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Synthesis and Characterization of a Stable Cyclic *gem*-Bis(phosphaylide): a 4π-Electron Three-Membered Heterocycle

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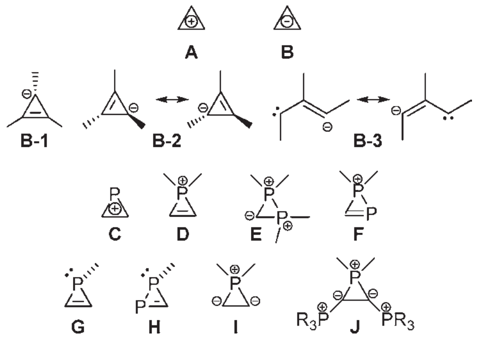
S *Supporting Information*

ABSTRACT: The mixed P,S-bisylide **1** reacts with phosphenium salts, affording phosphoniophosphinocarbenes, with elimination of diphenyl sulfide. Using a more compact cyclic phosphenium cation, the reaction leads to the formation of an original three-membered heterocycle featuring a *gem*-bisylide function. This molecule represents the first isolable analogue of the phosphirenyl anion derivative.

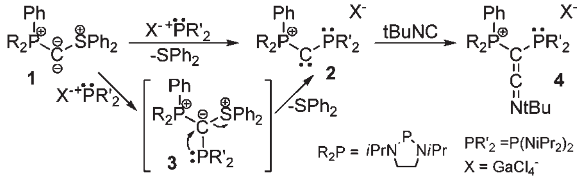
The cyclopropenium cation **A** (Chart 1) and the cyclopropenyl anion **B** are the smallest aromatic and antiaromatic compounds.[1] Since the synthesis of the first cyclopropenium cation in 1957,[2] numerous experimental and computational studies have been realized on aromatic derivatives of type **A**. In contrast, because of its instability and high reactivity, the antiaromatic species **B** remains elusive. Indeed, a series of pioneering works by Breslow showed that the parent molecule ($C_3H_3^-$) shows a pK_a value higher than those of simple alkyl anions.[3,4] To date, substituted cyclopropenyl anions have only been detected in the gas phase.[5] Computational studies[6] predicted that the D_{3h}-symmetric molecule with a cyclic electron delocalization is not a minimum in the energy surface but "ethenyl"-type **B-1** and "allyl"-type **B-2** with pyramidalized carbon atoms are the two most stable cyclic structures, and the open-chain structure **B-3** is close in energy.

In the case of phosphorus-containing analogues,[7] in addition to the classical π-aromatic species such as σ^2,λ^3-phosphirenium cation **C**,[8] hyperconjugative σ^* aromaticity can also be considered.[9] Several types of three-membered two-π-electron cyclic species such as mono- and diphosphirenium cations containing σ^4-phosphorus atoms (**D**[10] and **E**[11]) as well as a diphosphirenium cation including mixed-valence **F**[12] have been synthesized. However, potentially antiaromatic derivatives with 4π electrons are extremely rare molecules. In fact, the only known examples are 2*H*-phosphirene **G**[13] and diphosphirene **H**,[14] which are not antiaromatic systems because of the strongly pyramidalized tricoordinate phosphorus center.[15] The cyclic *gem*-bisylide **I** can be considered as a potentially σ^*-antiaromatic version of the unknown phosphirenyl anion. Here, we report the synthesis and isolation of the first stable three-membered cyclic *gem*-bis(phosphaylide) **J**, a σ^4-phosphirenyl anion stabilized by two phosphonio fragments.

Chart 1



Scheme 1. Electrophilic Substitution Reaction of P,S-Bisylide 1 with Phosphenium Cations



Recently, we reported the synthesis of a stable mixed P,S-bisylide **1** featuring two different ylide functions (phosphonium and sulfonium), which behaves as an unsymmetrical atomic carbon source.[16] Taking advantage of the neutral sulfide ligand as an excellent leaving group, we considered reactions with electrophiles possessing a lone pair on the reactive site, such as a phosphenium cation.

