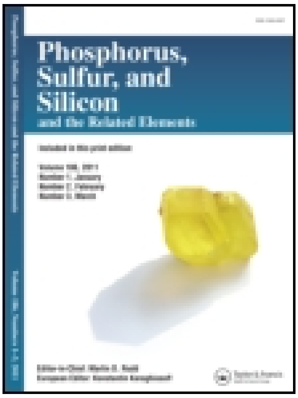

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

The Reaction of Cyclopropenylphosphonium Bromides with Sodium Polyphosphides as an Advanced Method of Synthesis of Sodium 1,2-Diphosphacyclopentadienides: Scope and Limitations

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To cite this article: Il'ya Bezkishko , Vasili Miluykov , Oleg Sinyashin & Evamarie Hey-Hawkins (2011): The Reaction of Cyclopropenylphosphonium Bromides with Sodium Polyphosphides as an Advanced Method of Synthesis of Sodium 1,2-Diphosphacyclopentadienides: Scope and Limitations, Phosphorus, Sulfur, and Silicon and the Related Elements, 186:4, 657-659

To link to this article: http://dx.doi.org/10.1080/10426507.2010.508061

Phosphorus, Sulfur, and Silicon, 186:657–659, 2011
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426507.2010.508061

THE REACTION OF CYCLOPROPENYLPHOSPHONIUM BROMIDES WITH SODIUM POLYPHOSPHIDES AS AN ADVANCED METHOD OF SYNTHESIS OF SODIUM 1,2-DIPHOSPHACYCLOPENTADIENIDES: SCOPE AND LIMITATIONS

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Abstract *A new ring expansion reaction based on the interaction between 1,2,3-triarylcyclopropenylphosphonium bromide (**1**) and sodium polyphosphides gives sodium 3,4,5-triaryl-1,2-diphosphacyclopentadienides (**2**) containing various substituents in the para-position of the aryl groups with a high yield. However, this reaction of trialkylcyclopropenylphosphonium bromide (i.e., tri(tert-butyl)- or triisopropylcyclopropenylphosphonium bromide) does not result to the formation of sodium 1,2-diphosphacyclopentadienides.*

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Keywords Phosphonium bromide; sodium 1,2-diphosphacyclopentadienides; sodium polyphosphides

There is significant interest in alkali metal phosphacyclopentadienides due to their high synthetic potential. As an isolobal anologue of Cp^-, they can form η^1- or η^5-coordinated complexes. However, the presence of a lone pair of electrons at the phosphorus atoms permits other more complicated coordination modes with transition metals. Thus, polymetallic complexes and clusters can be obtained that are useful as catalysts in organic reactions such as Suzuki,[1] propene polymerization,[2] diethylacetylene trimerization,[3] and asymmetric hydrogenation of amino acids.[4] Moreover, alkali metal phosphacyclopentadienides can be employed as starting materials for preparation of cage phosphanorbornadienes that exhibit good activity as anticancer reagents[5] or can be employed as ligands in catalysts for asymmetric organic reactions.[6–8]

Among numerous alkali metal phosphacyclopentadienides the 1,2-diphosphacyclopentadienide anion is especially attractive due to being isolobal to Cp^-, showing predominantly η^5-coordination with transition metals, and a pyrazolate anion, exhibiting

Received 21 June 2010; accepted 9 July 2010.

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predominantly bridging μ:η^1,η^1-coordination to form binuclear or polymeric metal complexes. Recently we have demonstrated for the first time that the 3,4,5-triaryl-1,2-diphosphacyclopentadienide anion forms bimetallic manganese complexes that exhibit large anti-ferromagnetic exchange interaction due to metal-to-ligand charge transfer.[9] Thus, the 3,4,5-triaryl-1,2-diphosphacyclopentadienide anion may be considered as a novel type of non-innocent ligand combining the ability of both the metal-to-ligand charge transfer and the exchange interaction between the metals.

