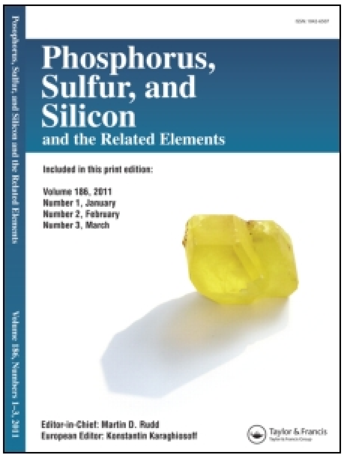

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New Advances in the Chemistry of the Phosphirene Ring

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NEW ADVANCES IN THE CHEMISTRY OF THE PHOSPHIRENE RING

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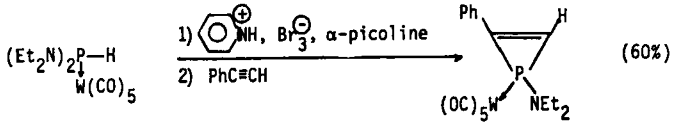
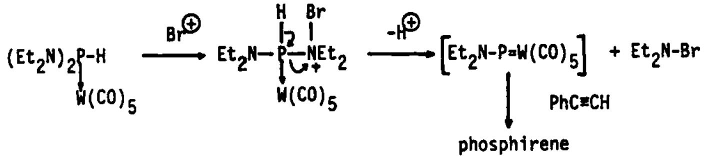
Abstract : Some recent developments of the chemistry of phosphirenes are reviewed. They include two new syntheses of the ring, a preliminary investigation on the reactivity of 1-chlorophosphirenes and various ring expansions.

The phosphirene ring occupies a very peculiar position among phosphorus heterocycles. Firstly, it is by far the most strained carbon-phosphorus heterocycle ever described in the literature. As a consequence, its intracyclic P-C bonds are bent and show an abnormal reactivity. Secondly, it forms the basis of a whole series of potentially aromatic 2π- and antiaromatic 4π-systems containing phosphorus. Thirdly, it is an ideal synthon for building larger heterocycles. Thus, since its discovery in our laboratory[1], we have devoted a lot of efforts to the study of this ring and we wish to summarize here our latest results in this field.

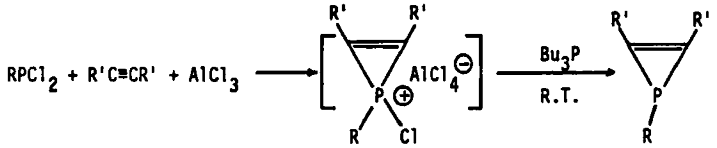
The initial synthesis of this ring[1] started from phosphole P-complexes and consequently was rather sophisticated. Since then we have devised an alternate synthesis which uses more classical starting products[2] :



We think that the first step of the mechanism of this synthesis involves the attack of positive bromine at a nitrogen lone pair. Then, the abstraction of a proton by α-picoline leads to a terminal phosphinidene complex which reacts as usual with the acetylenic compound to give a phosphirene :

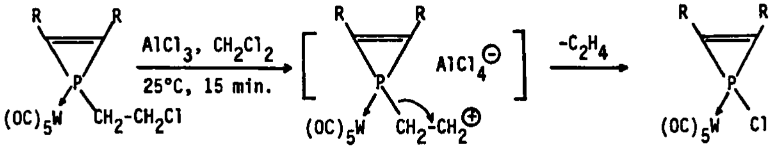


More recently, we have found[3] an even simpler synthesis of tervalent phosphirenes which relies on the in situ reduction of the Hogeveen's adducts[4] :

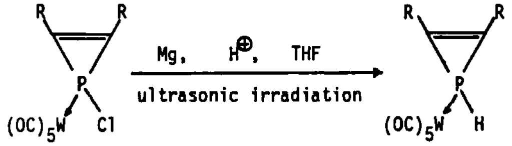


This route is obviously the shortest one for the non functional compounds but it does not work when $R = OR''$, NR''_2, Cl, etc...