The reaction of bisylide **1** with bis(diisopropylamino) phosphenium salt in tetrahydrofuran cleanly affords the phosphonio(phosphino) carbene **2** (Scheme 1), which is stable up to −30 °C. It can be trapped by reaction with *tert*-butyl isocyanide, leading to the corresponding ketenimine derivative **4**. The process can be rationalized by the first addition of phosphenium salt to the central carbon of **1**, leading to the transient formation of cationic ylide **3**. Because of π donation of the phosphino group, intermediate **3** undergoes sulfide elimination to give **2**.[17]

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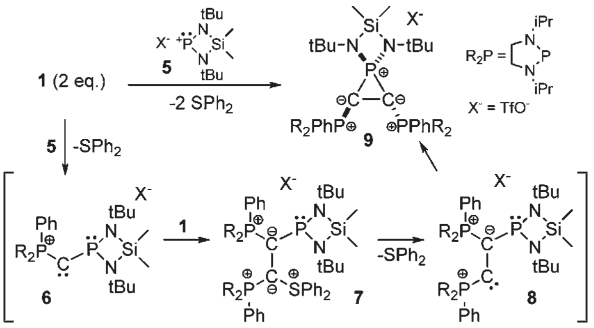
Scheme 2. Electrophilic Substitution Reaction of P,S-Bisylide **1** with Phosphenium Salt **5**



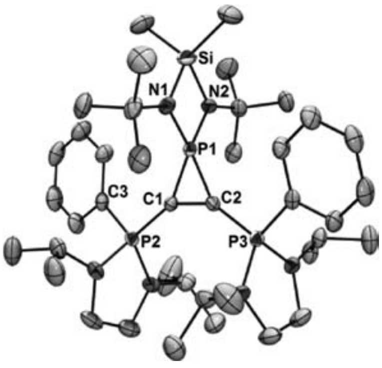


Figure 1. Molecular structure of **9**. Thermal ellipsoids represent 30% probability. Hydrogen atoms and the triflate anion are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−C1 1.680(4), P1−C2 1.682(4), P2−C1 1.677(4), P3−C2 1.673(4), C1−C2 1.558(6); C1−P1−C2 55.22(19), C2−C1−P2 143.9(3), C2−C1−P1 62.4(2), P2−C1−P1 151.4(3), C1−C2−P3 142.8(3), C1−C2−P1 62.3(2), P3−C2−P1 152.0(3).

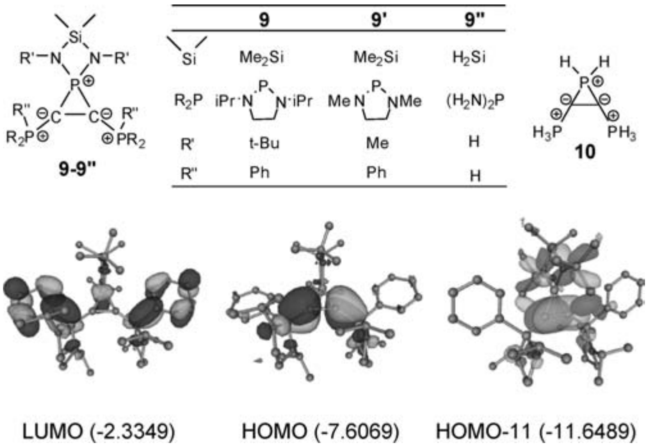
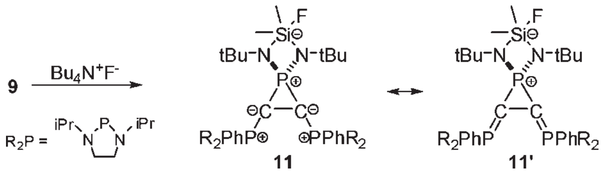


Figure 2. Selected molecular orbitals of **9** calculated at the M05-2X/6-31G(d) level. The energies of the molecular orbitals are given in electronvolts.

Scheme 3. Reaction of **9** with Tetrabutylammonium Fluoride



Using the more compact four-membered cyclic phosphenium cation **5**, the reaction consumes 2 equiv of bisylide **1**, leading to a three-membered heterocycle **9** featuring a *gem*-bisylide function (Scheme 2). In ^{31}P NMR, **9** exhibits a typical AX_2 system in agreement with a symmetrical structure, and the ring carbon atoms appear at 41.0 ppm as a doublet of doublet of doublets (J_{CP} = 245.6, 58.1, and 10.0 Hz) in the ^{13}C NMR spectrum. Like in the precedent reaction, here again it is reasonable to postulate the transient formation of carbene **6**, which could react with a second 1 equiv of bisylide **1**, leading to phosphonio ylide carbene **8**, after elimination of a second molecule of diphenyl sulfide. Then, an intramolecular interaction between the phosphine and carbene centers leads to **9**. However, we could not detect any intermediate by NMR spectroscopy, even at low temperature, probably because of the rapid reaction of transient carbene **6** with phosphenium cation **5**. Indeed, the reaction of **1** with only 1 equiv of **5** results in the formation of **9**, with 0.5 equiv of phosphonium salt **5** remaining intact.

