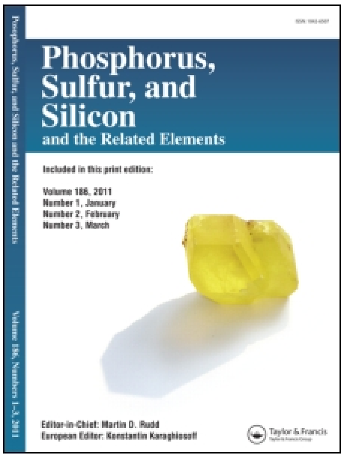

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Three-Membered Phosphorus Heterocycles by Phosphanediyl Transfer-Reactions

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THREE-MEMBERED PHOSPHORUS HETEROCYCLES BY PHOSPHANEDIYL TRANSFER-REACTIONS

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Abstract Reactions of the chloro(trimethylsilyl)phosphane $iPr_2NP(SiMe_3)Cl$ with $Cl-P=C(SiMe_3)_2$, $Et_3CP=NtBu$, $P\equiv CN(SiMe_3)iPr$, $tBuB\equiv NtBu$, as well as an intramolecular reaction of $Cl(Me_3Si)P-P=C(SiMe_3)_2$ have been carried out. We obtained in every reaction the corresponding [2+1]-cycloadducts with the iPr_2NP-unit except the latter case, there we obtained a dimer of a *3H*-diphosphirene.
The products have been characterized by means of ^{31}P- and ^{13}C-NMR, as well as single crystal X-ray crystallography.

INTRODUCTION

Several methods have been reported in the literature which give access to three-membered λ^3-phosphorus heterocycles$^{1)}$.
The usefulness of phosphanediyl-complex transfer as a new method has been demonstrated, with the synthesis of the first *1H*-phosphirene, by Mathey and coworkers$^{2)}$.
During the following years the trapping of electron-deficient species, such as substituted-silanediyl$^{3)}$ and -methanediyl$^{4)}$, by multiple bond systems became a well established synthetic method. In this work we report on the syntheses of a variety of phosphorus heterocycles according to a general route starting from substituted chloro(trimethylsilyl)phosphanes $R-P(SiMe_3)Cl^{5)}$, which serve as a synthon of phosphanediyl fragments {R-P], and multiple bond systems.

REACTIONS AND PRODUCTS

The chloro(trimethylsilyl)phosphanes have been obtained by an exchange reaction of the corresponding bis(trimethylsilyl)phosphanes with hexachloroethane[6).

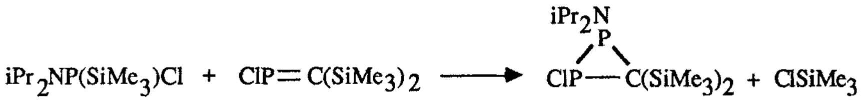
$$RP(SiMe_3)_2 + C_2Cl_6 \longrightarrow R{-}P(SiMe_3)Cl + ClSiMe_3 + C_2Cl_4 \quad (1)$$

Most of them are pale yellow oils and their ^{31}P-NMR shifts are found to be in the range 80 - 140 ppm.

As a good case in point we have used $iPr_2NP(SiMe_3)Cl$ for all further reactions with multiple bond systems. They have been carried out with a slight excess of the trapping reagent, small amounts of HMPT, and without any solvent at 20°C.

All ring products exhibits typically ^{31}P-NMR shifts and coupling constants.

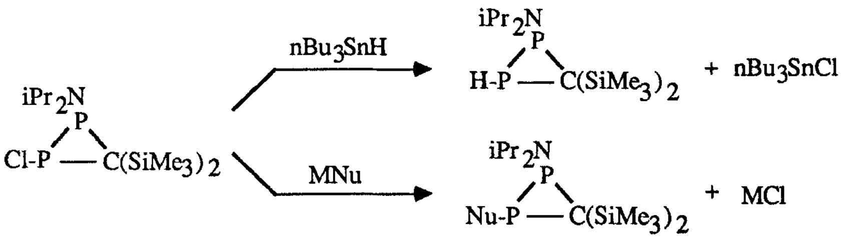
When $ClP{=}C(SiMe_3)_2$ was treated with $iPr_2NP(SiMe_3)Cl$ the following reaction occured:



(2)

The reaction is obviously more complicated, because in another case[6) a compound $Cl(R)P{-}P{=}C(SiMe_3)_2$ was observed as intermediate at low temperature by ^{31}P-NMR spectrum.

