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Synthesis of Poly(dialkylphosphazenes) from N-Silylphosphinimines

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ABSTRACT

Many N-silylphosphinimines $Me_3SiN{=}P(X)RR'$ undergo facile thermal decomposition with elimination of substituted silanes Me_3SiX and formation of cyclic or polymeric phosphazenes $(RR'PN)_n$. The process which is a new, general synthesis of phosphazenes has been used to prepare poly(dimethylphosphazene), $(Me_2PN)_n$, in nearly quantitative yield from $Me_3SiN{=}P(OCH_2CF_3)Me_2$. Convenient synthetic routes to the necessary silicon-nitrogen-phosphorus precursors are described and the results of their decomposition reactions are reported.

INTRODUCTION

Inorganic polymers with a backbone of alternating phosphorus and nitrogen atoms $\left(\overset{|}{\underset{|}{P}}{=}N\right)_n$ are known as polyphosphazenes [1]. Many such polymers with a variety of substituents at phosphorus have been prepared and they generally exhibit many useful properties including low temperature flexibility, resistance to chemical attack, flame retardancy, stability to UV and visible radiation, and moderate to high thermal stability.

Although numerous polyphosphazenes have been prepared, the only method that has proven generally useful for their synthesis is that developed by Allcock and coworkers [1,2]. This procedure involves the initial preparation of poly(dihalophosphazene) (halogen = F,Cl) from the cyclic trimers (eqs 1 and 2) and subsequent nucleophilic displacement of the halogens along the chain (eq 3). In each case, the substituents at phosphorus must be introduced after

$$nPCl_5 + nNH_4Cl \xrightarrow{-4nHCl} \frac{1}{n}(Cl_2PN)_n \qquad n = 3,4 \tag{1}$$

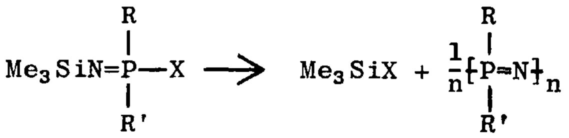
$$\underset{X = Cl,F}{(X_2PN)_3} \xrightarrow{\Delta} \underset{n = 15,000}{(X_2PN)_n} \tag{2}$$

$$(X_2PN)_n \left\langle \begin{array}{l} \xrightarrow{NaOR} [(RO)_2PN]_n \\ \\ \xrightarrow{RNH_2} [(RNH)_2PN]_n \end{array} \right. \tag{3}$$

polymerization since the substituted cyclic phosphazenes do not polymerize [3]. Until recently, no general method has been reported which allows the incorporation of the desired substituents before polymerization.

A common feature of the known phosphazene polymers is that the organic substituents are bonded to phosphorus through oxygen or nitrogen thereby providing pathways for decomposition or depolymerization on heating above about 200°C. It has long been speculated that directly P-C bonded alkyl or aryl groups might enhance the thermal and chemical stability of the polymers and give rise to interesting physical properties [3,4]. Furthermore, the alkyl substituted polyphosphazenes $(R_2PN)_n$ would be isoelectronic with the silicone polymers $(R_2SiO)_n$ which are an extremely versatile and useful class of polymers. The published attempts to prepare the directly P-C bonded polyphosphazenes have been largely unsuccessful. Treatment of poly(dihalophosphazenes) with organometallic reagents (e.g. RMgX or RLi) results in either incomplete substitution under mild conditions or chain cleavage and and molecular weight reduction under more vigorous conditions [4,5].

In this context, we report here a new, general, and direct method for the synthesis of polyphosphazenes. The new synthesis is based on the premise that suitably constructed N-silylphosphinimines will eliminate substituted silanes to form cyclic and/or polymeric phosphazenes (eq 4). This method has several potential advantages, the most important of which is the ability to incorporate the desired phosphorus substituents directly into the starting Si-N-P com-

