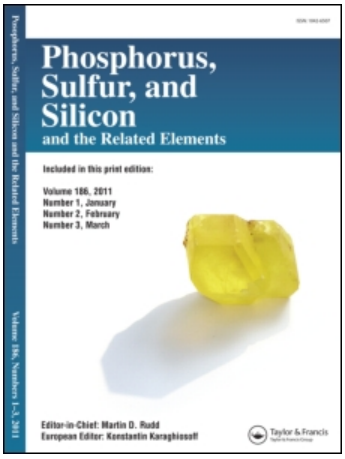

Phosphorus, Sulfur, and Silicon and the Related Elements

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On Derivatisation Reactions of 2-Chloro-3-Dichlorophosphanyl-1-Methyl-1.3.2-Diazaphosphorinane

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ON DERIVATISATION REACTIONS OF 2-CHLORO-3-DICHLOROPHOSPHANYL-1-METHYL-1.3.2-DIAZAPHOSPHORINANE

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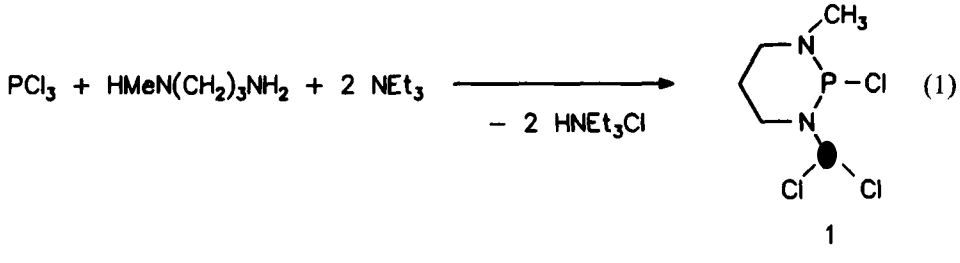
Derivatisation reactions of 2-chloro-3-dichlorophosphanyl-1-methyl-1.3.2-diazaphosphorinane **1** with protic nucleophiles like $HNEt_2$, CH_3OH, C_2H_5OH and the Franz-reagent $NEt_3 3HF$ forming the substituted N-phosphanyldiazaphosphorinanes **2–12** are described. The preferential nucleophilic attack on the exocyclic phosphanyl group of **1** in partial replacement reactions is discussed by means of ^{31}P-, ^{1}H- and ^{13}C-NMR data.

Key words: 2-Chloro-3-dichlorophosphanyl-1-methyl-1.3.2-diazaphosphorinane; N-phosphanyldiazaphosphorinanes, NMR-data.

INTRODUCTION

Recently we have shown that the reaction of PX_3 (X = Cl, Br) with bifunctional protic nucleophiles like propanolamine-1.3, propanediamine-1.3, ethylenediamine and ethanolamine in the presence of NEt_3 as base leads to the formation of N-halogenophosphanyl-1.3.2-oxaza- and -diazaphosphorinanes and -phospholanes.[1] Similarly the reaction of PCl_3 with a mixture of N-methyl-propanediamine-1.3 and NEt_3 was found to give 2-chloro-3-dichlorophosphanyl-1-methyl-1.3.2-diazaphosphorinane **1**; Equation (1).[1]



(1)

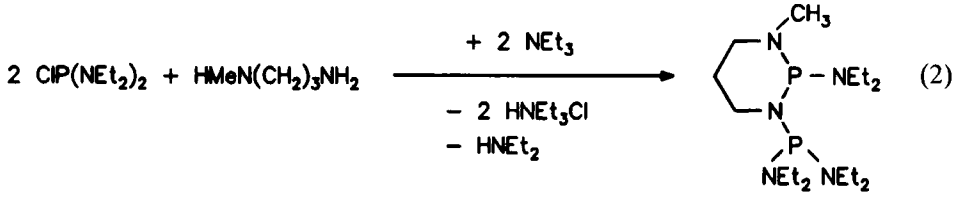
1

Further investigations concerning the derivatisation of the N-phosphanylated compound **1** with protic nucleophiles were carried out. In comparison with the reaction behaviour of 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane it was of special interest, on which of the two phosphorus atoms the nucleophilic attack takes place preferentially in partial replacement reactions.

RESULTS AND DISCUSSION

The investigations have shown, that a manifold derivatisation of **1** according to Scheme I is possible.

As expected in the reaction of **1** with $HNEt_2$ in a molar ratio of 1:6 the completely amidated, cyclic product **2** is obtained characterized by two doublets at δ = 100.8 and δ = 114.2 with a $^2J_{PNP}$ coupling constant of 312 Hz in the ^{31}P-NMR spectrum. The same diphosphorus compound is formed in the reaction of $ClP(NEt_2)_2$ with N-methyl-propanediamine-1.3 and NEt_3 in a molar ratio of 2:1:2; Equation (2).