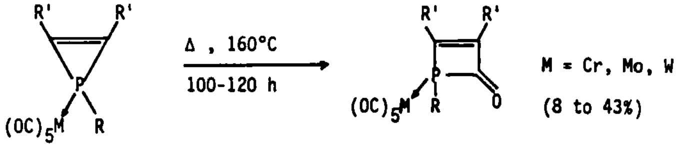
In order to have an access to potentially aromatic phosphirenyl cations, we needed to prepare 1-chlorophosphirenes. We have devised two methods for preparing their tungsten complexes. The first one relies on the HCl cleavage of the P-N bond of 1-aminophosphirene complexes prepared as described here before. The second one starts from 1-β-chloroethylphosphirene complexes[5] :



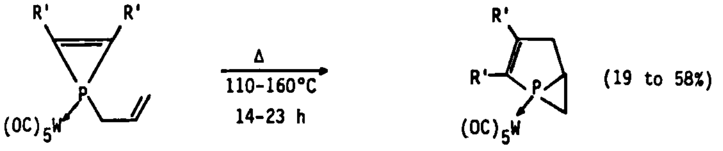
It seems clear that the driving force for this abnormal loss of ethylene is the "aromaticity" of the complexed phosphirenyl cation. At the present time, attempts at decomplexing these chloro species have given unsatisfactory results. The reduction of these complexed chlorophosphirenes has been successfully achieved using magnesium and a source of proton in THF. The chemistry of these P-unsubstituted species is described elsewhere.[6] Noteworthy in the context of this lecture is the fact that the complexed phosphirenyl anions seem to be highly unstable (the opening of the ring takes place upon metalation by n-BuLi at -70°C).



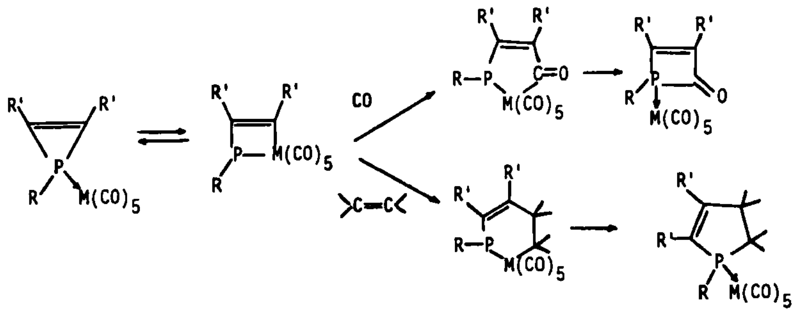
From a completely different standpoint, various ring expansions have been observed which can be related to the weakness or (and) to the π-character of the P-C intracyclic bonds (for a theoretical discussion on this topic, see ref 7). The first one was observed when heating phosphirene metal carbonyl complexes for long periods of time[8]:



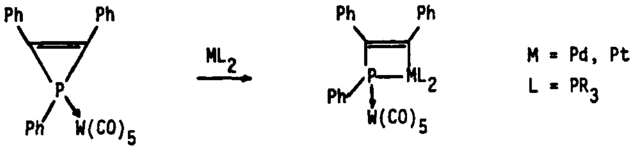
The second one was observed when heating 1-allylphosphirene complexes[9]:



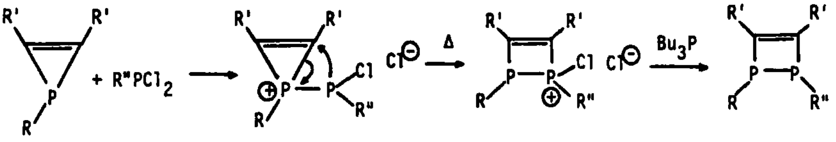
We believe that these two ring expansions have a common mechanism transiently involving an insertion of the metal into the ring :



Then, the second step would be a classical insertion of carbon monoxide or olefin into a transition metal-carbon bond. In collaboration with J.F. Nixon, we have demonstrated that it is indeed very easy to insert a transition metal such as platinum into the internal P-C bonds of phosphirenes[10]:



Finally, we have also been able to formally insert phosphinidenes into the phosphirene ring[11] :



In such a way, we have an easy and versatile access to a wide range of new 1,2-diphosphetenes.

It seems quite obvious that numerous other developments of the organic and coordination chemistry of phosphirenes will take place in the near future.

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