product with the aryl lithium reagent demonstrates that the reaction pathways are controlled by the substituent on the phosphazene ring. The copolymerization of the non-geminal or geminal propenylphenyl/phenylacetylene derivatives (1 and 2) with styrene leads to copolymers with pendent alkynylphosphosphazenes as shown for 1 in Scheme I. The maximum degree of incorporation of the phosphazene was



**Scheme I**

larger in the case of 1. We employed two approaches to

the formation of organometallic derivatives of these copolymers. The first route, which was unsuccessful, involved synthesis of the dicobalt hexacarbonyl complex of the monomer (4) and attempting to copolymerize this material with styrene. The alternative, successful, route involved adding the cobalt carbonyl to the copolymer (3). Variable levels of cobalt carbonyl loading could be obtained by this route. The organometallic polymer derivative (5) undergoes a chemically reversible one electron reduction at a potential very near that of  $\text{N}_3\text{P}_3\text{F}_5\text{C}\equiv\text{CPh}\cdot\text{Co}_2(\text{CO})_6$ .<sup>6</sup>

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