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## Phosphorus, Sulfur, and Silicon and the Related Elements

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## Synthesis, Structures and Reactivities of Dicoordinated Phosphorus Compounds

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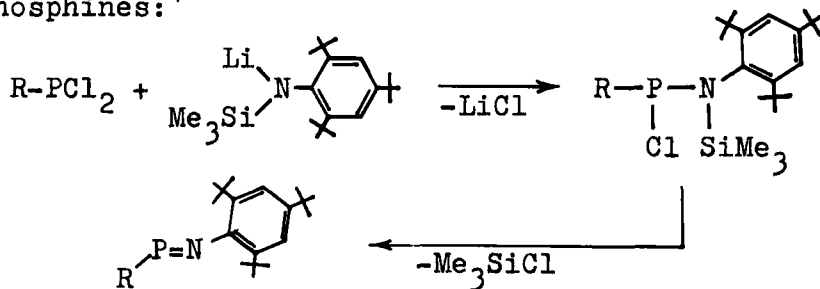
## SYNTHESIS, STRUCTURES, AND REACTIVITIES OF DICOORDINATED PHOSPHORUS COMPOUNDS

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**Abstract** The results of experimental investigations by the authors in the area of the chemistry of two-coordinate phosphorus compounds are discussed. Main attention is devoted to a consideration of the new methods for the synthesis of compounds with P=N, P=P, P=As, P=Sb bonds and their conversions.

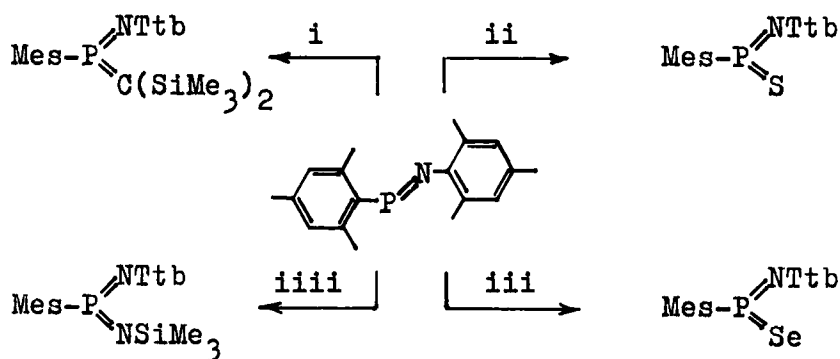
Starting in 1973 (with synthesis of the first two-coordinate phosphorus compound with a bond system N-P=N), approximately forty stable aminoiminophosphines have been synthesized so far, the stability of which is due primarily to the presence of such bulky substituents as Me<sub>3</sub>Si, t-Bu, i-Pr, t-Bu<sub>2</sub>P groups on the nitrogen atoms. However, up to date, a very few compounds with a bond system C-P=N have been described. We have extended synthetic borders of the reactions of 1,2-elimination of halosilanes in compounds of the type -P(Cl)-N(SiMe<sub>3</sub>)- for the synthesis of iminophosphines:<sup>1</sup>



R = Ph, Mes, t-Bu, 1-Ad

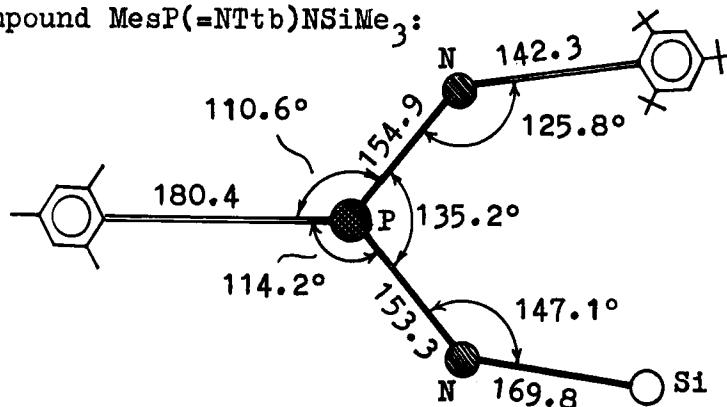
The steric shielding of the nitrogen atom appears to be the most rational approach for the stabilization of the C-P=N bond system.

The iminophosphines demonstrate rare and diverse chemical properties. A particular interest to these compounds lies in the synthesis of stable metaphosphonimidates. Some of the reactions realized by us are given on the scheme:<sup>2</sup>

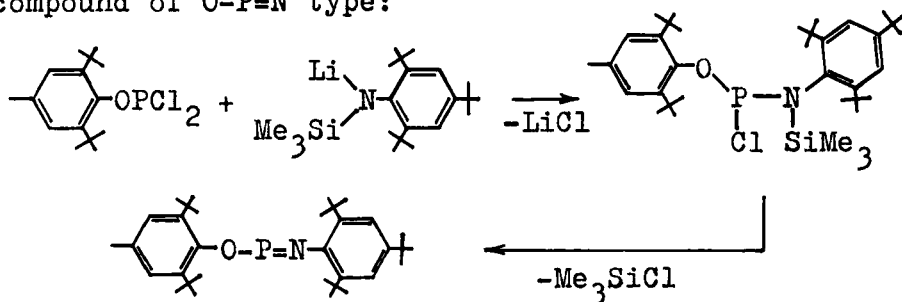


Reagents and conditions: i,  $\text{LiClC(SiMe}_3)_2$ ,  $\text{Et}_2\text{O}$ ,  $-78^\circ\text{C}$ ; ii, sulphur,  $20^\circ\text{C}$ , 10 h; iii, selenium,  $\text{C}_6\text{H}_6$ ,  $20^\circ\text{C}$ , 24 h; iv,  $\text{ClN(SiMe}_3)_2$ ,  $\text{C}_6\text{H}_6$ ,  $5^\circ\text{C}$ , 3 h

