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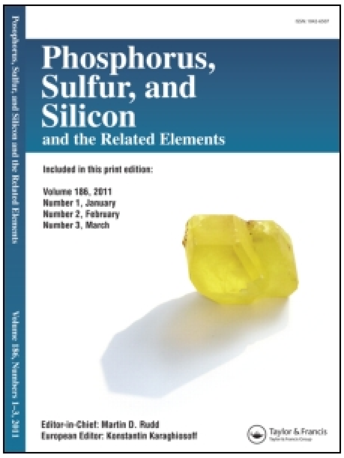

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NOVEL ASPECTS IN THE SYNTHESIS OF CARBENOIDS CONTAINING P/C-pπ-BONDS

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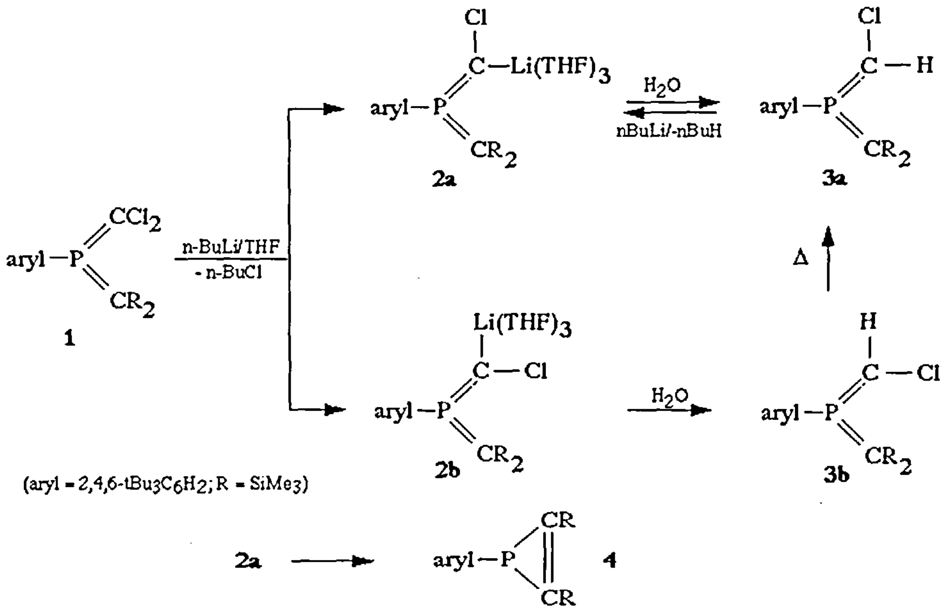
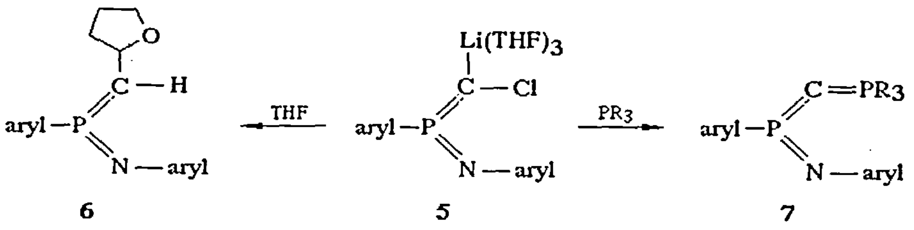
Abstract The synthesis and x-ray structure analysis of a novel type of carbenoids, aryl-P(=E)=C(Cl)Li(thf)$_3$ (E=N-aryl, C(SiMe$_3$)$_2$), as well as the first example of a 1,3-diphosphetane-2,4-diyl, (aryl-PCCl)$_2$, is reported and on the basis of quantum chemical calculations its bonding situation is discussed. Furthermore, selected examples for the varying reaction behavior of both types of compounds are presented.

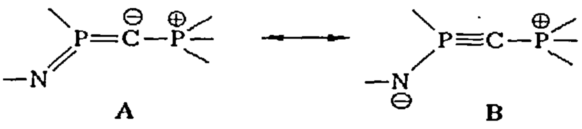
Carbenoids with a carbenoid center incorporated in a π-system have been attributed a great deal of interest. With respect to the existence of a heteroatom substituted species of this type , a phosphanyl carbenoid has been detected recently by nmr spectroscopy and its chemistry has been exploited in some detail[1].

Now we found that the bis(methylene)phosphorane **1**, acts as a suitable starting compound to a novel type of carbenoids , which upon reaction with *n*-butyl lithium afforded the two isomers **2a,b**; their constitution has been proven by NMR spectroscopy. Quenching the reaction with water results in the hydrogen substituted bis(methylene)phosphoranes **3a,b**, of which **3a** could be isolated in pure form. Hydrogen/lithium exchange with this isomer (**3a**) led selectively to the carbenoid **2a** and the structures of **2a** and **3a** were subjected to X-ray crystallographic studies[2]. Quantum chemical calculations on the model compounds, $HP(=CH_2)=CClLi$, $HP(=CH_2)=CClLi(H_2O)_3$, $HP(=CH_2)CCl^-$, indicate the importance of the donor solvent for the stabilization of the carbenoid and reveal a formal relationship between the solvated carbenoid with the free carbanion. LiCl elimination of **2a** occured at -10°C and resulted in the formation of the phosphirene, **4**.

