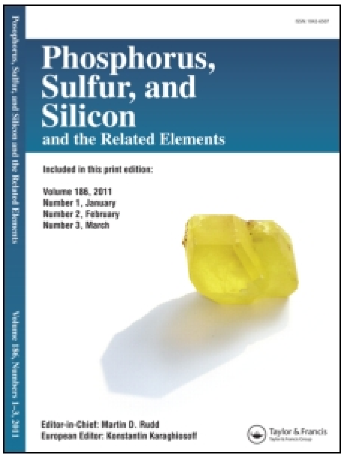

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P-*Functionalized Phosphaalkenes and Iminophosphines: New Results*

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P-FUNCTIONALIZED PHOSPHAALKENES AND IMINOPHOSPHINES: NEW RESULTS

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Abstract Synthesis, structures, spectroscopic data, and novel reactions of P-[bis(dialkylamino)methyleneamino]- and P-[bis(dialkylamino)methylenephosphino]-substituted phosphaalkenes, iminophosphines and phosphenium ions are discussed.

INTRODUCTION

In recent years we and other authors have reported the synthesis of a number of stable, highly reactive two-coordinate phosphorus derivatives including those with the P-Si, P-Hlg, P-P and P-O bonds.[1] These species were shown to be of considerable interest as important precursors for a broad spectrum of products which can be obtained by nucleophilic or electrophilic substitution without affecting the P=C,P=N or P=P bonds. We have since extended our researches to reaction chemistry of the functionalized phosphenium ions and dienic like systems of the type $(R_2N)_2C{=}E{-}P{=}X$ (E = N, P).[2-5]

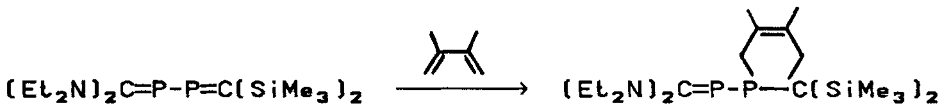
RESULTS AND DISCUSSION

Dienic like systems including dicoordinated phosphorus

Novel stable 2-aza-3-phospha- and 2,3-diphosphabutadienes have been prepared via condensation of the compounds $(R_2N)_2C{=}ESiMe_3$ (E = N, P) with $ClP{=}X$ ($X = CTms_2$, NAr). The structures and properties of these dienic like compounds are of special interest because they can be considered as potentially conjugated systems:

$$(R_2N)_2C{=}E{-}P{=}X \quad \longleftrightarrow \quad (R_2N)_2{}^{+}C{-}E{=}P{-}X^{-}$$

NMR data and X-ray structure determinations show that effective delocalization of the electron density takes place in the compounds $(R_2N)_2C=E-P=NAr$ (**1**: E = N; **2**: E = P). Thus, in the molecule $(Me_2N)_2C=P-P=NAr$ (Ar = 2,4,6-*tert*-$Bu_3C_6H_2$) the P-P distance (213 pm) is noticeably shorter than the normal P-P single bond. A strong elongation is observed for formally double P=C bond (181 pm) in relation to the standard P=C double bond length. Unlike the compounds **1** and **2** in the compounds $(R_2N)_2C=E-P=CTms_2$ (**3**: E = N; **4**: E = P; Tms = Me_3Si) a conjugation is mainly localized within the $(R_2N)_2C=E-$ fragment. In the molecule **4a** the P-P bond length (215.5 pm) is close to a usual P-P single bond length and only a slight elongation is observed for the P=C double bonds. It is essential that the backbone $N_2C=P-P=CSi_2$ is non-planar; the dihedral angle between the planes of the double bonds is equal to 51°. Apart from X-ray structure investigations this conclusion is supported by chemical behavior of the 2,3-diphosphabutadienes. In particular, the compounds **4a** easily reacts with 2,3-dimethylbutadienes to give [2+4]-cycloaddition product:



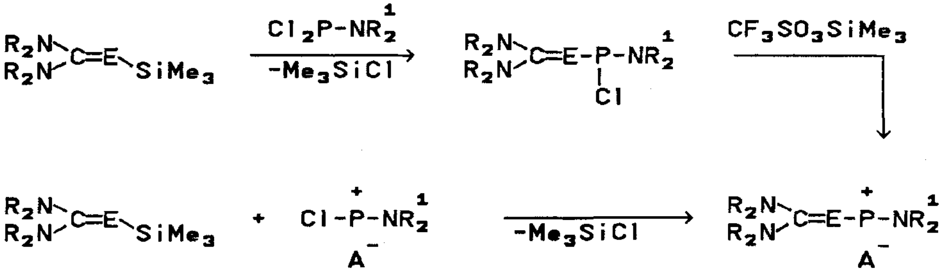
4a

Generation and transformations of bis(amino)methyleneamino- and bis(amino)methylenephosphino-substituted phosphenium cations