The X-ray structure of **9** reveals a spiro[2,3]cyclic structure with a quaternary phosphorus as the spiroatom (Figure 1).[18] The exocyclic P−C bonds (1.677 and 1.673 Å) are shorter than those observed for phosphonio−phosphonium ylides (1.70−1.73 Å) and are as short as those for a nonstabilized ylide (H_2CPMe_3: 1.67 Å),[19] suggesting a strong interaction of the lone pairs with the two adjacent phosphonio centers. The two cyclic carbon centers are almost planar with a sum of bond angles of 357.19°, but the P2−C1−C2−P3 fragment is slightly twisted (torsion angle: 31.88°). The C1−C2 bond (1.558 Å) is substantially long for a $C_{sp^2}-C_{sp^2}$ single bond in a three-membered cyclic structure (1.43−1.47 Å).[20]

To gain more insight into the electronic structure of **9**, density functional theory calculations were performed (see the Supporting Information). The geometry optimization at the M05-2X/6-31G(d) level closely reproduced the X-ray structure.[21,22,23] The π-symmetry orbitals in the three-membered ring are found in LUMO, HOMO, and HOMO−11 (Figure 2). The HOMO of the molecule is mainly localized on the carbon atoms in antibonding π symmetry, which delocalize toward exocyclic phosphorus atoms. The Wiberg bond indexes for P1−C1 (0.948) and P2−C1 (1.158) are significantly small in spite of the short P−C bond distances. The bond index for C1−C2 (0.957) corresponds to a single bond, indicating the absence of cyclic delocalization of π electrons. In contrast to the almost planar carbon centers in the three-membered ring **9**, the calculated geometries of the parent molecules **10** and **9''** show strongly pyramidalized tricoordinate carbon centers ($\Sigma\theta_C$: 310° and 312°, in contrast with the 359° and 340° computed for **9** and **9'**, respectively). These results suggest that the planar structure of **9** is mainly due to steric interactions.

To assess the (anti)aromatic character of **9**, the out-of-plane component of the NICS tensor was calculated (see the Supporting Information). NICS$(0)_{zz}$ is +5.4 ppm, thus indicating an antiaromatic character. However, NICS$(1)_{zz}$ is −2.2 ppm, probably because of the influence of substituents. Indeed, for **9'** both values are positive (+3.5 and +0.4 ppm, respectively).

In contrast, for **9″** and **10**, where the carbon centers are strongly pyramidalized, all values are negative. It is interesting to note that, for model geometries of **9′** and **9″** with nearly planar rings, all values become positive, which indicates their increased antiaromatic character.

Although **9** is relatively inert probably because of significant steric protection, the fluoride anion attacks at the silicon atom, affording the corresponding neutral three-membered cyclic product **11** featuring a pentacoordinate silicon center (Scheme 3).

The X-ray structure of **11**[18] shows two elongated endocyclic P−C bonds (1.7136 Å; 1.7175 Å) and shortened exocyclic P−C bonds (1.6603 Å; 1.6576 Å) compared to those observed for **9**, indicating significantly weakened P−C π interactions in the ring probably due to the increased electron density on the spirophosphorus atom. Thus, **11** can be best represented as an exocyclic bisylide, **11′**. However, it is interesting to note that the C−C bond length (1.548 Å) remains on the same order and even is slightly shorter than that in **9** (1.558 Å) in spite of an expected enhanced electrostatic repulsion between the negatively charged carbon atoms.

In conclusion, we have demonstrated that the mixed P,S-bisylide **1**, because of the lability of the sulfide ligand, undergoes substitution reactions with phosphenium cations, which transform the C(0) complex into transient carbene species. Furthermore, this methodology was successfully applied to the synthesis of the first isolable phosphirenyl anion derivative stabilized by two phosphonio substituents. Further research on other applications of this new methodology and on the chemical behavior of the new phosphorus heterocycles **9** and **11** is under active investigation.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental procedures, selected NMR data, X-ray crystallographic files for **9** and **11** (CIF), computational details, geometry parameters, and NICS values of the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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