(2)

2

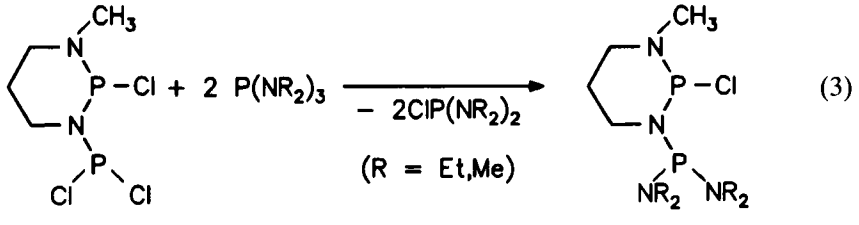
In the reaction of the cyclic chlorine compound **1** with diethyl amine and NEt_3 in a molar ratio of 1:2:2 the double amidated compound **3** was nearly quantitatively formed. The ^{31}P-NMR spectrum of **3** shows two doublets at δ = 115.5 and δ = 159.9 with a $^2J_{PNP}$ coupling constant of 214 Hz (see Table IV).

The ^{1}H-NMR data of **3** are represented in Table I.

The assignment of the first two signals was carried out by a comparison with the ^{1}H-NMR spectrum of compound **1**.[1] The signals at δ = 2.9 and at δ = 3.05 surprisingly represent an equivalence of nearly all NCH_2-groups (with the exception of 1 H). The ^{13}C-NMR data of **3** are summarized in Table II.

With the exception of the signals at δ = 14.0 and δ = 40.2 the spectrum agrees with the spectrum of the cyclic chlorine compound **1**.[1]

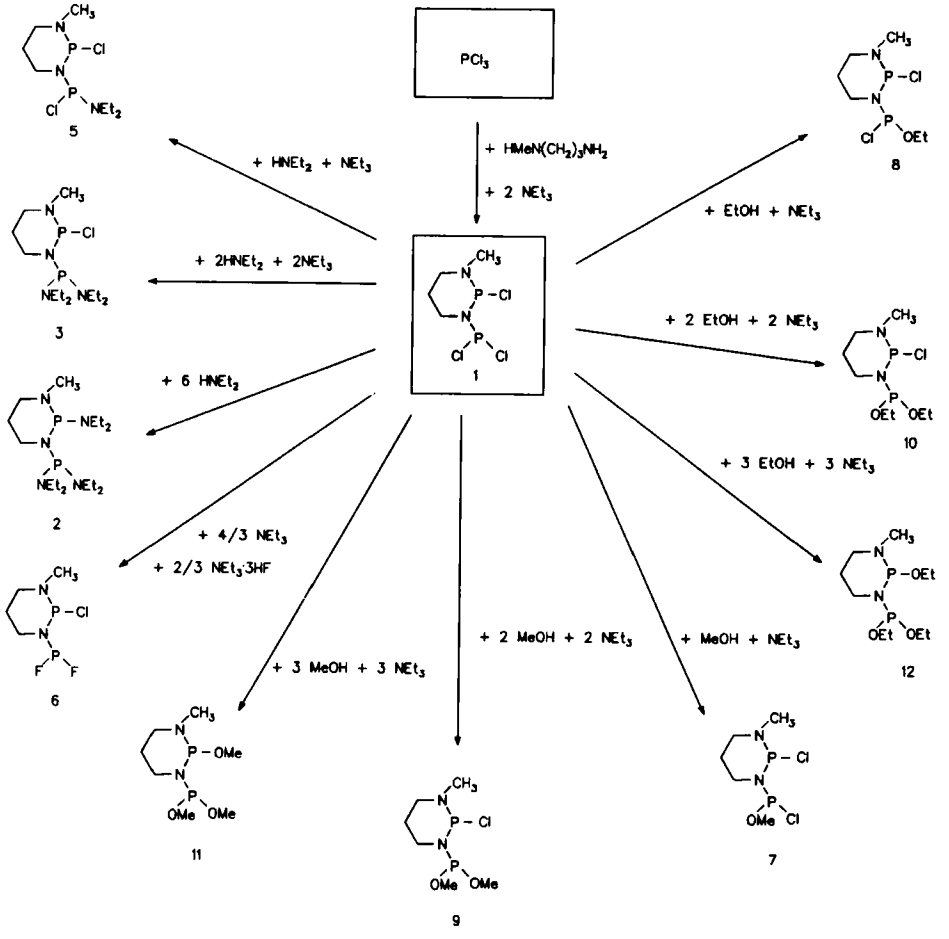
The preparation of the double amidated compound **3** was successfully demonstrated by the reaction of **1** with $P(NEt_2)_3$, too. Likewise the analogous dimethyl derivative **4** is formed by the corresponding reaction with $P(NMe_2)_3$; Equation (3).



(3)

3,4

The ^{31}P-NMR spectrum of the reaction of **1** with $HNEt_2$ and NEt_3 in a molar ratio of 1:1:1 indicated the formation of two diphosphorus compounds characterized by two doublets at δ = 136.0 and δ = 140.0 with a $^2J_{PNP}$ coupling constant of 326 Hz as well as two doublets at δ = 141.8 and δ = 145.2 with a $^2J_{PNP}$ coupling



SCHEME I Derivatisation reactions of 2-chloro-3-dichlorophosphanyl-1-methyl-1.3.2-diazaphosphorinane **1**.

