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## Phosphorus, Sulfur, and Silicon and the Related Elements

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## 2-Π- and 3-Π-Electron Diphosphorus-Containing 3-Membered Heterocycles

YVES CANAC<sup>a</sup>, DIDIER BOURISSOU<sup>a</sup>, HEINZ GORNITZKA<sup>a</sup>,  
WOLFGANG W. SCHOELLER<sup>b</sup>, ANTOINE BACEIREDO<sup>a</sup> and  
GUY BERTRAND<sup>a</sup>

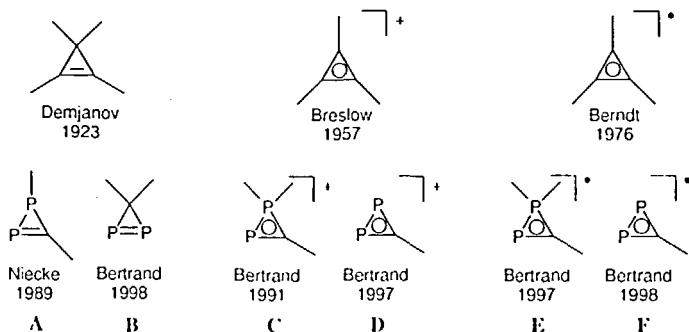
<sup>a</sup>Laboratoire de Chimie de Coordination, 205 route de Narbonne, 31077 Toulouse  
cedex (France) and <sup>b</sup>Fakultät für Chemie der Universität,  
Postfach 10 01 31 D-33615 Bielefeld (Germany)

The heterolytic cleavage of the P-N bond of the coordinated 1*H*-diphosphirene **5** gives the corresponding diphosphirenium complex **6**, while the homolytic cleavage of the P-N bond of the free 1*H*-diphosphirene **4** affords the transient diphosphirenyl radical **7** and the ensuing stable dimer **8** which features original half P-P bonds.

**Keywords:** three-membered rings; aromaticity; half bonds; singlet diradical; benzene valence isomers

### INTRODUCTION

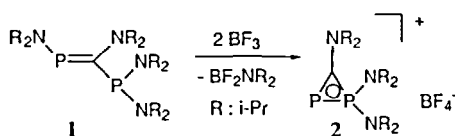
The chemistry of phosphorus often lags behind its analogues in carbon chemistry. For example, cyclopropenes,<sup>1</sup> cyclopropenyl cations<sup>2</sup> and cyclopropenyl radicals<sup>3</sup> have been known for some considerable time, while before our work,<sup>4</sup> compound **A**<sup>5</sup> was the only known diphosphorus-containing unsaturated three-membered ring system (Scheme 1). Here we report on the synthesis of derivatives of type **A**, **C**, **D** and **F**, and give an example of a type of compound which is not yet known in the carbon series.



SCHEME 1

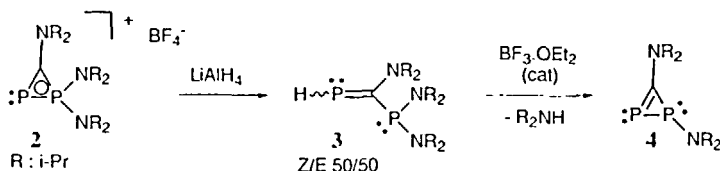
## RESULTS AND DISCUSSION

Treatment of the phosphalkene **1** with two equivalents of  $\text{BF}_3 \cdot \text{Et}_2\text{NH}$  complex at room temperature afforded the diphosphirenium salt **2**, the first derivative of type C, as non-air sensitive pale-yellow crystals (mp  $118^\circ\text{C}$ ) in 60 % yield (Equation 1). This compound was fully characterized including an X-ray diffraction study.<sup>6</sup> Due to the presence of a  $\sigma^4$  phosphorus center, the delocalization of the two  $\pi$ -electrons is much less effective than in cyclopropenyl cations.