Two different methods are employed for preparation of alkali metal 1,2-diphosphacyclopentadienides. One is based on the cleavage of a P-C bond of 1-phosphetene by lithium, followed by reaction with PCl_3 and finally reduction of the formed 1,2-diphosphole by lithium.[10] However, this method does not allow isolation of the pure lithium 1,2-diphosphacyclopentadienide. A more convenient synthesis of sodium 1,2-diphosphacyclopentadienide is based on reaction of triphenylcyclopropenyl nickel complexes with sodium polyphosphides.[11,12] However, this method demands the use of expensive [Ni(cod)$_2$] and does not allow the isolation of large amounts of sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide. Recently, we have found that sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide can be easily obtained by reaction of 1,2,3-triphenylcyclopropenylphosphonium bromides with sodium polyphosphides in high yield.[13] This method is scalable and allows preparation of sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide in significant amounts (up to 20 g) from common starting materials. In continuation of this work we were interested in the possibility of using the same method for the preparation of other derivatives of sodium 1,2-diphosphacyclopentadienide.

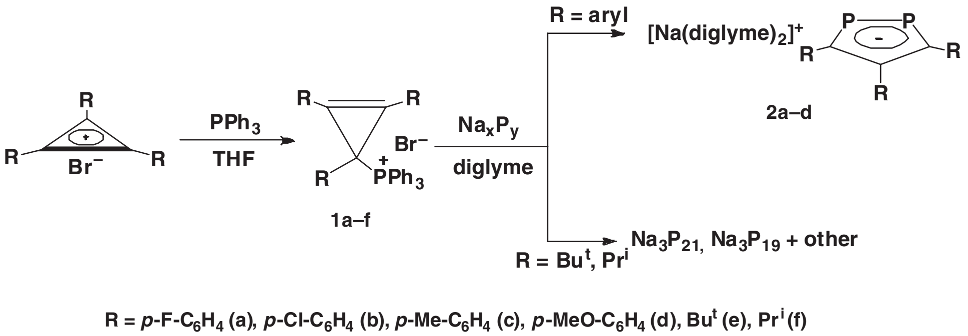
For this purpose we have synthesized a series of 1,2,3-triarylcyclopropenylphosphonium bromides (**1**), containing both acceptor or donor substituents in the *para*-position of the aryl group, by reaction of the corresponding 1,2,3-triarylcyclopropenyl bromides with PPh_3. The structure of compounds **1a–f** was confirmed by NMR spectroscopy. Thus, the $^{31}P\{^1H\}$-NMR spectrum of **1a** contains a singlet at +33 ppm typical for phosphonium salts. The $^{13}C\{^1H\}$-NMR spectrum consists of a doublet for the carbon atom C1 at +26 ppm, characteristic for sp^3-hybridized carbon atoms, with a coupling constant $^1J_{CP}$ = 72 Hz.

The phosphonium salts (**1**) were treated with a mixture of polyphosphides obtained *in situ* from sodium and white phosphorus containing mainly NaP_5 and Na_3P_7.[14]

Only the signals of sodium 3,4,5-triaryl-1,2-diphosphacyclopentadienides (**2a–d**) and PPh_3 were detected in the $^{31}P\{^1H\}$-NMR spectrum of the reaction mixture after refluxing for 3 h (Scheme 1). Compounds **2a–d** can easily be isolated from the reaction mixture by filtration. After washing with *n*-hexane, **2a–d** were obtained in good purity and can be used for following reactions without further purification.

However, no 1,2-diphosphacyclopentadienide anions were formed in the reaction of sodium polyphosphides with 1,2,3-tri(*tert*-butyl)- or 1,2,3-tri-isopropylcyclopropenylphosphonium bromides (**1e**,**f**); the $^{31}P\{^1H\}$-NMR spectra of the reaction mixtures contain only signals in the range of +50 to −100 ppm typical for sodium polyphosphides such as Na_3P_{21}, Na_3P_{19}, and others.[15]

In summary, we have found that reactions of cyclopropenylphosphonium bromides with sodium polyphosphides can be successfully used for the preparation of sodium 3,4,5-triaryl-1,2-diphosphacyclopentadienides containing acceptor or donor substituents in the *para*-position of an aryl group.



Scheme 1

Supporting information for this article containing details of experiments is available on the journal Website or from the authors.

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