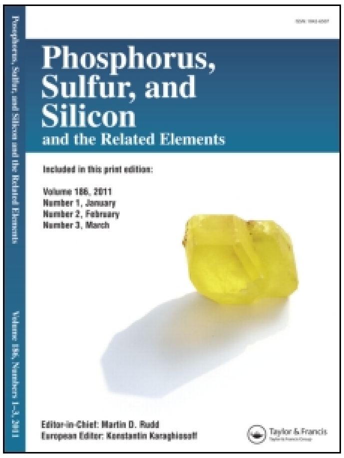

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FROM 1,3-DIPHOSPHETANE-2,4-DIYLS TO CYCLIC ANIONS AND CATIONS

M. Sebastian[a]; O. Schmidt[a]; A. Fuchs[a]; M. Nieger[a]; D. Szieberth[a]; L. Nyulaszi[a]; E. Niecke[a]
[a] Universität Bonn, Bonn, Germany

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FROM 1,3-DIPHOSPHETANE-2,4-DIYLS TO CYCLIC ANIONS AND CATIONS

M. Sebastian, O. Schmidt, A. Fuchs, M. Nieger, D. Szieberth,
L. Nyulaszi, and E. Niecke
Universität Bonn, Bonn, Germany

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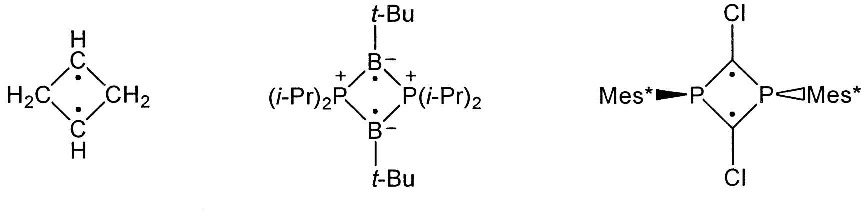
*The interest in diradicals has grown by the increasing number of stable diradicals which have been synthesized during the last few years. The diphosphacyclobutane-diyles have a diradicaloid molecular structure and they were the first diradicals to be prepared in the gramme scale. The combination of stability and high yield synthesis creates the opportunity both to change the substitution pattern or to prepare different valence isomers. Current experimental and computational studies reveal that electron transfer reactions of maintain the cyclic system. In the contribution, the oxidation reaction of **1** to the radical cation **2** and the cyclic diphosphaallyl cation **3** will be reported. Additionally, the remarkable mechanism of the reaction of **1** at first to the radical anion **4** but particularly to the diphosphacyclobutadiene dianion **5** under reductive conditions will be presented in detail.*

Keywords: Diphosphallyl cations; diphosphetane diyls; diradicals

Traditionally, singlet-diradicals like the cyclobutane-1,3-diyl **1**[1] have been characterized as short-lived molecules, that exist for only a few fractions of a second or are only isolable at low temperatures in a matrix (Figure 1). It was astonishing, therefore, when the first stable singlet diradicals were produced. A 1,3-diphospha-2,4-diboracyclobutane-2,4-diyl **2** has recently been reported by Bertrand et al.[2] In 1995, we reported the synthesis of a singlet diradical 1,3-diphosphetane-2,4-diyl **3** with an untypically high stability.[3]

For these diradicals **I** the transannular ring closing to the bicyclic isomer **II** is thermally forbidden,[4] however, it is possible to perform the ring closing reaction, photochemically[5] (Scheme 1). Under thermolysis,

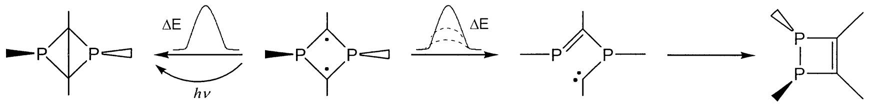
Address correspondence to E. Niecke, Institut fur Anorganische Chemie, Rheinische Friedrich Wilhelms, Universität Bonn, Gerhard-Domagk Str. 1, 53121 Bonn, Germany. E-mail: enicke@uni-bonn.de



1 **2** **3**

FIGURE 1 Cyclic diradicals.

