Derivatives of cis-NPCL$_2$(NSOCl)$_2$ and (NPCL)$_2$NSOCl, Part XIII [1]

**Methyl- and Ethylamino Derivatives of the Ring System cis-NPCL$_2$(NSOX)$_2$ with X = Chlorine and Fluorine**

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Methylamino Derivatives, Ethylamino Derivatives, Preparation, NMR

Aminolysis of cis-NPCL$_2$(NSOX)$_2$, with X = Cl or F, by MeNH$_2$ and EtNH$_2$ proceeds via a geminal substitution pattern. Preparation of the mono- and disubstituted derivatives is described. The NMR data are discussed.

**Discussion**

**Reaction pattern**

The ring systems 1 and 2 yield in a reaction with methyl- and ethylamine (molar ratio 1:2) in diethyl ether as well as in acetonitrile only mono derivatives with the amino substituent attached to the phosphorus atom. No sulphur substitution was observed in the $^{31}$P NMR spectra of the crude reaction mixtures, all $^{31}$P-signals were affected by $^{1}$H-$^{31}$P-coupling. This is in agreement with the results obtained by Van den Berg et al.: a small primary amine will react at the phosphorus atom [6].

Both in diethylether and in acetonitrile compound 1 forms two isomers in a ratio 1:5 whereas compound 2 gives two isomers in a ratio 3:7.

In view of the free space available at the oxygen atoms [7, 8] we suppose that in the isomer formed in the highest yield the amino and oxygen ligands are in cis-position.

* The first prefix is related to the position of the amino group with respect to the oxygen atoms, the second prefix to the position of the oxygen atoms with respect to each other.
Ring system 2 probably reacts less stereospecifically because of the smaller fluorine atoms. In contrast to the results obtained by Klingebiel and Heider [4, 5] we found that the cis- and trans-isomers have quite different δ^31P values (Table I).

The most abundant isomers could be isolated in a pure state and in all cases they appear to be white crystalline solids.

The second substitution step also takes place at the phosphorus atom. In these reactions, using four moles of amine per mole of the ring compound and diethylether as a solvent, cis-NPCl₂(NSOF)₂ is completely converted into cis-NPAm₂(NSOF)₂, but cis-NPCl₂(NSOCl)₂ the crude reaction product appears to be a 4:1 mixture of mono- and disubstituted products. Two reasons can be advanced for this difference in reactivity. First, from geometrical considerations the cis-isomer of NPClAm(NSOX)₂ leans itself less readily to the formation of a transition state with phosphorus in 5-coordination, than the trans-isomer. For X = Cl the relatively largest amount of cis-isomer is formed in the 1:2 reaction. The increase of the ratio cis/trans from 5 (2 mmoles ratio of amine) to 7 (4 mmoles ratio of amine) supports this view. Secondly, due to the smaller size of the fluorine atoms in comparison with the chlorine atoms, both isomers of cis-NPClAm(NSOF)₂ are more reactive to further substitution than the corresponding chlorine analogues.

To force the 1:4 reaction with cis-NPCl₂(NSOCl)₂ to completeness a more polar solvent has to be used. However, reactions carried out in acetonitrile yield large amounts of resinous material. In this case the best results are acquired with a 3:1 mixture of acetonitrile and diethylether.

Attempts to prepare the tri- and tetrasubstituted derivatives of cis-NPCl₂(NSOCl)₂ gave only very

