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

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

1986

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Winter, H. (1986). *The application of alkyllithium and alkylmagnesium reagents in cyclo(thia)phosphazene chemistry*. s.n.

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

ic, Pna2₁

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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ast-squares techniques
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1.0 Å from their cen-
assuming sp² or sp³
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=F, Cl, 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=F, 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=Cl, Ph) with H₂O 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=F, Cl, Ph) with KSO₂F (Chapter III) lead to a variety of fluorocyclothiaphosphazenes, the ³¹P and ¹⁹F NMR spectra of which are analyzed by means of spectrum simulation. Trans-NPF₂(NSOPh)₂ reacts with ^tBuLi via nucleophilic substitution to give (1 α , 3 β , 5 α)-NPF^tBu(NSOPh)₂. No reactivity is observed towards ^tBuMgCl.

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 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 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 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 Et_3N 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.