TABLE I

^{1}H-NMR data of 2-chlor-3-bis(diethylamino)phosphanyl-1-methyl-1.3.2-diazaphosphorinane **3**

δ^1H [ppm]	intensity	assignment
0.95	14 H	4x $C\underline{H}_3$; $CH_2C\underline{H}_2CH_2$
2.4	3 H	$NC\underline{H}_3$
2.9	11 H	4x $NC\underline{H}_{2\ exo}$
3.05	1 H	2x $NC\underline{H}_{2\ endo}$

constant of 150 Hz. The ratio of the two compounds was found to be 3:2. A separation of the products by distillation was impossible. Because of the small and constant shift difference of 5–6 ppm the products are assumed to be diastereomeric compounds in connection with a cis/trans-isomerism.

It is well established that the shift differences between those isomers may be very different.[2-4] While in some cases a shift difference is not visible in the ^{31}P-NMR spectrum, in most of the cases a difference of some ppm may be observed. For the 4.6-dimethyl-2-phenyl-1.3.2-dithiaphosphorinanes even a difference of 26.5 ppm was found.[4]

When compound **1** undergoes a partial amidation reaction with $P(NEt_2)_3$ in a molar ratio of 1:1, only one diphosphorus product, which is characterized by two doublets at δ = 136 and δ = 140 ($^2J_{PNP}$ = 326 Hz) in the ^{31}P-NMR spectrum, is formed. This was proved to be the monoamidated derivative **5**.

Concerning the ^{1}H- and ^{13}C-NMR spectra there are some similarities compared to the double amidated compound **3**, whereby the signals of the ^{13}C-NMR spectrum of **5** can be assigned easily (see Table III).

The ^{1}H-NMR spectrum of **5** shows a multiplet at δ = 0.9 for the exocyclic CH_3-groups, two multiplets at δ = 0.1 and δ = 1.2 for the two ring protons of the central CH_2-group, one doublet at δ = 2.15 for the NCH_3 protons as well as two multiplets at δ = 2.95 and δ = 3.2 for the endo- and exocyclic NCH_2-groups (intensity ratio: 6:1:1:3:5:3). The essential difference in comparison with compound

TABLE II

^{13}C-NMR data of 2-chlor-3-bis(diethylamino)phosphanyl-1-methyl-1.3.2-diazaphosphorinane **3**

δ^{13}C [ppm]	multiplicity	assignment
14.0	S	$\underline{C}H_3$
25.9	S	CH_2-$\underline{C}H_2$-CH_2
37.8	M	CH_2-$\underline{C}H_2$-N-P
39.7	D	$N\underline{C}H_3$
40.2	D	$N(\underline{C}H_2)_{exo}$
47.5	D	$\underline{C}H_2$-$N(CH_3)$

TABLE III

^{13}C-NMR data of 2-chlor-3-(diethylaminomonochlor)phosphanyl-1-methyl-1.3.2-diazaphosphorinane **5**

δ^{13}C [ppm]	multiplicity	assignment
13.7	S	$\underline{C}H_3$
25.9	S	CH_2-$\underline{C}H_2$-CH_2
39.5	D	$N\underline{C}H_3$
40.3	M	CH_2-$\underline{C}H_2$-N-P
41.1	D	$N(\underline{C}H_2)_{exo}$
46.6	S	$\underline{C}H_2$-$N(CH_3)$

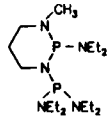
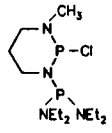
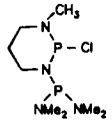
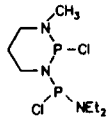
3 was therefore found to be a nonequivalence of the two ring protons of the central CH_2-group in **5**. The ^{31}P-NMR results of the reactions of **1** with amines are summarized in Table IV.

Considering the ^{31}P-NMR chemical shifts, similar values should be obtained for the completely amidated, exocyclic phosphanyl groups in **2**, **3** and **4**. As expected the corresponding values marked in Table IV by underlining are nearly constant. This result is assumed to be a reference for the preferential attack of nucleophiles on the exocyclic phosphorus atom of 2-chloro-3-dichlorophosphanyl-1-methyl-1.3.2.-diazaphosphorinane **1**. In contrast to that for the monoamidated compound **5** an assignment of the measured ^{31}P-NMR chemical shifts to a single phosphorus atom by a comparison with other NMR-data is impossible.

Proceeding on this assumption it is furthermore impossible to decide, whether the amino group is situated on the endo- or the exocyclic phosphorus atom. However, since during a double replacement obviously a twofold attack takes place on the exocyclic phosphorus atom, also in the case of the monoamidated compound **5** the most probable substitution is assumed to take place on the exocyclic phosphorus atom.

TABLE IV

^{31}P-NMR data of the reaction products of **1** with $HNEt_2$

compound	$\delta^{31}P$ [ppm]	$^2J_{PNP}$ in Hz
	100.8	312
	<u>114.2</u>	
2		
	<u>115.5</u>	214
	151.9	
3		
	<u>117.7</u>	283
	151.4	
4		
	136.0	326
	140.0	
	141.8	150
5	145.2	

Furthermore some evidence for the substitution on the exocyclic phosphorus atom was found by the ^{31}P-NMR spectroscopic proof of the existence of diastereoisomers.

