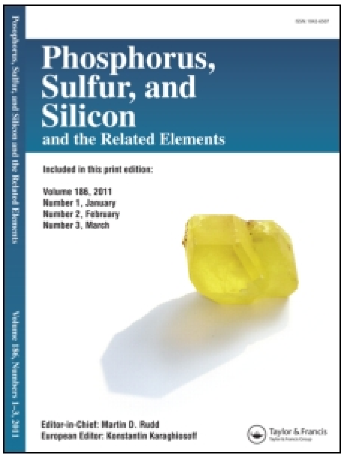

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Diphosphetane-Diyles: Diradical or Hückel-Aromatic ? from Orbital and Structural Isomerism to Radical Cations and Anionic Carbenes

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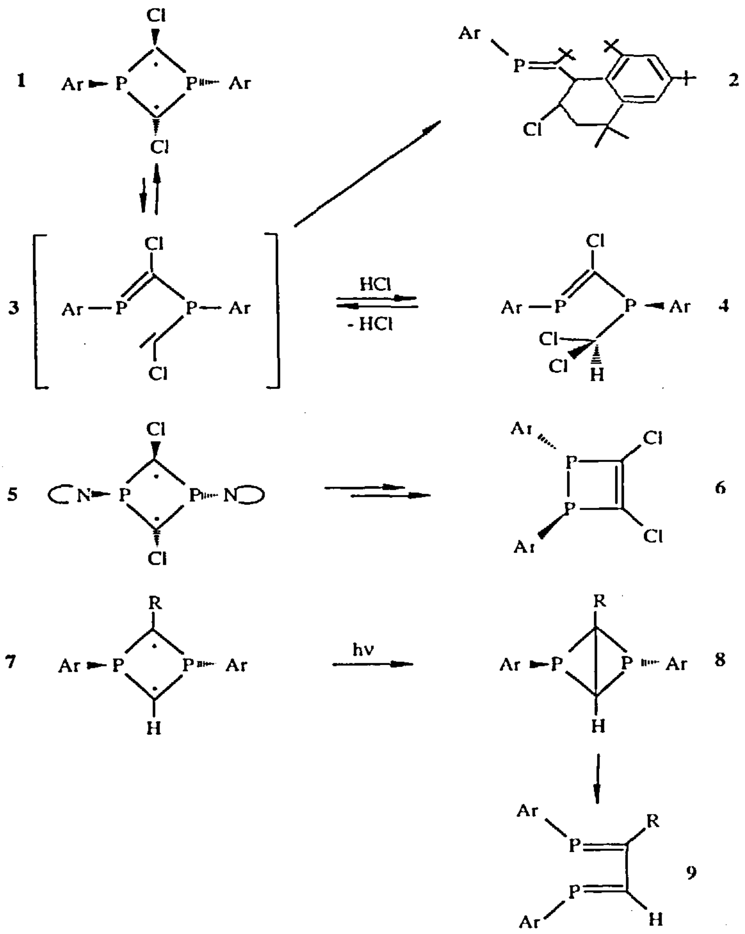
The synthesis, crystal structure and bonding properties of various diphosphetane-diyles are discussed and compared with those of other valence isomers. Experimental studies revealed that interconversion of different isomers are possible. Furthermore, it will be shown that diphosphetane-diyles can serve as building blocks in organo phosphorus as well as metal organic chemistry.