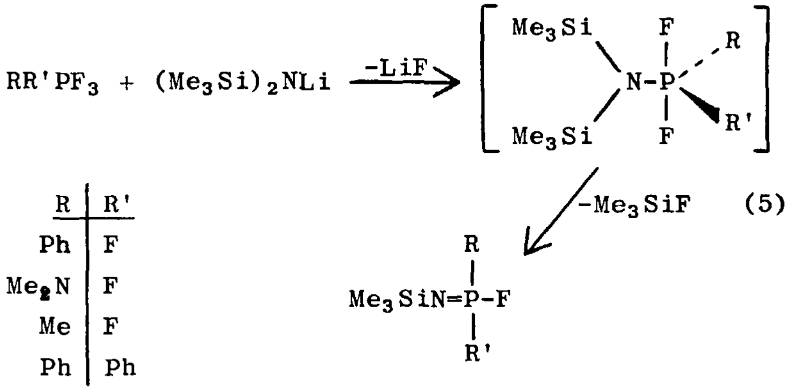


$$\mathrm{Me_3SiN{=}\overset{R}{\underset{R'}{P}}{-}X} \longrightarrow \mathrm{Me_3SiX} + \frac{1}{n}\left[\overset{R}{\underset{R'}{P}}{=}N\right]_n \qquad (4)$$

pound. Therefore, by designing the appropriate precursors, it should be possible to widely vary the pattern of substituents in the phosphazene products. It is this procedure which has resulted in the successful preparation of the first fully P-C bonded poly(dialkylphosphazene), $(Me_2PN)_n$ [6].

SILICON-NITROGEN-PHOSPHORUS COMPOUNDS

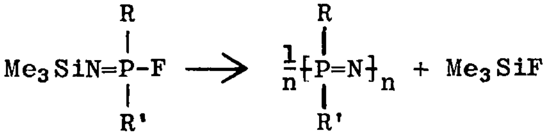
Studies of the chemistry and stereochemistry of silicon-nitrogen-phosphorus compounds [7-13] have led us into the phosphazene area in the following manner. In an attempt to prepare the first example of an acyclic pentacoordinate phosphorus compound containing a silylamino substituent, lithium bis(trimethylsilyl)amide was treated with some substituted fluorophosphoranes [13]. The desired silylaminophosphoranes, however, were not isolated. Instead, the reaction (eq 5) proceeded with elimination of fluorotrimethylsilane as well as lithium fluoride to produce a new series of P-fluoro-N-silylphosphinimines. Furthermore,



(5)

R	R'
Ph	F
Me_2N	F
Me	F
Ph	Ph

it was soon established that these phosphinimines would readily undergo further fluorosilane elimination (eq 6) to form phosphazenes [13]. Closer examination of these phosphazenes has indicated that only smaller



$$Me_3SiN{=}\overset{R}{\underset{R'}{P}}{-}F \longrightarrow \frac{1}{n}\left[\overset{R}{\underset{R'}{P}}{=}N\right]_n + Me_3SiF \qquad (6)$$

R	Ph	Ph	Me	Me	Me_2N
R'	F	Ph	F	Me	F

cyclic compounds (i.e., trimer and tetramer) are obtained. Nonetheless, these decompositions appeared to be a novel synthesis of phosphazene rings, especially non-geminally substituted compounds in which each phosphorus bears two different substituents.

These preliminary results led us to speculate on the generality of such silane eliminations and, hence, to propose the general phosphazene synthesis outlined above (eq 4). A most obvious variable in this new method is the effect of changing the leaving group (X) in the precursor N-silylphosphinimines. With this in mind we have prepared a number of new "suitably constructed" N-silylphosphinimines with a variety of leaving groups, and a mixture of alkyl, aryl, and alkoxy substituents at phosphorus.

The synthesis of the new N-silylphosphinimines was contingent upon the availability of relatively large amounts of another type of Si-N-P compound, the bis(trimethylsilyl)aminophosphines, $(Me_3Si)_2NPRR'$.

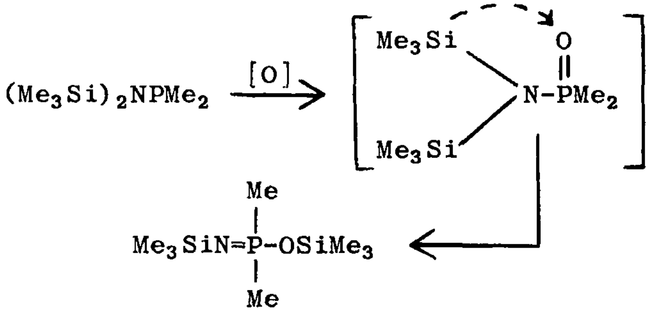
Initially, the synthesis of such compounds involved reactions of $(Me_3Si)_2NLi$ with chlorophosphines R_2PCl [12]. The preparation and handling of the latter reagents, however, is often tedious, especially where R = alkyl. These problems have been avoided by our development of a convenient, "one-pot" synthesis (eq 7) which uses readily available starting materials [11]. The silylaminophosphines can be prepared