Concerning the fluorination of **1** we carried out reactions with $NEt_3$3HF as fluorinating agent in the presence of an excess of NEt_3 in acetonitrile at -20°C. It was attempted to obtain the monofluorinated and the completely fluorinated compound. However, only mixtures of products were obtained, which could not be identified. But the preparation of the double fluorinated compound **6** was successful (see Scheme I).

The ^{31}P-NMR spectrum of **6** is of higher order with an ABX_2-pattern (see Figure 1a).

The ^{31}P-NMR chemical shift values and PP- and PF-coupling constants were determined by a simulation of the spectrum (see Figure 1b).

The A-part of the spectrum consists of a triplet further splitted in doublets at $\delta = 140.2$ for the exocyclic phosphorus atom, whereas for the endocyclic phosphorus atom a doublet at $\delta = 131.0$ is obtained. For the $^2J_{PNP}$ coupling constant a positive value of 404 Hz is observed. The one-bond $^1J_{PF}$ coupling constant is negative and amounts to -1227.7 Hz, the three-bond $^3J_{PF}$ coupling constant is positive and amounts to 42.5 Hz.

The ^{19}F-NMR spectrum of the considered compound **6** shows the expected doublet at $\delta = -63.9$.

Due to the splitting pattern of the ^{31}P-NMR - and ^{19}F-NMR spectra it could be proved, that the two fluorine atoms are bound on the exocyclic phosphanyl group, which was therefore recognized as the most reactive, electrophilic centre in compound **1**.

Accordingly also in replacement reactions of **1** with amines and alcohols the nucleophilic attack should primarily take place on the exocyclic phosphorus atom.

The alcoholysis of 2-chloro-3-dichlorophosphanyl-1-methyl-1.3.2-diazaphosphorinane **1** with methanol and ethanol leads to the corresponding, new cyclic alkoxy derivatives (see Scheme I). For preventing side reactions it was of special importance, that the alcohol was added dropwise to a mixture of **1** and NEt_3 at 0°C in benzene. In the reaction of **1** with ethanol and NEt_3 in a molar ratio of 1:1:1 two diphosphorus compounds were formed in a proportion of 1:1.5 represented by similar chemical shift values in the ^{31}P-NMR spectrum. The main product is characterized by two doublets at $\delta = 164.2$ and $\delta = 133.7$ with a $^2J_{PNP}$-coupling constant of 454 Hz, whereas the second diphosphorus compound is characterized by two doublets at $\delta = 163.7$ and $\delta = 133.0$ with a $^2J_{PNP}$-coupling constant of 413 Hz. Due to their similar chemical shifts the two compounds are assumed to be diastereomers. Diastereomers of that type, however, should occur only in that case, in which the nucleophilic substitution by the alcohol takes place on the exocyclic phosphorus atom.

Analogeous results were also obtained in the corresponding reactions with methanol. In the reactions of **1** with the alcohol and NEt_3 in a molar ratio of 1:2:2 mixtures of products are obtained consisting of the dialkoxy- and the trialkoxy derivatives. Even with a deficit of the alcohol the formation of the cyclic triester could not be avoided. However, in the corresponding ^{31}P-NMR spectra no signals for diastereomeric compounds were observed, i.e. the substitution should again

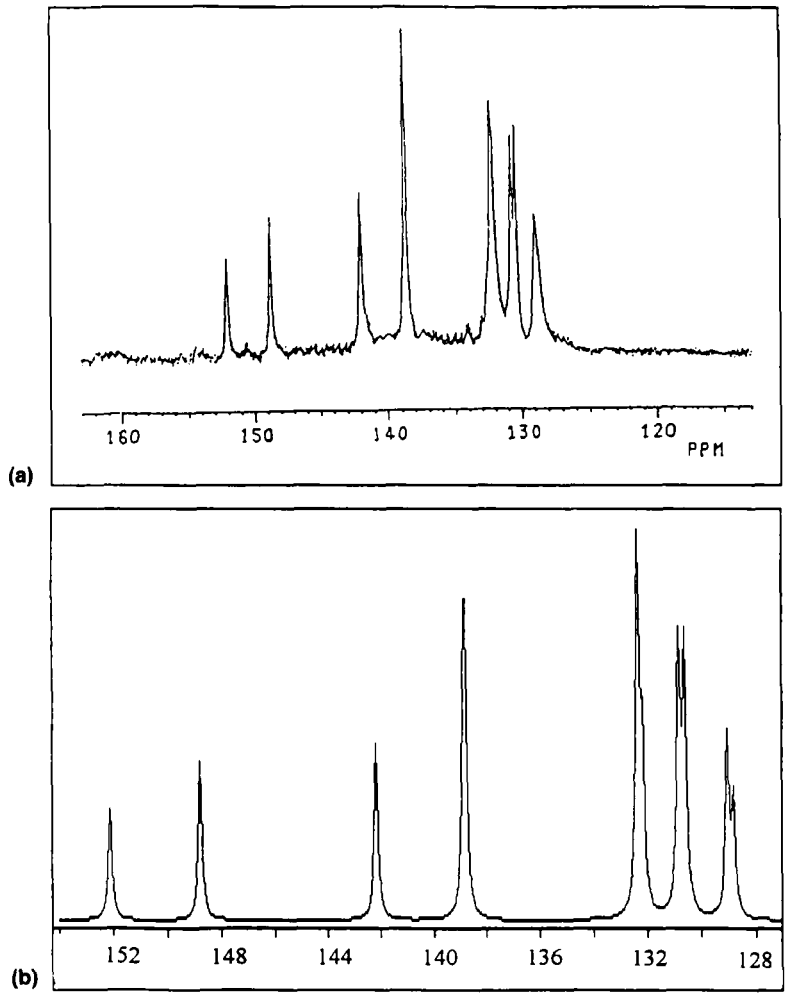


FIGURE 1 (a) ^{31}P-NMR spectrum of **6**; (b) simulation of the ^{31}P-NMR spectrum of **6**.