New reactions including the fast valence isomerization of phosphenium cations to λ^3-iminophosphines and diphosphenes have been discovered:

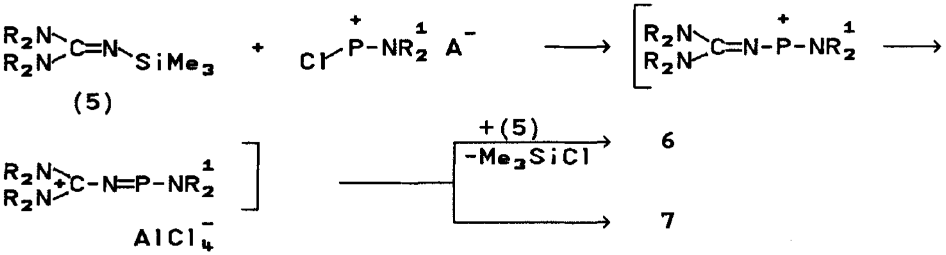
E = N,P

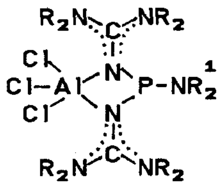
The following pathways for generation of the bis(amino)methyleneamino- and bis(amino)methylenephosphino-substituted phosphenium cations have been employed:



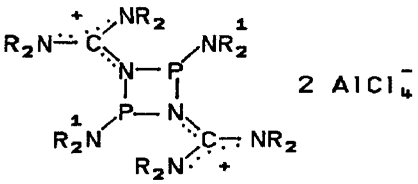
E = N, P; A = $AlCl_4$, CF_3SO_3

Depending on the ratio of reactants and the order of their mixing the coupling reactions of $(R_2N)_2C{=}NSiMe_3$ with $Cl\text{-}P^+\text{-}NR_2\ A^-$ give various products. If the chloro(amido)-phosphenium salt is slowly added into the imine solution, the reaction proceeds in a molar ratio of 1:2 and results in the formation of the cyclic compounds 6. A quite different result is observed in those cases when the imine 5 is added to chloro(amido)phosphenium salt. Addition of 1 equiv of $(R_2N)_2C{=}NSiMe_3$ at -78°C to $Cl\text{-}P^+NR_2\ AlCl_4^-$ leads to the 1,2,3,4-diazadiphosphetidines 7. We have not been able to detect the intermediate species spectroscopically, however, it seems very plausible that the reactions under consideration include the generation of methyleneamino-substituted phosphenium cations and their subsequent valence isomerization into λ^3-iminophosphines.



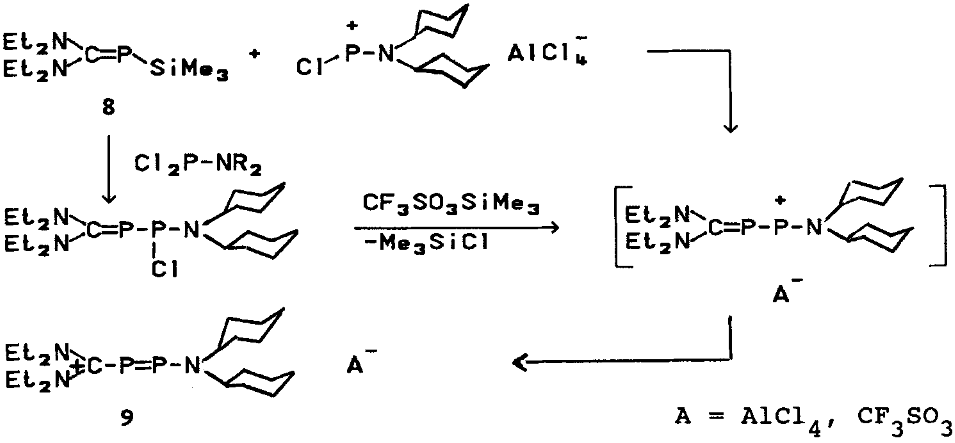


(6)



(7)

Evidence for the transient formation of the compounds $[(R_2N)_2C\text{-}E\text{=}P\text{-}NR^1_2]^+ A^-$ was given in the series of diphosphenes. Treatment of the phosphaalkene 8 with equimolar amount of $Cl_2P\text{-}NCy_2$ and the following reaction with $CF_3SO_3SiMe_3$ lead to formation of the diphosphene 9. Alternatively, the methyleneamino-phosphenium cation can be generated by coupling reaction of 8 with $Cl\text{-}P^+\text{-}NCy_2$ $AlCl_4^-$.



The compound 9 has been clearly characterized by NMR spectroscopy (δ_P 465 and 210 ppm, $^1J_{PP}$ 525 Hz) and chemical transformations.

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