$$\begin{tikzcd}(Me_3Si)_2NH \arrow[r, "n\text{-}BuLi", "Et_2O"'] & (Me_3Si)_2NLi \arrow[r, "PCl_3", "-78\,^\circ C"'] & (Me_3Si)_2NPCl_2 \arrow[dl, "2RMgBr", "0\,^\circ C"'] \\ & (Me_3Si)_2NPR_2 & \end{tikzcd} \qquad (7)$$

$$R = Me,\ Et$$

in molar quantities and are isolated in 70-75% yields by vacuum distillation.

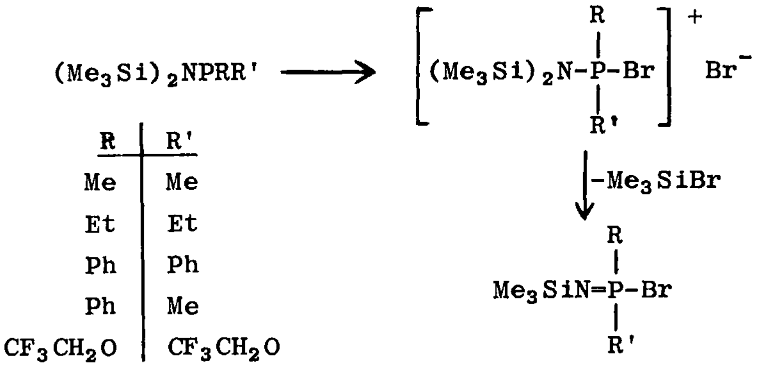
One of the first appropriately substituted N-silylphosphinimines was obtained in a related study of the oxidation of silylaminophosphines [7,12]. When $(Me_3Si)_2NPMe_2$ is oxidized by either oxygen or <u>tert</u>-butyl(trimethylsilyl) peroxide, the structurally rearranged siloxyphosphinimine $Me_3SiN{=}P(OSiMe_3)Me_2$ is isolated in high yield (eq 8). Indeed, the lability



(8)

of silyl groups toward intramolecular migrations is a dominant feature of the chemistry of such compounds [7,9,11,12].

A much more important development in the synthesis of potential phosphazene precursors was the preparation of a new series of P-bromo substituted phosphinimines [14]. This was accomplished by the simple reaction of bromine with bis(trimethylsilyl)-aminophosphines in benzene (eq 9). Unlike trialkyl- and triarylphosphines which react with bromine to give

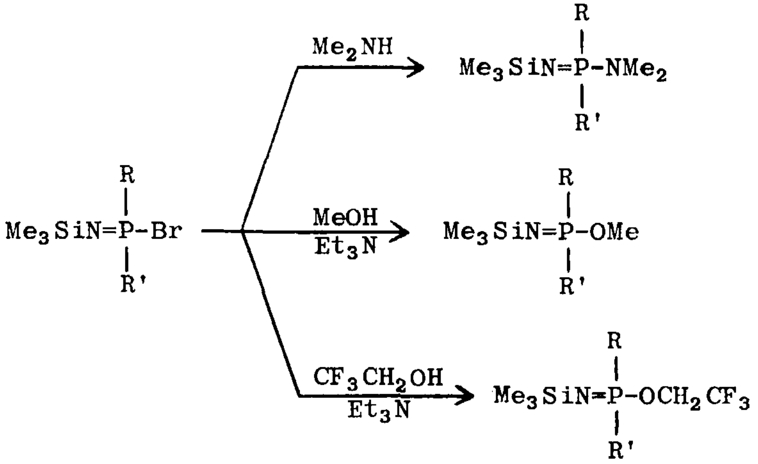


$$(Me_3Si)_2NPRR' \longrightarrow \left[(Me_3Si)_2N-\overset{R}{\underset{R'}{P}}-Br\right]^{+} Br^{-} \xrightarrow{-Me_3SiBr} Me_3SiN{=}\overset{R}{\underset{R'}{P}}-Br \tag{9}$$

R	R'
Me	Me
Et	Et
Ph	Ph
Ph	Me
CF_3CH_2O	CF_3CH_2O

phosphonium salts $[R_3PBr]^+Br^-$, the analogous silylaminophosphonium salts are not isolated. Instead, Me_3SiBr is eliminated, giving high yields of the P-bromo-N-silylphosphinimines. These compounds are hydrolytically unstable liquids which are usually sufficiently volatile to permit purification by vacuum distillation. They have been fully characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analysis.