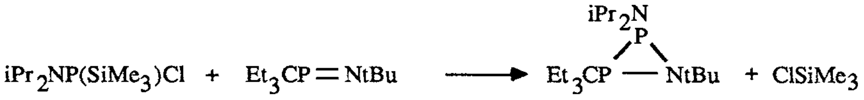
The chlorine atom in the diphosphirane has been substituted by various nucleophiles as well as hydrogen[7).



(3)

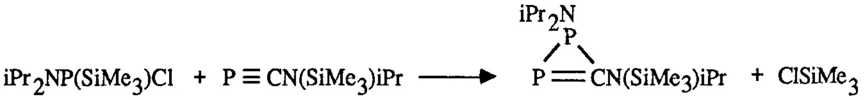
(4)

The reaction with $Et_3CP{=}NtBu$ afforded under very mild conditions the corresponding azadiphosphiridine[8].



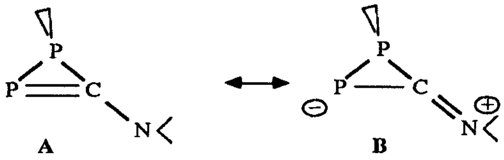
(5)

There is evidence for a 1,1-oxidation of the phosphorus atom in the iminophosphane in the first step[8]. This product would then isomerize to form the azadiphosphiridine.
The first *1H*-diphosphirene[9] was accessible by treating the phosphaalkyne $P{\equiv}CN(SiMe_3)iPr$ with the chloro(silyl)phosphane.

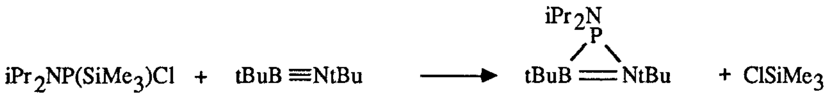


(6)

The product was confirmed by X-ray structure analysis. The bonding is interesting because the almost planar arrangement of the P(1)-C(1)-N(1)-Si(1) atoms (dihedral angle 177.6°) enables a significant π-donation of the amino nitrogen atom and this indicates a substantial participation of resonance structure **B** as well as that of resonance structure **A** in the ground state of this diphosphirene.

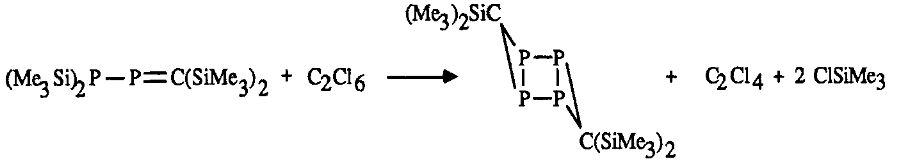


Interestingly $iPr_2NP(SiMe_3)Cl$ and $tBuB{\equiv}NtBu$ also react to give the azaphosphaboriridine[8].



(7)

Treatment of the persilylated 1,2-diphospha-2-propene with hexachloroethane under mild conditions afforded a trans-1,2,4,5-tetraphosphatricyclo[3.1.0.0$^{2.4}$]hexane.



(8)

The formation can be explained by two different reaction pathways[10)] via a diphosphirane or a diphospha-analogue of a diazoalkane leading, however, to a *3H*-phosphirene, which dimerizes spontaneously.

The conformation of the dimer was confirmed by an X-ray structure analysis.

The bonding in the diphosphirane framework exhibits an interplanar angle of 105° with respect to the planar P_4 framework. The two P-P-distances (220.4(1) and 224.5(1) ppm) are significantly different; the longer distance points to the formation of the cycloadduct from two molecules of the *3H*-diphosphirene.

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REFERENCES

1) M. Baudler, Angew.Chem.Int.Ed.Engl. 21, 492 (1982).
2) A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, J.Chem.Soc. Chem.Commun., 45 (1984).
3) A. Schäfer, M. Weidenbruch, W. Saak, S. Pohl, Angew.Chem.Int.Ed. Engl. 26, 776 (1987).
4) O. Wagner, M. Ehle, M. Regitz, Angew.Chem.Int.Ed.Engl. 28, 225 (1989).
5) R. Appel, W. Paulen, Angew.Chem.Int.Ed.Engl. 20, 869 (1981).
6) R. Streubel, E. Niecke, Chem. Ber. 123, 1245 (1990).
7) R. Streubel, E. Niecke, M. Nieger, Chem. Ber., submitted for publication.
8) R. Streubel, E. Niecke, P. Paetzold, Chem. Ber. 124, 765 (1991).
9) E. Niecke, R. Streubel, M. Nieger, D. Stalke, Angew.Chem.Int.Ed. Engl. 28, 1673 (1989).
10) E. Niecke, R. Streubel, M. Nieger, Angew.Chem.Int.Ed.Engl. 30, 90 (1991).