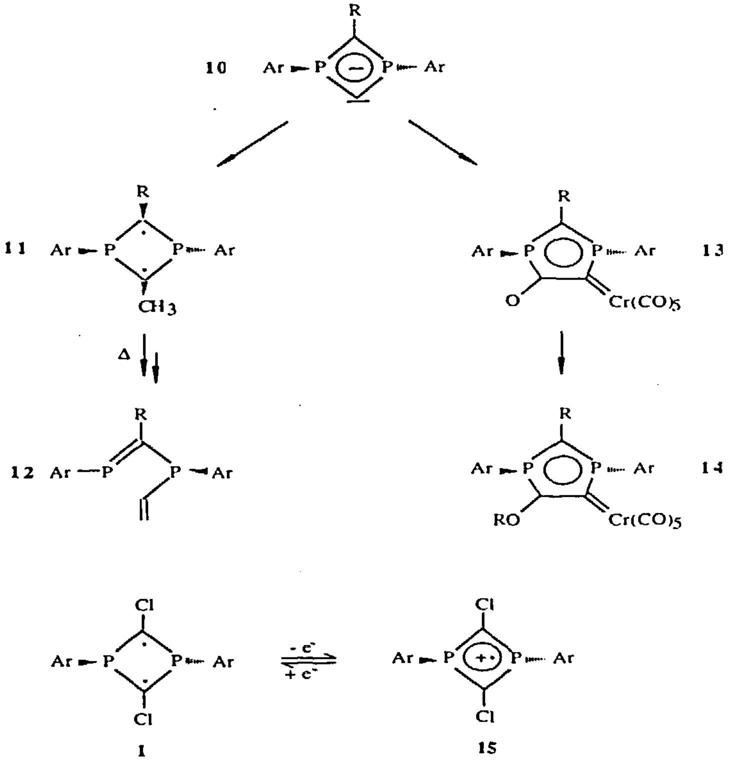
It is well established that within the series 2,4-diphosphabicyclobutane, 1,4-diphosphabutadiene, and 1,2-diphosphetene, the bicyclic sytem is the least and the cyclic butene derivative is the most stable isomer/1/. Recently we have proven the existence of a further valence isomer, viz. the 1,3-diphosphacyclobutane-2,4-diyle ($[Mes^*PCCl]_2$ **1**), which possess a diradicaloid molecular structure with a low lying triplet state/2/. Even if the diradicaloid is the least stable member of the whole family of isomers, their existence owes to the fact that the thermal isomerisation yielding the 2,4-diphosphabicyclobutane is forbidden according to the Woodward-Hoffmann rules. While compound **1** is stable at ambient temperatures, it isomerizes on heating to give the corresponding diphosphapropene derivatives **2** /2/. Phosphinocarbene **3** is assumed to be an intermediate. of this reaction. The existence of the latter was further proven indirectly by the formation of a 1,3-diphosphapropene **4** by addition of hydrogen halide/3/. The HCl-addition product **4** of the transient "carbene" **3** can be used itself as a precursor for **1**, in the presence of a suitable base/3/.



To prove the substitution effect on the chemical behaviour we have synthesized a series of biradicaloids with σ-acceptor (σ-donor) substituents at the phosphorus (carbon) positions, which were expected to increase the inversion barrier at phosphorus (lower the inversion barrier at carbon) and bringing the biradical character (cyclic delocalisation) to the fore. Characteristic examples of both types are the 1,3-diphosphacyclobutane-2,4-diyles, **5** and **7**, which exhibit quite different thermal stabilities. While **5** isomerizes even in the solid state at ambient temperatures to produce the *trans*-1,2-diphosphetene **6** /4/, compound **7** exhibits a remarkable thermal stability. However, UV-treatment results spontaneously in a *trans*-annular C-C linkage to give the 2,4-diphosphabicyclobutane **8**, which can be considered as an orbital isomer of the 1,3-diphosphacyclobutane-2,4-diyle **5**. Heating of the bicyclus **8** results in a valence isomerization giving the *cis/gauche*-1,4-diphosphabutadiene **9** in accordance with quatum chemical calculations /5/.

Deprotonation of compound **7** results in the formation of the "carbenic like" anion **10**. As a strong nucleophile this anion can serve as a precusor for a variety of derivatives, as it is compound **11**, which slowly isomerizes thermally at ambient temperatues via ring opening and formation of a 1,4-phosphapentadiene **12** /3/. However, of more interest is the smooth reaction with transition metal carbonyls, e.g. $Cr(CO)_6$, resulting, via CO-insertion, in the formation of the anionic cylic phosphinocarbene complex **13** /3/. Consecutive reaction with suitable electrophiles leads to neutral carbene complexes **14**/3/.

Furthermore, the redox properties of the diphosaphetane-diyle **1**, will be given. The reversible formation of the radical cation **15** is proven by CV as well as ESR experiments/6/.



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