Not only are these P-bromo compounds potential phosphazene precursors themselves, but they also can be derivatized at the P-Br bond, thereby facilitating the introduction of other functional groups [14]. The P-bromo-N-silylphosphinimines react with dimethylamine and with alcohols in the presence of Et_3N (to scavenge HBr) giving the amino and alkoxy substituted phosphinimines in good yields (eqs 10-12). These products are



$$Me_3SiN{=}P(R)(R')\text{-}Br \xrightarrow{Me_2NH} Me_3SiN{=}P(R)(R')\text{-}NMe_2 \quad (10)$$

$$Me_3SiN{=}P(R)(R')\text{-}Br \xrightarrow[Et_3N]{MeOH} Me_3SiN{=}P(R)(R')\text{-}OMe \quad (11)$$

$$Me_3SiN{=}P(R)(R')\text{-}Br \xrightarrow[Et_3N]{CF_3CH_2OH} Me_3SiN{=}P(R)(R')\text{-}OCH_2CF_3 \quad (12)$$

colorless liquids which can be purified by vacuum distillation and which have been characterized by NMR spectroscopy and elemental analysis.

These simple reactions have, therefore, produced a new series of potential phosphazene precursors $Me_3SiN{=}P(X)RR'$ (eq 4) with a variety of leaving groups (X = $OSiMe_3$, Br, NMe_2, OMe, and OCH_2CF_3). Moreover, these are all easily prepared in synthetically useful quantities, while quantities of the original P-fluoro-N-silylphosphinimines are often limited by difficulties in the synthesis and handling of the starting fluorophosphoranes (eq 5).

PHOSPHAZENE SYNTHESIS

Cyclic Phosphazenes

The thermal stability of each of the new N-silylphosphinimines has been investigated. Typically, the compounds were sealed in evacuated heavy-walled glass ampoules and heated either in an oil bath or an oven. At relatively high temperatures of 200° to 250 °C, the compounds $Me_3SiN{=}P(X)R_2$, where X is NMe_2, $OSiMe_3$, or OMe and R is Et or Me, showed no signs of any decomposition even after several days. In each case none of the expected silane Me_3SiX was formed and the phosphinimines were recovered unchanged.

The P-bromo-N-silylphosphinimines, however, are much less stable and readily eliminate Me_3SiBr on heating under a variety of conditions. For example, when $Me_3SiN{=}P(Br)Me_2$ is heated in refluxing benzene for 5 days, a ^{31}P NMR spectrum of the white solids remaining after removal of benzene and Me_3SiBr indicate that nearly equal amounts of tetrameric (δ 27.1) and pentameric (δ21.5) $(Me_2PN)_n$ [15] are formed. On heating a neat sample of the same compound in a sealed ampoule at 190 °C for 2 days the principle ^{31}P NMR signal corresponds to tetramer with only traces of trimer and pentamer. On heating in a sealed ampoule at 250 °C for one day, slightly larger proportions of trimer and pentamer relative to tetramer are observed.

Some related P-bromo-N-silylphosphinimines $Me_3SiN{=}P(Br)RR'$ (R = R' = Me; R = R' = Et; R = R' = Ph; and R = Me, R' = Ph) also smoothly eliminate Me_3SiBr on heating in sealed glass ampoules. In all cases only the smaller cyclic products are obtained and, indeed, this appears to be an effective new synthetic route to such compounds.

