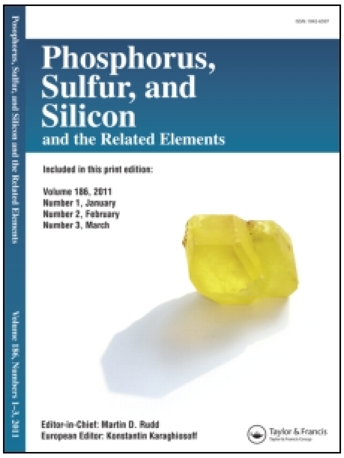


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

4-π-Electron 4-Membered Phosphorus Heterocycles

Regis Reau; Antoine Baceiredo; Guy Bertrand

To cite this Article Reau, Regis , Baceiredo, Antoine and Bertrand, Guy(1996) '4-π-Electron 4-Membered Phosphorus Heterocycles', Phosphorus, Sulfur, and Silicon and the Related Elements, 109: 1, 429 — 432

To link to this Article: DOI: 10.1080/10426509608545182

URL: http://dx.doi.org/10.1080/10426509608545182

Phosphorus, Sulfur, and Silicon, 1996, Vols. 109–110, pp. 429–432
Reprints available directly from the publisher
Photocopying permitted by license only

4-π-ELECTRON 4-MEMBERED PHOSPHORUS HETEROCYCLES

REGIS REAU, ANTOINE BACEIREDO and GUY BERTRAND*
Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne, 31077
Toulouse Cédex, France

Abstract The synthesis and reactivity of 4-π-electron 4-membered heterocycles possessing a phosphazene moiety is described.

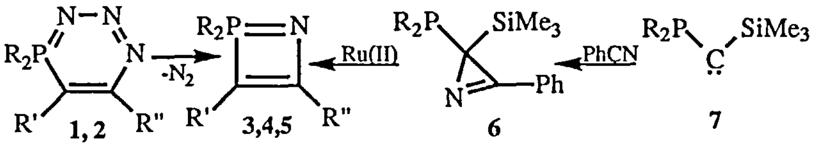
Key Words *Heterocycles, phosphazene rings, Aza-Wittig reactions, diazirines.*

INTRODUCTION

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

SYNTHESIS

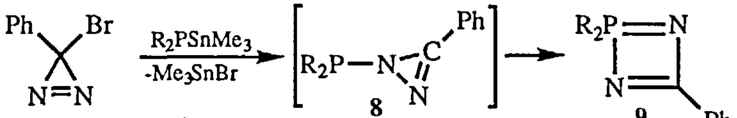
The target phosphazene rings have been obtained via ring contraction or ring expansion reactions. Extrusion of dinitrogen from 1,2,3,4λ^5-triazaphosphinine **1** and **2** occured in refluxing toluene giving 1,2λ^5-azaphosphetes **3** and **4** in 80 and 90% yield, respectively (Scheme 1)[1]. Phosphinocarbene **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 1,2λ^5-azaphosphete **5** in 95% yield (Scheme 1)[3a].



1, 3: R = i-Pr_2N, R' = R" = CO_2Me 5: R = i-Pr_2N, R' = $SiMe_3$, R" = Ph
2, 4: R = c-Hex_2N, R' = R" = CO_2Me 6, 7: R = c-Hex_2N

Scheme 1

The key step of the synthetic route used for the preparation of the 1,3,2λ^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].



R = c-Hex_2N

Scheme 2

CHARACTERIZATION AND STRUCTURE

Derivatives 3, 4, 5 and 9 exhibit some common spectroscopic data. Their ^{31}P NMR chemical shifts are around + 52 ppm (± 2 ppm) and the β carbon with respect to the phosphorus atom gives a signal at very low field in ^{13}C NMR spectra [$\underline{\delta}^{13}C$ β: +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-π-electron 4-membered heterocycles possessing a phosphazene moiety are best described as cyclic ylides (Figure 1).

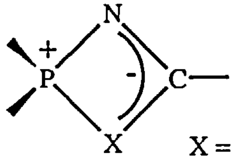
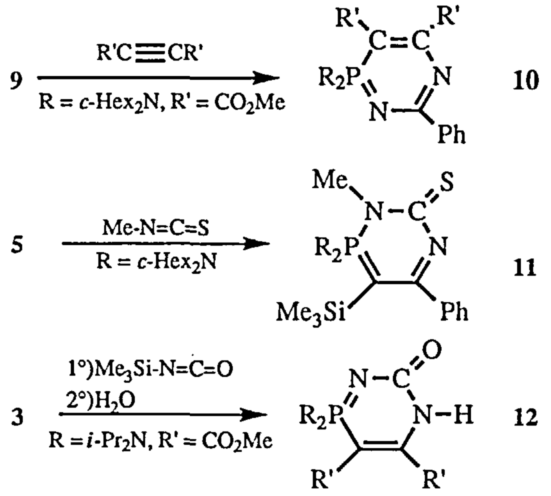


Figure 1

X = N or C-R

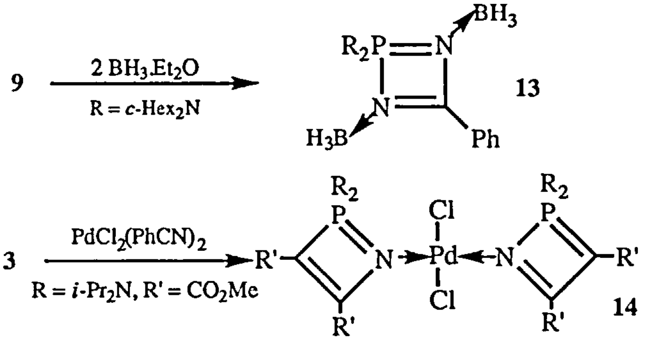
REACTIVITY

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 hydrogen-bonded 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.



Scheme 3

Complexation of the nitrogen atom of the phosphazene moiety occured on adding Lewis acids or transition metal fragments. Two equivalents of BH_3 react with diazaphosphete 9 leading to double adduct 13[4b], while azaphosphete 3 reacts at room temperature with half an equivalent of $PdCl_2(PhCN)_2$ giving the bis(η^1-azaphosphete)palladium(II) complex 14 in 65% yield[1c]. From the spectroscopic data and X-ray analyses, it appears that the 4-π-electron 4-membered ring structures are only slightly perturbated by the complexation of the ring nitrogens (scheme 4).



Scheme 4

CONCLUSION

These results demonstrate that 4-π-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.

REFERENCES

1. (a) J. Tejeda, R. Réau, F. Dahan and G. Bertrand, *J. Am. Chem. Soc.*, **115**, 7880 (1993).
   (b) K. Bieger, J. Tejeda, R. Reau, F. Dahan and G. Bertrand, *J. Am. Chem. Soc.*, **116**, 8087 (1994).
   (c) Unpublished results
2. G. Alcaraz, R. Reed, A. Baceiredo and G. Bertrand, *J. Chem. Soc. Chem. Commun.*, 1354 (1993).
3. G. Alcaraz, U. Wecker, A. Baceiredo, F. Dahan and G. Bertrand, *Angew. Chem. Int. Ed. Engl.*, **34**, 246 (1995).
   (b) Unpublished results.
4. (a) G. Alcaraz, A. Baceiredo, M. Nieger and G. Bertrand, *J. Am. Chem. Soc.*, **116**, 2159 (1994).
   (b) Unpublished results.
5. A. W. Johnson, W. C. Kaska, K. A. O. Starzewski and D. A. Dixon (Wiley and Sons, New York, 1993), p. 403.