EQUATION 1

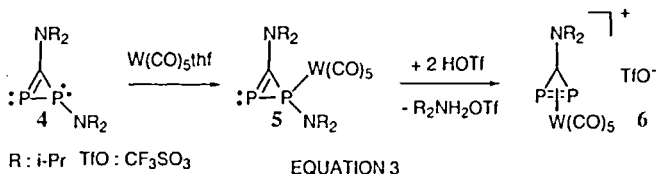
Addition of one equivalent of lithium aluminium hydride to a thf solution of **2** afforded the corresponding *P*-hydrogenophosphaalkene **3** as a 50/50 mixture of *Z* and *E* isomers in 80% total yield. Then, to induce the 1,3-elimination reaction of diisopropylamine, a thf solution of **3** was treated at room temperature with a catalytic amount (5%) of  $\text{BF}_3 \cdot \text{OEt}_2$ . After work up, derivative **4**, a compound of type A, was obtained as a light yellow oil in 65% yield (Equation 2).<sup>7</sup> Note that the  $\sigma^3$  phosphorus center of *1H*-diphosphirenes is strongly pyramidalized<sup>5</sup> and therefore these cyclic four- $\pi$ -electron systems are in fact non anti-aromatic.



EQUATION 2

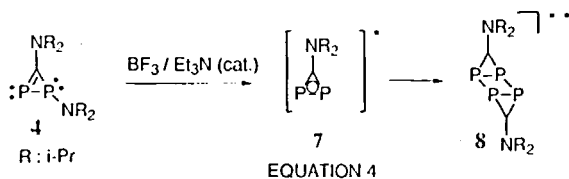
The corresponding coordinated *1H*-diphosphirene **5** was obtained in 65% yield by treating **4** with  $\text{W}(\text{CO})_5(\text{thf})$ .<sup>7</sup> The heterolytic cleavage of the P-N bond of **5** was achieved with two equivalents of trifluoromethanesulfonic acid at  $-78^\circ\text{C}$  affording **6**, the first diphosphirenium salt **D**, as a highly air and water sensitive red oil, stable for days in solution at room temperature (Equation 3).<sup>8</sup> The  $\eta^2$ -coordination mode of the heterocycle in **6** (via the P=P bond) was deduced from the spectroscopic data: the  $^{31}\text{P}$

NMR spectrum shows only one singlet at -157.4 ppm in the range expected for a three-membered phosphorus heterocycle. In contrast with diphosphirenium salts **C**, diphosphirenium salts **D** are strongly related to cyclopropenyl cations (P is isolobal to the CH fragment) and are therefore potentially aromatic systems.



The homolytic cleavage of the P-N bond of **4** was achieved with catalytic amounts of BF<sub>3</sub> (5%) and Et<sub>3</sub>N (5%) in tetrahydrofuran at 50°C for 2 hours leading to a diamagnetic red solution. After evaporation of the solvent and extraction with pentane, compound **8** was isolated in 45% yield as red crystals (mp 140°C) (Equation 4).<sup>9</sup> The molecular weight, obtained by mass spectrometry corresponded to a dimer of the diphosphirenium radical **7**. The <sup>31</sup>P proton coupled NMR spectrum showed only a singlet at -164.5 ppm, suggesting the presence of a three-membered ring framework and the absence of an amino group at phosphorus. The high symmetry of the structure was confirmed by the <sup>1</sup>H and <sup>13</sup>C NMR spectra.

Additionally, a single crystal X-ray diffraction study of **8** was performed. In the solid state, the molecule is organised around an inversion centre located at the middle of a rectangular P<sub>4</sub> framework, which is almost perpendicular to two three-membered rings. Interestingly, the PP bonds between the two three-membered rings [2.634(3) Å] are by far the longest PP bonds ever reported, but are clearly less than twice the phosphorus van der Waals radii (3.8 Å). This unusual value was readily rationalized by *ab initio* calculations which predict that the two three-membered rings are linked by two P-P half bonds, or formally one-electron P-P bonds.



Interestingly, compound **8** is the first valence isomer derivative of a tetraphosphabenzene and can be related, in the corresponding carbon series, to *anti*-tricyclohexylene **G**. Up to now, only *cis*-Dewar benzene **H**, benzvalene **I**, prismane **J**, and bicycloprop-2-enyl **K** have been observed experimentally (Scheme 2). The singlet biradical **G** has not yet been discovered, although it is calculated to be only 83 kJ/mol higher in energy than **K**.



SCHEME 2

## CONCLUSION

Derivatives **2**, **4** and **6** are diphosphorus-containing analogues of the well-known cyclopropenes and cyclopropenyl cations whereas compound **8** is related to the hitherto unknown singlet biradical **G**. The isolation of **8** suggests that in phosphorus chemistry, half bonds should play an important role.

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