Polymeric Phosphazenes

While the N-silylphosphinimines where the potential leaving group is F, Br, NMe_2, $OSiMe_3$ or OMe are either stable compounds or give exclusively cyclic phosphazenes when heated, markedly different results are obtained when the leaving group is trifluoroethoxy, CF_3CH_2O. On investigating the thermal stability of $Me_3SiN{=}P(OCH_2CF_3)Me_2$, we find that $Me_3SiOCH_2CF_3$ is eliminated from the compound under a variety of conditions. In each case, the product is a solid material which analyzes for Me_2PN but bears no physical resemblance to the cyclic dimethylphosphazenes $(Me_2PN)_n$ (n = 3,4,5). Although this decomposition occurs slowly at room temperature or under a neat reflux at atmospheric pressure, best results are obtained by heating the phosphinimine in a sealed glass ampoule at 190 °C for 2 days. Removal of the volatile silane under vacuum leaves an off-white solid which, unlike the trimer and tetramer, is quite insoluble in water but is highly soluble in CH_2Cl_2 or $CHCl_3$. The ^{31}P NMR spectrum contains a sharp singlet at $\delta 8.26$ (in $CDCl_3$, relative to H_3PO_4) which is far upfield from that of the cyclic dimethylphosphazenes. Based on elemental analysis, which confirms the molecular formula as Me_2PN, the reaction yield is virtually quantitative. A weight average molecular weight ($\overline{M}_w$) of 50,000 was determined by light scattering techniques. This value corresponds to an average chain length of about

660 monomer units and although this is significantly less than the typical 10,000-15,000 units reported for polyphosphazenes with alkoxy, amino, or halo substituents, it is, nevertheless, the first example of a well-characterized poly(dialkylphosphazene) with directly P-C bonded substituents.

Other physical data for poly(dimethylphosphazene) include a glass transition temperature (T_g) of -42 °C a melting point (T_m) of 158 °C, and an intrinsic viscosity, $[\eta]$, of 0.44 dl/g (in $CHCl_3$ at 25 °C). When a CH_2Cl_2 solution of $(Me_2PN)_n$ is allowed to evaporate slowly, a thin film of the polymer is formed. Pouring a CH_2Cl_2 solution into hexane results in precipitation of a white powder-like form of the polymer and serves as a means of purification.

Prepared in this manner, poly(dimethylphosphazene) is superficially similar to some lower molecular weight (3,500-12,500) products reported by Sisler and coworkers [16]. Their compounds, however, were obtained in low yields from the thermolysis of $Me_2P(NH_2)_2Cl$ after a tedious preparation and purification. The reproducibility of their results has also been questioned [3]. Our method, on the other hand, utilizes easily prepared starting materials, affords excellent yields, and gives considerably higher molecular weights for $(Me_2PN)_n$.

The elimination of $Me_3SiOCH_2CF_3$ from N-silylphosphinimines appears to be fairly general. Flindt and Rose [17] have reported that this silane elimination from $Me_3SiN{=}P(OCH_2CF_3)_3$ gives low molecular weight oligomers ($\overline{M}_n \sim 10{,}000$) of $[(CF_3CH_2O)_2PN]_n$. Our preliminary results indicate that $Me_3SiOCH_2CF_3$ will also eliminate from some other N-silylphosphinimines. Although $Me_3SiN{=}P(OCH_2CF_3)Ph_2$ is stable on heating for prolonged periods at 250 °C, both $Me_3SiN{=}P(OCH_2CF_3)RR'$ (R = R' = Et; and R = Me, R' = Ph) show quantitative formation of $Me_3SiOCH_2CF_3$. The solid product of the decomposition of the diethyl compound gives a satisfactory elemental analysis for Et_2PN, but its insolubility in all common solvents has thus far prevented further characterization. The phenyl/methyl substituted compound decomposes to form a sticky solid, the ^{31}P NMR spectrum of which consists of a sharp singlet at δ1.67. Like $(Me_2PN)_n$, this is significantly upfield from the signals of the small ring compounds (δ ~27).

Another interesting system under investigation in our laboratory is a polymeric phosphazene with a mixture of Me and Et substituents at phosphorus. By allowing $(Me_3Si)_2NPCl_2$ (eq 7) to react with equimolar amounts of MeMgBr and EtMgBr, we obtain 1:2:1 proportions of the phosphines $(Me_3Si)_2N{-}PMe_2$, -PMeEt, and $-PEt_2$. Subsequent reactions as described previously provide mixtures of $Me_3SiN{=}P(OCH_2CF_3)RR'$ which decompose readily to give phosphazene products characterized by 3 broad signals in the ^{31}P NMR spectrum at δ7.8, 13, and 18 in approximately 1:2:1 proportions. Presumably these correspond to the PMe_2, PMeEt, and PEt_2 centers, respectively, distributed in a random fashion along the phosphazene chain. Further characterization of these materials is underway.

