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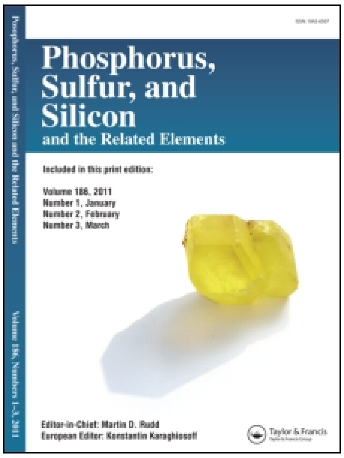

Phosphorus, Sulfur, and Silicon and the Related Elements

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Novel Cations and Molecules from Phosphaalkynes, 1H-Phosphirenes and from Tetraphosphacubane

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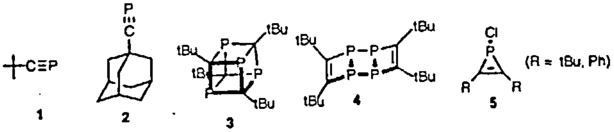
Generation and trapping (counter ion) of the phosphavinyl cation (the P-analog of vinyl cation) by low temperature protonation of kinetically stable phosphaalkynes in super acid media led to the formation of the corresponding phosphaalkenes without direct observation of a long-lived cation. Reactions of RCP (R = tBu, 1-Ad) with "PhSeF" and with PhSeCl resulted in bis-phenylselenenylation and chlorophenylselenenylation respectively, forming novel Se-containing phosphaalkenes. Ionization of 1-H-triflato-phosphirene with $B(OTf)_3/SO_2$ led to the direct observation of a persistent phosphirenylium cation. The $(CO)_5$ W-complexed phosphirenylium cation was subsequently generated from the $(CO)_5$ W-complexed triflate and trifluoroacetate derivatives. Progress in P-functionalization of tetraphosphacubane by reactions with potent electrophiles (i.e. MeOTf, EtOTf"$PhCH_2OTf$", $TMSCH_2OTf$), alkynyl-iodonium triflates and with protic superacids are briefly summarized.

Keywords: phosphaalkynes; 1H-phosphirenes; tetraphosphacubane; electrophilic chemistry; superacids; stable phosphorus cations; Se-containing phosphaalkenes

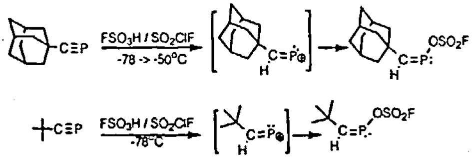
Thanks to the highly versatile chemistry of phosphaalkynes, they have developed into an important class of low-coordination organophosphorus compounds which can function as building blocks for the rapid assembly of numerous new molecules and cations. Several review articles and book chapters have summarized the progress which has been achieved in this field over the past two decades.[1-7] Utilizing the synthetic methods developed by Regitz and coworkers, beginning with two kinetically stable phosphaacetylenes **1-2** which are more conveniently accessible, various cyclooligomers (such as **3** and **4**) can be synthesized chemoselectively via cycloaddition reactions. Cycloaddition also provides access to **5** as a key derivative for phosphirene chemistry (Fig 1). In relation to our work in carbocation and onium ion chemistry, we have been involved in electrophilic chemistry of the above compounds and their derivatives as a means to generate interesing phosphorus cations and molecules.[8-14]

Fig 1



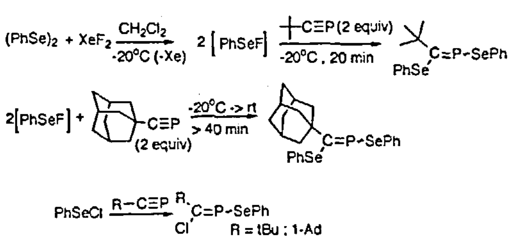
A persistent phosphavinyl cation has not yet been directly observed; low temperature protonation of **1-2** produced the corresponding phosphaalkenes by initial C-protonation and counter ion quenching to give phosphaalkenes by *anti* addition (Fig. 2). High level theoretical calculations showed that C-protonation is favored over P-protonation and at higher levels a cyclic cation was found to be the minimum.[12]

Fig 2



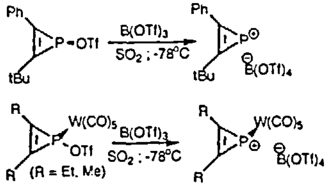
In experiments designed to produce phosphaalkenes by fluoroselenenylation of **1-2** with "PhSeF" via $(PhSe)_2/XeF_2$, double phenyl selenenylation was observed, whereas with PhSeCl, chloroselenenylation was the outcome but with "$PhSe^+$" attacking at P (Fig 3):[13]

Fig 3



In the field of phosphirene chemistry, ionization of the triflate derivative with $B(OTf)_3$ in SO_2 produced a persistent phosphirenylium cation, deshielded by 313 ppm relative to the precursor (Fig 4)[11] ; multinuclear NMR and theory suggest aromatic character. Solvation with SO_2 is a key factor in lowering the energy barrier to ionization. The topic has been examined in detail computationally.[15] The W-complexed analogue has also been generated and studied by multinuclear NMR (Fig 4).[16]

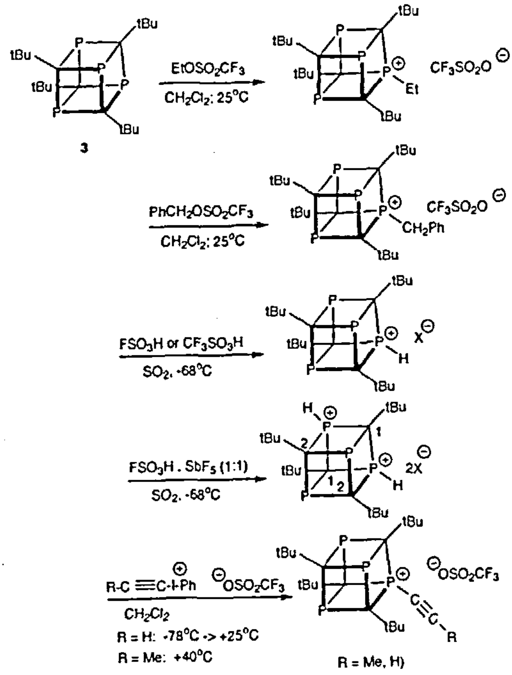
Fig 4



Focusing on the electrophilic chemistry of **3**, decreased basicity/nucleophilicity at P is due to n P -> σ PC delocalization, thus showing a novel P/C bonding state with net positive charge at P and net negative charge at the cage carbons.[4]

Monoalkylation at P was achieved using potent alkylating agents such as MeOTf, EtOTf, "$PhCH_2OTf$" and $TMSCH_2OTf$ to furnish stable mono-phosphonium salts, mono- and diprotonation were effected in superacids at low temperature, and monoalkynylation was achieved with electron-deficient alkynes to give the P-alkynylated salts (Fig 5):[8,9]

Fig 5



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