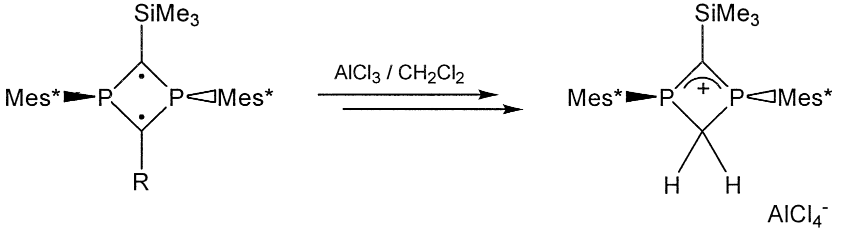
a ring-opening is observed, forming a cryptocarbene **III** which rearranges to the most stable valence isomer, the diphosphete **IV**.[6]



II I III IV

SCHEME 1

The barrier to this ring opening is dependant on the substitution pattern of the ring atoms.[7] By varying this substitution the diradical then becomes stable against isomerization under ambient conditions. This extraordinary stability, and the fact that the compound can be prepared in gram quantities, allowed us to examine the chemistry of these diradicals.



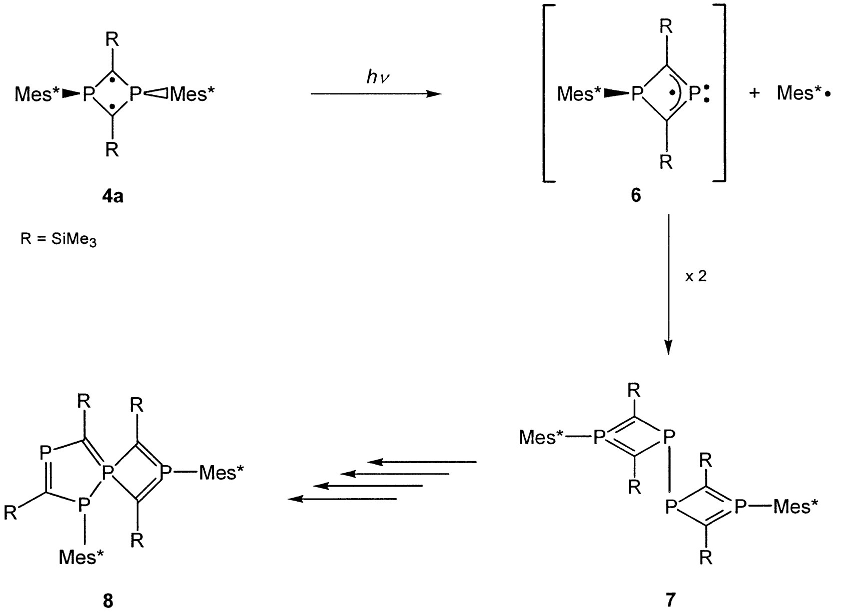
4a **5**

R = SiMe$_3$

SCHEME 2

A cyclovoltametric experiment on the persilylated diradical **4a** (R = SiMe$_3$) shows that the compound can undergo a reversible oxidation (by

0.85 V) and the radical cation has been identified by EPR spectroscopy.* To see whether this oxidation could also be carried out by chemical methods, $AlCl_3/CH_2Cl_2$ was chosen as an oxidizing agent (Scheme 2). The cyclic 1,3-Diphosphaallyl cation **5** could be isolated from the reaction mixture.[8] The cationic nature of **5** is confirmed by NMR investigations. The ^{13}C-NMR shows a signal lying in the range of carbenium ions, which can be assigned to the ring carbon atom with the $SiMe_3$ substituent. The low field shift of the signal in the ^{29}Si-NMR spectrum in comparison to **4a** indicates that the $SiMe_3$ group is also deshielded. The crystal structure shows that the $(P_2)C$—Si bond length significantly increased by about 4 pm compared to **4b** (R = H). The possibility of cleaving the electrophilic trimethylsilyl group is currently being investigated.