takes place on the exocyclic phosphorus atom. Otherwise diastereomeric compounds should occur, if the replacement takes place both on the endocyclic and the exocyclic phosphorus atom. Accordingly the reaction of the diester **9** characterized by two doublets at δ = 140.9 and δ = 144.7 in the ^{31}P-NMR spectrum with an excess of methyl iodide in nitromethane solution should only lead to a Michaelis-Arbuzov-reaction on the exocyclic phosphorus atom.

As expected the ^{31}P-NMR spectrum of the reaction solution showed besides a constant signal at δ = 140.9 characterizing the endocyclic phosphorus atom a shift to higher field of the signal for the exocyclic phosphorus atom.

This result is a further reference for an alcoholysis primarily taking place on the exocyclic phosphorus atom.

In contrast to the partially alkoxylated compounds the formation of the corresponding trialkoxyester **11** and **12** proceeded nearly quantitatively in the presence of an excess of NEt_3.

The ^{31}P-NMR spectroscopic data of the alcoholysis products of 2-chloro-3-dichlorophosphanyl-1-methyl-1.3.2-diazaphosphorinane **1** are summarized in Table V.

As can be seen from Table V there are only small differences of the ^{31}P-NMR chemical shift values and the $^{2}J_{PNP}$ coupling constants between the cyclic methoxy- and ethoxy derivatives. Considering the ^{31}P-NMR chemical shifts a nearly constant value for the completely alkoxylated exocyclic phosphanyl group is observed. Compared with the values for the ethoxy derivatives at δ = 142 and 143 the chemical

TABLE V

^{31}P-NMR data of the reaction products of **1** with alcohols

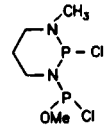
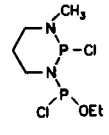
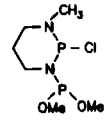
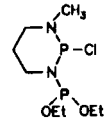
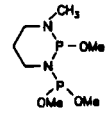
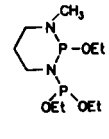
compound	δ^{31}P [ppm]	$^{2}J_{PNP}$ in Hz
	133.4 (D) 166.9 (D)	454
	132.7 (D) 166.4 (D)	412
7		
	133.7 (D) 164.2 (D)	454
	133.0 (D) 163.7 (D)	413
8		
	140.9 (D) 144.7 (D)	337
9		
	139.8 (D) 142.8 (D)	343
10		
	121.0 (D) 145.2 (D)	329
11		
	118.4 (D) 141.6 (D)	336
12		

TABLE VI
^{13}C-NMR data of **11**

δ^{13}C [ppm]	multiplicity	assignment
27.0	S	CH_2-$\underline{C}H_2$-CH_2
33.5	S	CH_2-$\underline{C}H_2$-N-P
40.0	D	N-$\underline{C}H_3$
46.9	D	$\underline{C}H_2$-N(CH_3)
50.5	M	O-$\underline{C}H_3$

TABLE VII
Results of the {^{13}C—^{1}H}-COSY experiment of **11**

δ^{13}C [ppm]	δ^1H [ppm]	intensity	assignment
27.0	1.29	1 H	CH_2-$\underline{C}H_2$-CH_2
	1.78	1 H	
33.5	3.19	1 H	CH_2-$\underline{C}H_2$-NP($OMe)_2$
	3.49	1 H	
40.0	2.51	3 H	N-$\underline{C}H_3$
46.9	2.39	1 H	$\underline{C}H_2$-NCH_3
	3.02	1 H	
50.5	3.31	9 H	O-$\underline{C}H_3$

shifts for the methoxy derivatives ($\delta \approx 145$) are weakly shifted (by about 3 ppm) to lower field. In this context it is known from the literature,[5] that the ^{31}P-NMR chemical shifts for $P(OR)_2(NR_2)$-compounds range from $\delta = 140$ to $\delta = 148$ depending on R; for example for $P(OEt)_2NEt_2$ a value of $\delta = 146$ is typical.[5] These data are a further reference for a substitution taking place primarily on the exocyclic phosphorus during the alcoholysis and are in agreement with the results obtained from the replacement reactions with amines and $NEt_3$3HF.

For the ^{31}P-NMR spectrum of compound **11** two doublets at $\delta = 121$ and $\delta = 145.2$ with a $^2J_{PNP}$ of 329 Hz were found to be typical.