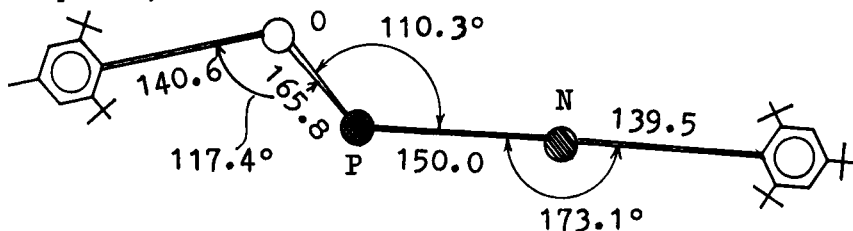
X-Ray crystallographic data have been obtained for the compound  $\text{MesP(=NTtb)NSiMe}_3$ :



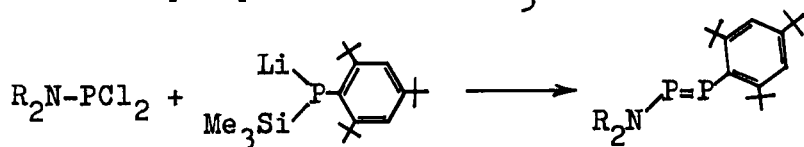
The method of reducing the coordination number of trivalent phosphorus based on the elimination of a halosilane in a sterically overloaded diad  $-P(Cl)-N(SiMe_3)-$ , has also been used successfully by us for the synthesis of the first thermally stable compound of  $O=P=N$  type:



Structural details for the resulting oxy-imino-phosphine, are summarized below:



Only two types of diphosphenes have been known up to this moment: carbosubstituted diphosphenes and bis(amino)diphosphenes. The compounds having  $N=P=P-C$  bond system have been synthesized by the reaction of aminodichlorophosphines and  $Li(Me_3Si)PTtb$ .<sup>3</sup>

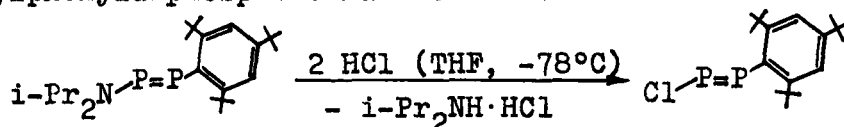


$R = Me_3Si, t-BuMe_2Si, i-Pr$

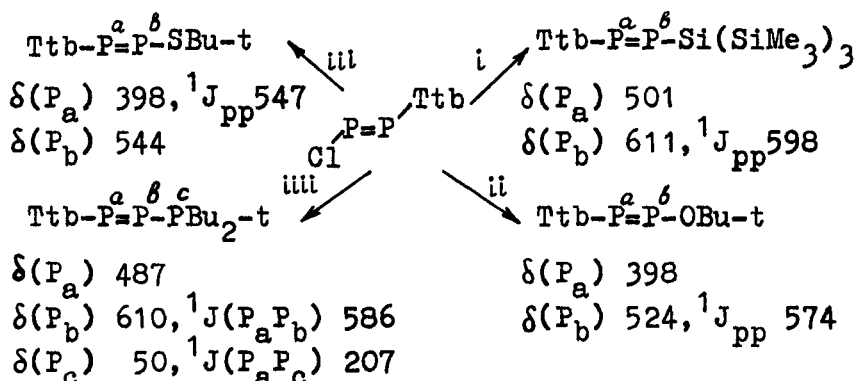
The use of  $Li(Me_3Si)PTtb$  in reactions with aminodichloroarsines  $R_2N-AsCl_2$  and aminodichlorostibines

$R_2N-StCl_2$  makes it possible to obtain aminoarsinidenphosphines  $R_2N-As=PTtb$  and aminostibulenephosphines  $R_2N-St=PTtb$ .<sup>4</sup>

In order to synthesize diphosphenes containing P-Cl bond, a route to the P-chloro-P -2,4,6-tri-tert-butylphenyldiphosphene had to be found:



P-Chlorodiphosphene retains stability at  $-30^\circ C$  and can be used as a key product in the synthesis of other types of heterosubstituted diphosphenes. The examples of the preparative use of such reactions are given on the scheme:



Reagents: i,  $(Me_3Si)_3SiLi$ ; ii,  $t-BuOLi$ ;  
iii,  $t-BuSLi$ ; iiiv,  $t-Bu_2PLi$

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