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# Phosphorus, Sulfur, and Silicon and the Related Elements

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## 4-π-Electron 4-Membered Phosphorus Heterocycles

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#### 4-π-ELECTRON 4-MEMBERED PHOSPHORUS HETEROCYCLES

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Abstract The synthesis and reactivity of  $4-\pi$ -electron 4-membered heterocycles possessing a phosphazene moiety is described. Key Words Heterocycles, phosphazene rings, Aza-Wittig reactions, diazirines.

#### INTRODUCTION

We have recently shown that the presence of only one phosphorus atom possessing no available p-orbital is sufficient to stabilize a  $4-\pi$ -electron 4-membered ring[1]. Here, we report on the synthesis, structure and reactivity of such heterocycles possessing a phosphazene moiety.

#### SYNTHESIS

The target phosphazene rings have been obtained via ring contraction or ring expansion reactions. Extrusion of dinitrogen from  $1.2.3.4\lambda^5$ -triazaphosphinine 1 and 2 occured in refluxing toluene giving  $1,2\lambda^5$ -azaphosphetes 3 and 4 in 80 and 90% yield, respectively (Scheme 1)[1]. Phosphinocarbene 7[2] reacts with benzonitrile in toluene, at room temperature, affording 3-phenyl-2,2-[bis(dicyclohexylamino)phosphino](trimethylsilyl)-2H-azirine 6 in 85% isolated yield. Interestingly, addition at room temperature of a catalytic amount of (p-cymene)ruthenium(II)chloride to a dichloromethane solution of 6, leads to the 1,2 $\lambda^5$ -azaphosphete 5 in 95% yield (Scheme 1)[3a].



The key step of the synthetic route used for the preparation of the  $1,3,2\lambda^5$ diazaphosphete 9 is also a ring expansion from a transient N-phosphinoisodiazirine 8. This anti-aromatic three-membered ring 8 is transiently formed in the reaction of bromophenyldiazirine with bis(dicyclohexylamino)trimethylstannylphosphine, and spontaneously rearranges to 9 in 26 % isolated yield (Scheme 2)[4a].



#### CHARACTERIZATION AND STRUCTURE

Derivatives 3, 4, 5 and 9 exhibit some common spectroscopic data. Their <sup>31</sup>P NMR chemical shifts are around + 52 ppm ( $\pm$  2 ppm) and the  $\beta$  carbon with respect to the phosphorus atom gives a signal at very low field in <sup>13</sup>C NMR spectra [ $\underline{\delta}^{13}$ C  $\beta$ : +182.4 (3), +181.7 (4), +192.4 (5), +194.7 (9)]. Derivatives 3[1a] and 9[4b] have been characterized by X-ray diffraction studies. Both four-membered rings are nearly planar and, of particular interest, the exocyclic P-N bonds are shorter than the endocyclic ones. On the other hand, the values of the endocyclic bond lengths are halfway between those of single and double bonds. These data as a whole indicate that there is a positive charge located at the phosphorus atom and that the NCX part of the molecule can be regarded as an allylic anion. Thus, in agreement with ab initio calculations [4b], 4- $\pi$ -electron 4-membered heterocycles possessing a phosphazene moiety are best described as cyclic ylides (Figure 1).

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#### REACTIVITY

Derivatives 3, 4, 5 and 9 behave as aza-Wittig reagents as illustrated by the reaction involving diazaphosphete 9 and dimethyl acetylenedicarboxylate which gives rise to diazaphosphinine 10 in 70% yield[4b]. However, some unusual reactions are also observed. Phosphazenes react with isothiocyanates and isocyanates to give carbodiimides and the corresponding phosphine sulfide and oxyde, respectively[5]. In marked contrast, methyl isothiocyanate inserts into the phosphazene bond of 5 affording six-membered heterocycle 11. In the same veine, trimethylsilyl isocyanate reacts with 3 leading, after hydrolysis, to heterocycle 12 (scheme 3)[1b]. Compound 12 exists as a hydrogenbonded dimer in the solid state and of particular interest has a structure comparable to that of cytosine, the  $C(NH_2)_2$  being replaced by a  $P(NiPr_2)_2$  group.



Complexation of the nitrogen atom of the phosphazene moiety occured on adding Lewis acids or transition metal fragments. Two equivalents of BH<sub>3</sub> react with diazaphosphete 9 leading to double adduct 13[4b], while azaphosphete 3 reacts at room temperature with half an equivalent of PdCl<sub>2</sub>(PhCN)<sub>2</sub> giving the bis( $\eta^{1}$ azaphosphete)palladium(II) complex 14 in 65% yield[1c]. From the spectroscopic data and X-ray analyses, it appears that the  $4-\pi$ -electron 4-membered ring structures are only slightly perturbated by the complexation of the ring nitrogens (scheme 4).



#### CONCLUSION

These results demonstrate that  $4-\pi$ -electron 4-membered rings featuring a phosphazene moiety are thermodynamically stable but highly reactive; they are valuable building blocks in heterocyclic chemistry and ligands for transition metal complexes.

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