As expected the ^{13}C-NMR data of **11** could be easily analyzed (see Table VI) based on the assignments of the ^{13}C-NMR data of **1**.[1]

In contrast to that the ^{1}H-NMR spectrum, however, was found to be more complicated, since with the exception of the NCH_3- and the OCH_3- protons all CH_2-protons are characterized by different chemical shift values. In order to obtain an exact correlation between the ^{1}H-nuclei and the ^{13}C-nuclei of **11** an {^{13}C-^{1}H}-COSY experiment was carried out leading to the assignments represented in Table VII.

EXPERIMENTAL

All experiments were carried out under an atmosphere of nitrogen with dry solvents and starting materials. The solvents were dried by standard methods. Standard Schlenk procedures were used for all syntheses. The NMR-spectra were recorded on a Bruker AM 300 spectrometer (operating frequencies ^{31}P: 121.5 MHz; ^{1}H: 300 MHz; ^{13}C: 75 MHz and ^{19}F: 282 MHz). The resonance frequencies are given

in δ (ppm) and referenced to 85% H_3PO_4 (^{31}P) and tetramethyl silane (^1H, ^{13}C) and to fluorotrichloromethane (^{19}F), respectively. A positive value of δ corresponds to a shift to lower field.

1. *The preparation of 2-chloro-3-dichlorophosphanyl-1-methyl-1.3.2-diazaphosphorinane* **1** *was carried out by the published procedure.*[1]

2. *Preparation of 2-diethylamino-3-bis(diethylamino)phosphanyl-1-methyl-1.3.2-diazaphosphorinane* **2**. A solution of 0.24 mol (17.3 g) of $HNEt_2$ in 5 ml of benzene is dropwise added to a solution of 0.039 mol (10 g) of **1** in 15 ml of benzene under vigorous stirring at 0°C. After 2 h additional stirring the formed H_2NEt_2Cl is filtered. The ^{31}P-NMR spectrum of the reaction solution indicated the formation of the diphosphorus compound with an intensity of 50%. After removing the solvent an increase of the signals between δ = 110 and 150 and between δ = 5 and 15 was observed. Attempted vacuum distillation (0.05 Torr, 96°C) caused decomposition of the oily residue.

^{31}P-NMR data: δ: 101.1 (D), 114.4 (D); $^2J_{PNP}$ = 312 Hz

3. *Preparation of 2-chlor-3-bis(diethylamino)phosphanyl-1-methyl-1.3.2-diazaphosphorinane* **3**. A solution of 0.079 mol (5.8 g) of $HNEt_2$ and 0.079 mol (8.0 g) of NEt_3 in 20 ml of benzene is dropwise added to 0.039 mol (10 g) of **1** in 80 ml of benzene under vigorous stirring at 0°C. After 2 h of additional stirring the formed $HNEt_3Cl$ is filtered and washed 3 times with 10 ml of benzene. The combined liquid filtrates are evaporated. The residue is distilled under vacuum (0.05 Torr) yielding the product as a red, viscous oil (yield: 69% (6.9 g)).

B.p.: (0.05 Torr = 6,6 Pa): 98°C
Anal. Calcd. for $C_{12}H_{29}N_4P_2Cl$ (326.45):
C, 44.11; H, 8.88; N, 17.15; P, 18.99; Cl, 10.86
Found: C, 43.98; H, 8.95; N, 17.12; P, 18.50; Cl, 10.90
^{31}P-NMR data (benzene): δ: 115.5 (D); 151.9 (D); $^2J_{PNP}$ = 214 Hz
^1H-NMR data (C_6D_6): δ: 0.95 (M) (14 H); 2.4 (D, J = 20 Hz) (3 H); 2.9 (M) (11 H); 3.05 (M) (1 H)
^{13}C-NMR data (C_6D_6): δ: 14.0 (S); 25.9 (S); 37.8 (M); 39.7 (D, $^2J_{PC}$ = 11 Hz); 40.2 (D, $^2J_{PC}$ = 19.7 Hz); 47.5 (D, $^2J_{PC}$ = 6.4 Hz)

4. *Preparation of 2-chlor-3-(diethylaminomonochlor)phosphanyl-1-methyl-1.3.2-diazaphosphorinane* **5**. Under vigorous stirring 0.039 mol (9.76 g) of $P(NEt_2)_3$ in 20 ml of benzene are dropwise added to a solution of 0.039 mol (10 g) of **1** in 80 ml of benzene at room temperature. Immediately a discoloring of the reaction solution to dark-yellow is observed. After 2 h of stirring the solvent is removed by distillation. The residue is distilled under vacuum yielding the product as a clear, yellow liquid (yield: 71% (8.1 g).

B.p.: (0.05 Torr = 6.6 Pa): 70–72°C
Anal. Calcd. for $C_8H_{19}N_3P_2Cl_2$ (289.9):
C, 33.09; H, 6.55; N, 14.48; P, 21.37; Cl, 24.44
Found: C, 32.95; H, 6.66; N, 14.51; P, 21.50; Cl, 24.60
^{31}P-NMR data (C_6D_6): δ: 136,0 (D); 140,0 (D); $^2J_{PNP}$ = 326 Hz
^1H-NMR data (C_6D_6): δ: 0.9 (M) (6H); 1.0 (M) (1 H); 1.2 (M) (1 H); 2.15 (D, $^3J_{PH}$ = 19.9 Hz) (3 H); 2.95 (M) (5 H); 3.2 (M) (3 H)
^{13}C-NMR data (C_6D_6): δ: 13.7 (S); 25.9 (S); 39.5 (D, $^2J_{PC}$ = 12.1 Hz); 40.3 (M); 41.1 (D, $^2J_{PC}$ = 20.4 Hz); 46.6 (S)

5. *Reactions of* **1** *with* $P(NR_2)_3$ *(R = Me,Et).* The $P(NR_2)_3$ is dropwise added to a solution of **1** in benzene under stirring at room temperature. Immediately a discoloring of the reaction solution to dark-yellow is observed. The reaction solution is liberated from the solvent and the residue is investigated by ^{31}P-NMR-spectroscopy (see Table VIII).

