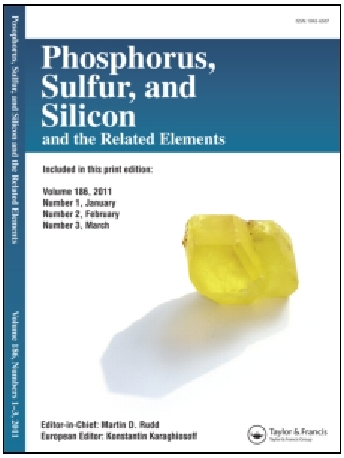

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Synthesis and investigation of new types of dicoordinated phosphorus compounds

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SYNTHESIS AND INVESTIGATION OF NEW TYPES OF DICOORDINATED PHOSPHORUS COMPOUNDS

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Abstract New synthetic methods for the preparation of stable compounds with P=N, P=C and P=P -linkages have been developed.

λ^3-IMINOPHOSPHINES

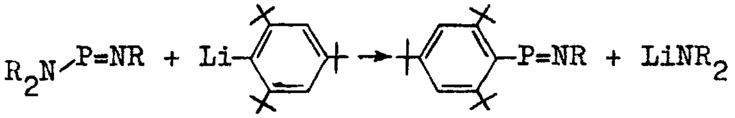
Thermal elimination of small, energetically stable molecules XHlg ($X{=}Me_3Si,Li$) from sterically crowded phosphorus-nitrogen dyad -P(Hlg)-N(X)- has been so far the only synthetic access to λ^3-iminophosphines.[1] We have elaborated a novel route to iminophosphines via nucleophilic displacement at the dicoordinated phosphorus atom in the aminoiminophosphine series.

Aminoiminophosphines undergo nucleophilic transamination with the retention of phosphorus coordination when treated with highly hindered lithium amides (Eq.1).[2]

$$R'_2N{-}P{=}NR \;+\; LiNR''_2 \;\rightleftharpoons\; R''_2N{-}P{=}NR \;+\; LiNR'_2 \qquad (1)$$

The equilibrium position mainly depends upon the relative nucleophilicity of starting and formed lithium amides and it is displaced toward the less nucleophilic lithium amide.

The reaction described offers a considerable potential for the preparation of new aminoiminophosphines that are difficult to prepare by classical method. The transfer of this reaction principle to hindered organolithium compounds and aminoiminophosphines provides a pathway to derivatives of dicoordinated phosphorus based on the skeleton C-P=N. The first thermally stable compound of C-P=N type has been synthesised by a nucleophilic displacement reaction between tris(trimethylsilyl)aminoiminophosphine and 2,4,6-tri-t-butylphenyl-lithium (Eq. 2).[3,4]



(2)

$R = Me_3Si$

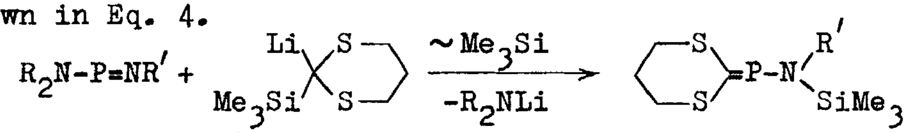
We have observed that aminoiminophosphines react with silyl functionalized organometallic species via nucleophilic displacement at the dicoordinated phosphorus atom with subsequent [1,3]-silyl migration from carbon to nitrogen. For example, treatment of aminoiminophosphines with an equimolar quantity of $(Me_3Si)_3CLi$ in THF at -78°C resulted in the formation of aminomethylenephosphines (Eq. 3).

$$R_2N\text{-}P{=}NR' + LiC(SiMe_3)_3 \xrightarrow[-R_2NLi]{} \left[(Me_3Si)_3C\text{-}P{=}NR'\right]$$

$$(Me_3Si)_2C{=}P\text{-}N(R')SiMe_3 \xleftarrow{\sim Me_3Si} \tag{3}$$

$R = Me_3Si$; $R' = Me_3Si$, t-Bu, 1-adamantyl

Recently this method has been successfully used by us to prepare aminomethylenephosphines containing thioalkyl-substituents at the methylene carbon atom, as shown in Eq. 4.



$R = Me_3Si$; $R' = Me_3Si$, t-Bu (4)

P-TRIMETHYLSILYL BIS(DIALKYLAMINO)METHYLENEPHOSPHINES

A number of compounds having the C=P-Si basic structure have been prepared by our group via the condensation of bis(dialkylamino)difluoromethanes with tris(trimethylsilyl)phosphine (Eq. 5).[5]

$$(R_2N)_2CF_2 + (Me_3Si)_3P \xrightarrow[-2Me_3SiF]{} (R_2N)_2C{=}P{-}SiMe_3 \quad (5)$$

$R = Me, Et, i\text{-}Pr$

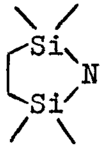
A noticeable feature of P-trimethylsilyl bis(dialkylamino)methylenephosphines in comparison with the known methylenephosphines having the C=P-C backbone structure is the upfield shift of the ^{31}P nmr signal (-27 to -47 ppm). The high reactivity of P-Si bond can be utilized for the synthesis of other types of functionalized dicoordinated phosphorus compounds. Thus, interaction of P-trimethylsilyl methylenephosphines with heterocumulenes (ketenes, isocyanates, isothiocyanates, carbodiimides) leads to compounds based on the skeleton $\rangle C{=}P{-}\overset{|}{C}{=}X$ ($X = R_2C$, RN, S).[6] Our investigations in this field are continuing.

AMINODIPHOSPHENES

On treatment of the sterically hidden aminodichlorophosphines with equimolar quantity of bis(trimethylsilyl)mercury in DME or THF at 20°C the bis(amino)diphosphenes were obtained in quantitative yields.

$$R_2N{-}PCl_2 + Hg(SiMe_3)_2 \xrightarrow[-Hg]{-2Me_3SiCl} \tfrac{1}{2}\ R_2N{-}P{=}P{-}NR_2 \quad (6)$$

R_2N =



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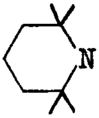
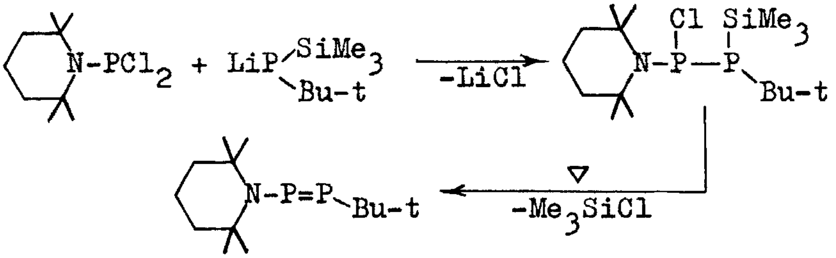


The composition and constitution of bis(amino)diphosphenes are confirmed by elemental analyses, molecular weight determinations and nmr data. A noteworthy characteristic of the compounds are their P-nmr signals which appear at extremely low field (>472 ppm). The reaction according to Eq. 6 is a general method of converting hindered aminodichlorophosphines into bis(amino)diphosphenes that can be effected under very mild conditions.

The synthetic approach to the first compound having the N-P=P-C molecular skeleton is outlined in Eq. 7.



(7)

The $^{31}P\{^1H\}$ nmr spectrum of 2,2,6,6-tetramethylpiperidino-tert-butyldiphosphene consists of an AB pattern with δ_A +508, δ_B +383 ppm, and $^1J(PP)$ 611 Hz.

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