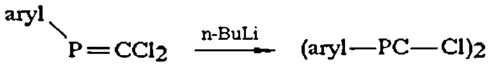


By analogy, starting from the imino(methylene)phosphorane, aryl-P(=Naryl)=CCl_2, the corresponding iminophosphoranylidene carbenoid **5** was obtained. The constitution of **5** was proven by NMR spectroscopy and suitable trapping experiments. On heating to -10°C **5** reacted by elimination of LiCl with addition of the solvent (thf) to **6**, while in the presence of phosphanes (Ph_3P, $(Me_2N)_3P$) a novel type of carbodiphosphoranes, **7** was obtained[3]. The X-ray structure analysis of **7a,b** indicated a high degree of P/C-multiple bonding (PC 158.8 [159.2 pm], ∢ PCP 149.3 [157.5°]), as summarized in the following canonical valence bond formula A and B[4].



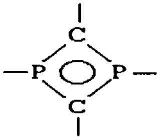


Surprisingly, starting from the methylenephosphane, aryl-P=CCl_2, reaction with *n*-butyl-lithium in the molar ratio of 2:1 afforded a novel type of PC-heterocycles 8[5].

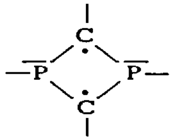

$$\text{aryl}{-}P{=}CCl_2 \xrightarrow{\text{n-BuLi}} (\text{aryl}{-}PC{-}Cl)_2$$

8

According to the x-ray analysis 8 forms a planar $(PC)_2$-skeleton with the substituents at the carbon and the phosphorus atoms suited in a *trans* configuration (PC 175.0°; CPC 87.8°; PCP 92.2°; $\Sigma \sphericalangle$ P 337°; $\Sigma \sphericalangle$ C 347°). Ab initio calculations (at MCSCF level) reveal for the parent structure, $(HPCH)_2$, a singlett ground state with C_i-symmetry, with a small singlet triplet energy separation (with MRCI correction). The configuration interaction procedure results in two dominant contributions. The first one accounts for delocalization within the ring system (as is found in S_2N_2) while the mixing in of the second contribution introduces biradical character within the ring system. Both contributions can be summarized by the two resonance structures **C** and **D**.

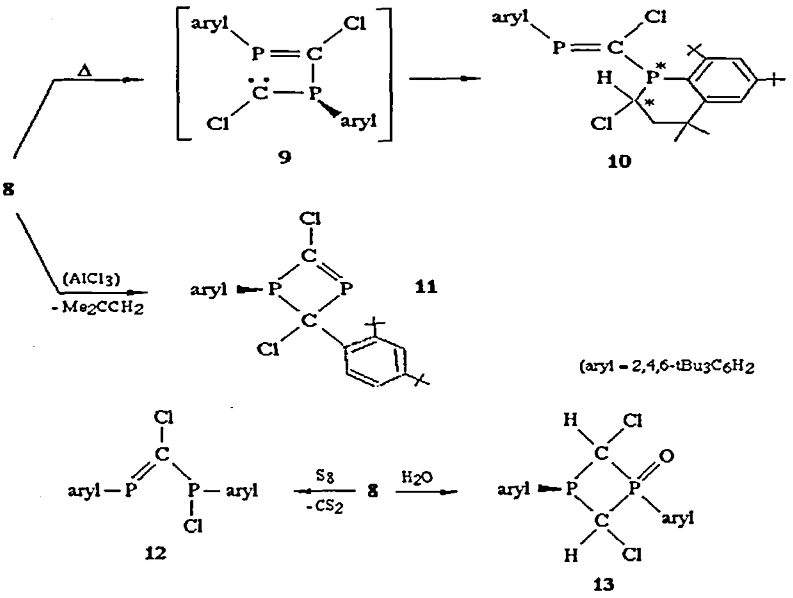


C



D

On heating the heterocycle 8 in toluene isomerized under cleavage of one PC-bond affording to two stereoisomeric diphosphapropene-derivatives **10**. The constitution of the main product was confirmed by x-ray structure analysis. As an intermediate the phosphinocarbene **9**, was assumed which stabilizes by CH-activation involving one of the *o*-tert.-butyl group of the aryl substituent. However, in the presence of a Lewis acid ($AlCl_3$), a 1,3-diphosphetene **11** was formed; by aryl shift from the phosphorus to the carbon atom and loss of Me_2CCH_2. Reaction of the heterocycle 8 with sulfur or water produced the 1,3-diphosphapropene **12** (via shift of the chlorine from the carbon to the phosphorus atom and loss of CS_2) and the 1,3-diphosphetane **13**. The latter was structurally confirmed by X-ray analysis (PC 184.5, 189.0, 187.9; CPC 82.3°, 84.5°; PCP 94.8°, 94.3°).



Furthermore, ab initio calculations on the different isomers of parent 1,3-diphosphetane-2,4-diyl yield the following relative energies: HP=CH-P(H)-C(H): (+14); HP-CH-CH-PH (-37); HP=CH-CH=PH(-49); HP-CH=CH-PH(-52); P=CH-P(H)-CH_2 (-54 kcal/mole).

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