6. *Preparation of 2-chlor-3-difluorophosphanyl-1-methyl-1.3.2-diazaphosphorinane* **6**. Under vigorous stirring a solution of 0.026 mol (3.19 g) of $NEt_3 \cdot 3HF$ and 0.09 mol (9.3 g) of NEt_3 in 20 ml of acetonitrile is dropwise added to a solution of 0.039 mol (10 g) of **1** in 90 ml of acetonitrile at −20°C. The $HNEt_3Cl$ is filtered and washed 2 times with 10 ml of acetonitrile. The solvent is removed in the vacuum and the resulting liquid is immediately distilled in the vacuum yielding the product as a colourless liquid (yield: 78% (6.8 g).

B.p.: (0.05 Torr = 6.6 Pa): 60–62°C
Anal. Calcd. for $C_4H_9N_2P_2F_2Cl$ (220.45): C, 21.77; H, 4.08; N, 12.70
Found: C, 21.54; H, 4.12; N, 12.57

TABLE VIII

Results of the reactions of **1** with $P(NR_2)_3$

amount of $P(NR_2)_3$	amount of 1	^{31}P-NMR data of the reaction solution
0.98 g (3.9 mmol) $P(NEt_2)_3$ in 5 ml benzene	1 g (3.9 mmol) in 10 ml benzene	**5**: 2 doubl. at δ= 135.6; δ= 139.7 J_{PNP} = 313 Hz, 40% intensity; δ = 154 $ClP(NEt_2)_2$ side prod.: 2 singl. at δ = 142 and 163
1.96 g (7.8 mmol) $P(NEt_2)_3$ in 5 ml benzene	1 g (3.9 mmol) in 10 ml benzene	**3**: 2 doubl. at δ= 115.1; δ= 151.6 J_{PNP} = 214 Hz, 60% intensity; 1 singl. at δ= 154 $(ClP(NEt_2)_2$
1.29 g (7.9 mmol) $P(NMe_2)_3$ in 5 ml benzene	1g (3.9 mmol) in 10 ml benzene	**4**: 2 doubl. at δ= 117.7; δ= 151.4 J_{PNP}= 283 Hz, 60% intensity 1 singl. at δ= 159.8 $(ClP(NMe_2)_2$

^{31}P-NMR data (CH_3CN): δ $^{31}P_{exo}$ = 140.2; δ $^{31}P_{endo}$ = 131.0; $^2J_{PNP}$ = 404 Hz; $^1J_{PF}$ = −1227.7 Hz; $^3J_{PF}$ = 42.5 Hz
^{19}F-NMR data (CH_3CN): δ = −63.9 (D)
^1H-NMR data (CD_3CN): δ: 1.3 (M) (1 H) $CH_2(C\underline{H}_A\underline{H}_B)CH_2$; 1.8 (M) (1 H) $CH_2(CH_A\underline{H}_B)CH_2$; 2.6 (M) (4 H) $NC\underline{H}_3$—$(C\underline{H}_A\underline{H}_B)$—$CH_2$; 3.0 (M) (2H) $NCH_3(CH_A\underline{H}_B)CH_2$, $N(C\underline{H}_A\underline{H}_B)P_{exo}$; 3.5 (M) (1 H) $N(CH_A\underline{H}_B)P_{exo}$
^{13}C-NMR data (CD_3CN): δ: 26 (S) $CH_2\underline{C}H_2CH_2$; 35.5 (S) $\underline{C}H_2NP$; 40 (D, $^2J_{PC}$ = 30.5) $N\underline{C}H_3$; 46.5 (S) $\underline{C}H_2N(CH_3)$

7. Alkoholysis of **1** *with methanol and ethanol.* A solution of the alcohol in benzene is dropwise added to a solution of **1** and NEt_3 in benzene at 0°C under vigorous stirring. After 2 h of additional stirring the formed $HNEt_3Cl$ is filtered and the solvent is removed under vacuum. The residue was investigated by ^{31}P-NMR spectroscopy (see Table IX).

8. *Preparation of 2-methoxy-3-dimethoxyphosphanyl-1-methyl-1.3.2-diazaphosphorinane* **11**. The reaction is carried out in a molar ratio of 1:4:4 of **1**: methanol: NEt_3 in order to prevent a partial formation of the double methoxylated compound. A solution of 0.095 mol (3 g) of methanol in 20 ml of benzene is dropwise added to a solution 0.024 mol (6 g) of **1** and 0.095 mol (9.6 g) of NEt_3 in 50 ml of benzene at 0°C under vigorous stirring. After 2 h of additional stirring the $HNEt_3Cl$ is filtered and washed 3 times with 20 ml of benzene. The combined filtrates are evaporated and the residue is distilled in the vacuum yielding the product as a colourless liquid (yield: 4.2 g (74%)).