CONCLUDING REMARKS

The research described herein demonstrates that the proposed phosphazene synthesis (eq 4) is, in fact, a generally useful one. Through the elimination of Me_3SiBr from N-silylphosphinimines, high yields of smaller cyclic phosphazenes are readily obtained. More significantly, the elimination of $Me_3SiOCH_2CF_3$ from other N-silylphosphinimines is a general approach to good yields of polymeric phosphazenes, many of which have evaded synthesis by other methods. This synthetic route is particularly applicable to the preparation of polyphosphazenes with directly P-C bonded substituents such as $(Me_2PN)_n$. The physical properties and potential applications of $(Me_2PN)_n$, particularly in view of its electronic similarity to poly(dimethylsiloxane) $(Me_2SiO)_n$, certainly are worthy of more detailed study. Other features of our synthesis which need to be further explored include the variation of substituents at phosphorus, methods of increasing molecular weight, and the possibility of crosslinking the polymer chains.

A number of obvious questions involving mechanistic aspects of the new synthetic method remain to be answered. Since the cyclic phosphazenes $(Me_2PN)_{3,4}$ do not polymerize [3] even under extreme conditions, it appears that the $Me_3SiOCH_2CF_3$ elimination reaction must bypass the cyclics, leading to speculation about the formation of the Me_2PN monomer. Another interesting but puzzling fact is that Me_3SiBr elimination gives only cyclic phosphazenes while $Me_3SiOCH_2CF_3$ elimination yields exclusively polymeric products.

Finally, it seems likely that the development of this new synthesis of polyphosphazenes, including some much-sought-after compounds, will serve to further stimulate the continued growth of phosphazene chemistry and, perhaps, to help bring it closer to the realm of commercial application.

ACKNOWLEDGMENTS

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REFERENCES

[1] H.R. Allcock, Phosphorus-Nitrogen Compounds, Academic Press, New York, 1972.

[2] H.R. Allcock, Angew. Chem. Int. Ed. Engl., 16, 147 (1977).

[3] H.R. Allcock and D.B. Patterson, Inorg. Chem., 16, 197 (1977).

[4] H.R. Allcock, D.B. Patterson, and T.L. Evans, J. Am. Chem. Soc., 99, 6095 (1977).

[5] H.R. Allcock and C.T.-W. Chu, Macromolecules, 12, 551 (1979).

[6] P. Wisian-Neilson and R.H. Neilson, J. Am. Chem. Soc., 102, 2848 (1980).

[7] R.H. Neilson, P. Wisian-Neilson, and J.C. Wilburn, Inorg. Chem., 19, 413 (1980).

[8] R.H. Neilson and D.W. Goebel, J. Chem. Soc. Chem. Commun., 769 (1979).

[9] J.C. Wilburn. P. Wisian-Neilson, and R.H. Neilson, Inorg. Chem., 18, 1429 (1979).

[10] R.H. Neilson and W.A. Kusterbeck, J. Organomet. Chem., 166, 309 (1979).

[11] J.C. Wilburn and R.H. Neilson, Inorg. Chem., 18, 347 (1979).

[12] J.C. Wilburn and R.H. Neilson, Inorg. Chem., 16, 2519 (1977).

[13] P. Wisian-Neilson, R.H. Neilson, and A.H. Cowley, Inorg. Chem., 16, 1460 (1977).

[14] P. Wisian-Neilson and R.H. Neilson, Inorg. Chem., in press (June, 1980)

[15] H.T. Searle, J. Dyson, T.N. Ranganathan, and N.L. Paddock, J. Chem. Soc., Dalton Trans., 203 (1975).

[16] H.H. Sisler, S.E. Frazier, R.G. Rice, and M.G. Sanchez, Inorg. Chem., 5, 327 (1966).

[17] E.-P. Flindt and H. Rose, Z. Anorg. Allg. Chem., 428, 204 (1977).