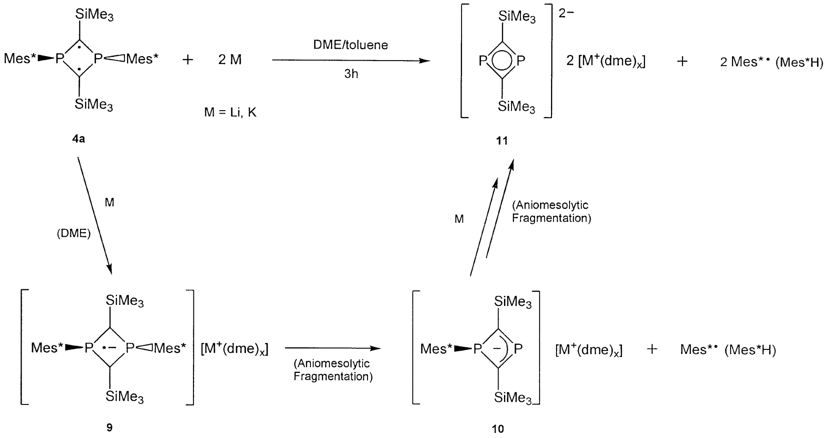
SCHEME 3

It has been mentioned previously that the irradiation of the diradicals **I** leads to the formation of bicyclic species **II**. In the case of **4a** (R = $SiMe_3$), the transannular ring closing has not been observed because of the very large steric interactions of the axial $SiMe_3$ groups.[5] Instead, the irradiation of compound **4a** leads to the cleavage of an aryl radical (Scheme 3). The resulting phosphaallyl radical **6** forms a dimer **7**, as

*EPR-measurements were carried out by A. Elvers, U. Zenneck, Universität Erlangen.

identified by ^{31}P-NMR investigations. Surprisingly, the spirocyclic compound **8** has been isolated from the reaction mixture and characterized by x-ray crystallography.

The discovery that the persilylated diradical **4a** can selectively undergo photochemical P—C_{aryl} bond cleavage stimulated our investigation to initiate the bond cleavage via electron transfer reagents such as alkali metals.



SCHEME 4

If **4a** is reacted under reducing conditions with alkali metals, remarkably, both aryl substituents are cleaved from the diradical, and the previously unknown lithium, or potassium salt of the 1,3-diphosphacyclobutadiendiide **11** is formed[9] (Scheme 4). In the case of the **11***[Li^+(dme)]$_2$, we were able to isolate x-ray quality crystals, and the crystal structure has been solved. This structure shows that the lithium complex can be described as a solvent stabilized ion pair and the four-membered P_2C_2-ring possesses C_i symmetry. The CSi-bonds are slightly shorter than similar bonds in the silyl substituted cyclobutadiene dianions, synthesized by Sekiguchi.[10]

To clarify the mechanism of this surprising reaction, extensive theoretical calculations (B3LYP/6-31+G*) have been carried out. These calculations show that this process occurs via an aniomesolytic fragmentation of the P—C_{aryl} bond. The diradical **4a** is reduced by one electron, forming a radical anion **9***[Li^+(dme)$_x$]. There is a slight barrier of about 6 kcal/mol before the aniomesolytic fragmentation occurs, forming an aryl radical (observed as 1,3,5-tri*tert*-butylbenzene and a cyclic phosphaallyl anion **10***[Li^+(dme)$_x$]. The phosphaallyl anion has been experimentally characterized by NMR spectroscopy. Reduction of **10***[Li$^+$(dme)$_x$] initiates the second fragmentation step leading to the dianion product **11***[Li$^+$(dme)]$_2$.

Besides of these oxidation, photochemical and reduction reactions the diversity of reactions is completed with substitution and cryptocarbene reactions, or valence isomerizations which have been reported previously.

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