B.p.: 60°C (0.05 Torr = 6.6 Pa)
Anal. Calcd. for $C_7H_{18}N_2O_3P_2$ (240): C, 34.97; H, 7.49; N, 11.66; P, 25.80
Found: C, 34.97; H, 7.45; N, 11.62; P, 25.60
^{31}P-NMR data (benzene): δ: 121.0 (D); 145.2 (D); $^2J_{PNP}$ = 329 Hz
^1H-NMR data (C_6D_6): δ: 1.29 (M) (1 H); 1.78 (M) (1 H); 2.39 (M) (1 H); 2.51 (D, J = 16.7 Hz) (3 H); 3.02 (M) (1 H); 3.19 (M) (1 H); 3.31 (9 H); 3.49 (M) (1 H)
^{13}C-NMR data (C_6D_6): δ: 27.0 (S); 33.5 (S); 40.0 (D, $^2J_{PC}$ = 31.3 Hz); 46.9 (D, $^2J_{PC}$ = 5.9 Hz); 50.5 (M)

9. *Preparation of 2-ethoxy-3-diethoxyphosphanyl-1-methyl-1.3.2-diazaphosphorinane* **12**. The reaction is carried out in a molar ratio of 1:4:4 of **1**: ethanol: NEt_3 in order to prevent a partial formation of the double ethoxylated compound. A solution of 0.095 mol (4.36 g) of ethanol in 20 ml of benzene is dropwise added to a solution of 0.024 mol (6 g) of **1** and 0.095 mol (9.6 g) of NEt_3 in 50 ml of benzene at 0°C under vigorous stirring. After 2 h of additional stirring the $HNEt_3Cl$ is filtered and washed 3 times with 20 ml of benzene. The combined filtrates are evaporated and the residue is distilled in the vacuum yielding the product as a light yellow liquid (yield: 3.5 g (46%)).

B.p.: 89°C (0.05 Torr = 6.6 Pa)
Anal. Calcd. for $C_{10}H_{24}N_2P_2O_3$ (282): C, 42.55; H, 8.51; N, 9.93; P, 21.98
Found: C, 42.23; H, 8.75; N, 9.73; P, 21.80

TABLE IX

Results of the alcoholysis reactions of **1**

amount of alcohol	amount of **1**	amount of NEt_3	^{31}P-NMR data of the reaction solution
0.13 g (4 mmol) methanol in 3 ml benzene	1 g (4 mmol) in 7 ml benzene	0.4 g (4 mmol)	**7**: 2 doubl. at δ= 166.9; 133.4 J_{PNP}= 454 Hz; 2 doubl. at δ= 166.4; 132.7 J_{PNP}= 412 Hz; 20% side prod.: singl. at δ= 141,142,143, 170
0.18 g (4 mmol) ethanol in 3 ml benzene	1 g (4 mmol) in 7 ml benzene	0.4 g (4 mmol)	**8**: 2 doubl. at δ= 164.2; 133.7 J_{PNP} = 454 Hz 2 doubl. at δ= 163.7; 133.0 J_{PNP}= 413 Hz; 20% side prod.: singl. from δ= 0 to 20
0.26 g (8 mmol) methanol in 3 ml benzene	1 g (4 mmol) in 7 ml benzene	0.8 g (8 mmol)	**9**: 2 doubl. at δ= 140.9; 144.7 J_{PNP}= 337 Hz 40% intensity; **11**: 2 doubl. at δ= 121.0; 145.2 J_{PNP}= 329 Hz; side prod.: signals from δ= 10 to 40
0.36 g (8 mmol) ethanol in 3 ml benzene	1 g (4 mmol) in 7 ml benzene	0.8 g (8 mmol)	**10**: 2 doubl. at δ= 139.8; 142.8 J_{PNP}= 343 Hz intensity: 40%; **12**: 2 doubl. at δ= 118.4; 141.6 J_{PNP}= 336 Hz intensity: 30% side prod.: signals from δ= 10 to 30

^{31}P-NMR data (benzene): δ: 118.4 (D); 141.6 (D); $^2J_{PNP}$ = 336 Hz
^1H-NMR data (C_6D_6): δ: 0.98 (M) (9H); 1.28 (M) (1 H); 1.75 (M) (1 H); 2.39 (M) (1 H); 2.51 (D, J = 16 Hz) (3 H); 2.95 (M) (1 H); 3.18 (M) (1 H); 3.5 (M) (1 H); 3.9 (M) (6 H)
^{13}C-NMR data (C_6D_6): δ: 14.2 (S) $\underline{C}H_3$; 27.2 (S) $CH_2\underline{C}H_2CH_2$; 33.6 (S) $CH_2\underline{C}H_2NP$; 40.1 (D, $^2J_{PC}$ = 30.1 Hz) $N\underline{C}H_3$; 46.9 (D, $^2J_{PC}$ = 5.8 Hz) $\underline{C}H_2$—$N(CH_3)$; 49.5 (M) $O\underline{C}H_2$.

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