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## The application of alkyllithium and alkylmagnesium reagents in cyclo(thia)phosphazene chemistry

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$(\text{NPI}^i\text{Pr}(\text{NSOPh})_2$

ic, Pna<sub>2</sub>,<sub>1</sub>

075

$2\theta < 50^\circ$

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decay; absorption using  
min. and max. applied  
factor (on F) 0.91 and  
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terson and Fourier  
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ast-squares techniques  
ropic thermal parame-  
e non-hydrogen atoms.  
ms were introduced at  
1.0 Å from their cen-  
assuming sp<sup>2</sup> or sp<sup>3</sup>  
on and refined in the  
with an overall iso-  
perature factor.

## Summary

This thesis describes a study of the reactivity of cyclo(thia)phosphazenes towards alkyllithium and alkyl Grignard reagents. Attention is focused on three types of starting materials, viz.  $(\text{NPF}_2)_n(\text{NSOX})_{3-n}$ ,  $(\text{NPCl}_2)_n(\text{NSOX})_{3-n}$  ( $n=1,2,3$ ;  $X=\text{F}, \text{Cl}, \text{Ph}$ ) and  $(\text{NPCl}_2)_4$ .

Chapter I provides information about the characteristics of cyclo(thia)phosphazenes; the literature on reactions of  $(\text{NPX}_2)_n$  ( $n=3,4$ ;  $X=\text{F}, \text{Cl}$ ) with the above-mentioned organometallic compounds is reviewed.

During attempts to synthesize fluorocyclothia-phosphazenes in the presence of KF/18-crown-6 ether in acetonitrile hydrolysis phenomena were observed. Chapter II describes reactions of  $(\text{NPCl}_2)_n(\text{NSOX})_{3-n}$  ( $n=1,2,3$ ;  $X=\text{Cl}, \text{Ph}$ ) with H<sub>2</sub>O in the presence of KCl and 18-crown-6 affording potassium crown ether salts of hydroxy derivatives of the ring compounds. Both mono- and disubstituted compounds could be isolated. It appears that in the case of  $(\text{NPCl}_2)_3$  a non-geminal substitution pattern occurs, whereas  $(\text{NPCl}_2)_2\text{NSOCl}$  reacts according to a geminal pathway. The latter observation has been confirmed by crystal structure determination of the compound  $(\text{KC}_{12}\text{H}_{24}\text{O}_6)^+(\text{NHPU}_2\text{NPCl}_2\text{NSOCl})^-$ .

Reactions of  $\text{NPCl}_2(\text{NSOX})_2$  and  $(\text{NPCl}_2)_2\text{NSOX}$  ( $X=\text{F}, \text{Cl}, \text{Ph}$ ) with KSO<sub>2</sub>F (Chapter III) lead to a variety of fluorocyclothiaphosphazenes, the <sup>31</sup>P and <sup>19</sup>F NMR spectra of which are analyzed by means of spectrum simulation. Trans-NPF<sub>2</sub>(NSOPh)<sub>2</sub> reacts with <sup>t</sup>BuLi via nucleophilic substitution to give (1 $\alpha$ , 3 $\beta$ , 5 $\alpha$ )-NPF<sup>t</sup>Bu(NSOPh)<sub>2</sub>. No reactivity is observed towards <sup>t</sup>BuMgCl.

Chapter IV and V provide a detailed discussion

of the reactions of  $(\text{NPCl}_2)_3$ , trans and cis- $\text{NPCl}_2(\text{NSOPh})_2$  and  $(\text{NPCl}_2)_2\text{NSOPh}$  with  $\text{RLi}$  ( $\text{R}=\text{Me}, ^t\text{Bu}$ ) and 2-propanol. The reaction products, e.g.

$\text{NP}(\text{H})\text{O}^i\text{Pr}(\text{NPCl}_2)_n(\text{NSOPh})_{2-n}$  ( $n=0,1,2$ ) are supposed to arise from a metal-halogen exchange process. Compound  $(1\alpha,3\beta,5\alpha)\text{-NP}(\text{H})\text{O}^i\text{Pr}(\text{NSOPh})_2$  was characterized by means of an X-ray structure determination. The tetramer  $(\text{NPCl}_2)_4$  also reacts with  $\text{MeLi}$  according to a metal-halogen exchange process, leading to unprecedented hydridocyclophosphazenes and bi(cyclophosphazenes); the X-ray structure determination of the bi(cyclophosphazene)  $(\text{N}_4\text{P}_4\text{Cl}_6\text{Me})_2$  is discussed (Chapter VI).

Chapter VII reports the reactivity of trans- $\text{NPCl}_2(\text{NSOPh})_2$  towards  $(\text{Bu}_3\text{PCuI})_4/\text{RMgCl}$  ( $\text{R}=\text{Pr}, ^i\text{Pr}$ ) or  $\text{RMgCl}$  ( $\text{R}=\text{Me}, ^t\text{Bu}$ ); again a metal-halogen exchange process is observed. The X-ray structure determinations of  $(1\alpha,3\beta,5\alpha)\text{-NP}^n\text{Pr}^i\text{Pr}(\text{NSOPh})_2$  and  $(1\alpha,3\beta,5\alpha)\text{-NPI}^i\text{Pr}(\text{NSOPh})_2$ , in combination with that of cis- $\text{NPCl}_2(\text{NSOPh})_2$ , provide information about the effects of the substituents on the ring skeleton. The difference in electronegativity between the sulfur and phosphorus centres within a PNS segment can be correlated with the difference between the NP and NS bond lengths.

The reactivity of the hydridocyclophosphazenes  $\text{NP}(\text{H})\text{R}(\text{NP}(\text{OCH}_2\text{CF}_3)_2)_2$  ( $\text{R}=\text{O}^i\text{Pr}, \text{Me}$ ) is discussed in Chapter VIII. Reactions of these compounds with p-nitrobenzaldehyde in the presence of small amounts of  $\text{Et}_3\text{N}$  or quinine afford  $\text{NP}(\text{CHOHC}_6\text{H}_4\text{NO}_2)\text{R}(\text{NP}(\text{OCH}_2\text{CF}_3)_2)_2$ . Asymmetric catalysis in the case of quinine is demonstrated.