Table I. NMR data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ^31P [ppm]</th>
<th>δ^1H [ppm]</th>
<th>2J_PH [Hz]</th>
<th>3J_PPH [Hz]</th>
<th>3J_NH_H [Hz]</th>
<th>3J_CH_H [Hz]</th>
<th>δ^19P [ppm]</th>
<th>δ^19P [Hz]</th>
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</thead>
<tbody>
<tr>
<td>cis-NPCl₂(NSOCl)₂ (1)</td>
<td>27.6</td>
<td>15.5</td>
<td>17.6</td>
<td>5.7</td>
<td></td>
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<tr>
<td>cis-cis-NPCINHMe₂(NSOCl)₂ (3)</td>
<td>17.5</td>
<td>2.82</td>
<td>CH₃</td>
<td>not detd</td>
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<tr>
<td>trans-cis-NPCINHMe₂(NSOCl)₂ (4)</td>
<td>20.3</td>
<td>2.90</td>
<td>CH₃</td>
<td>not detd</td>
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<tr>
<td>cis-NP(NHMe)₂₂(NSOCl)₂ (5)</td>
<td>10.9</td>
<td>2.68</td>
<td>NH</td>
<td>not detd</td>
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<tr>
<td>cis-cis-NPCINHET₂(NSOCl)₂ (6)</td>
<td>15.3</td>
<td>1.30</td>
<td>CH₃</td>
<td>16.6</td>
<td>15.1</td>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans-cis-NPCINHET₂(NSOCl)₂ (7)</td>
<td>17.9</td>
<td>1.20</td>
<td>CH₃</td>
<td>not detd</td>
<td></td>
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<td></td>
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<tr>
<td>cis-NP(NHET)₂₂(NSOCl)₂ (8)</td>
<td>7.2</td>
<td>1.30</td>
<td>CH₃</td>
<td>1.2</td>
<td>7.0</td>
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<tr>
<td>cis-NPCl₂(NSOF)₂ (2)</td>
<td>30.9</td>
<td>15.8</td>
<td>17.9</td>
<td>5.7</td>
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<tr>
<td>cis-cis-NPCINHMe₂(NSOF)₂ (9)</td>
<td>21.2</td>
<td>2.87</td>
<td>CH₃</td>
<td>15.8</td>
<td>15.0</td>
<td>5.0</td>
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<td>trans-cis-NPCINHMe₂(NSOF)₂ (10)</td>
<td>23.7</td>
<td>2.86</td>
<td>CH₃</td>
<td>not detd</td>
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<tr>
<td>cis-NP(NHMe)₂₂(NSOF)₂ (11)</td>
<td>13.0</td>
<td>2.71</td>
<td>CH₃</td>
<td>not detd</td>
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<tr>
<td>cis-cis-NPCINHET₂(NSOF)₂ (12)</td>
<td>18.9</td>
<td>1.31</td>
<td>CH₃</td>
<td>16.0</td>
<td>14.9</td>
<td>7.1</td>
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<td>trans-cis-NPCINHET₂(NSOF)₂ (13)</td>
<td>21.4</td>
<td>1.21</td>
<td>CH₃</td>
<td>not detd</td>
<td></td>
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<tr>
<td>cis-NP(NHET)₂₂(NSOF)₂ (14)</td>
<td>9.7</td>
<td>1.22</td>
<td>CH₃</td>
<td>1.0</td>
<td>7.3</td>
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</tbody>
</table>

a Centre of broad band; b hidden by N–CH₃ proton signal, hence positioned at ca. 3.0–3.2 ppm.
small yields of the substitution products together with large amounts of resinous material.

$^{31}$P NMR

The $^{31}$P NMR data are listed in Table I. As we can expect, in all cases the resonance signals shift to higher field on progressing aminolysis: $\delta_{\text{PCl}_2} > \delta_{\text{PClAm}} > \delta_{\text{PAm}_2}$. Examining the chemical shifts, there appears to be an almost constant difference (2.5–2.8 ppm) between the $\delta_{^{31}P}$ value of a cis-isomer and that of a trans-isomer, despite of the different ligands at the sulphur atoms (Cl or F). Plotting the $\delta_{^{31}P}$ value (or mean value if two isomers are present) against the degree of substitution (n) linear relationships are obtained (Fig. 1). Both for the methyaminio and ethylamino derivatives the graph for $X = \text{F}$ is found at the lowest field. This can be ascribed to the larger electron-withdrawing capacity of the SOF group compared to the SOCl group.

The slopes of the graphs show that an ethylamino group affects the $^{31}$P chemical shift more than a methylamino group. They seem to follow the base strengths of the amines concerned, although the differences are small ($pK_a(\text{MeNH}_2) = 10.66$; $pK_a(\text{EtNH}_2) = 10.81$).

$^1H$ NMR

The CH$_3$ proton signal of the methyaminio group is split into a doublet of doublets due to coupling with the phosphorus atom and the NH proton. The CH$_3$ resonance of the ethylamino group consists of a triplet of doublets because of coupling with the CH$_2$ protons and the phosphorus atom. The CH$_2$ signal is split by coupling with three centres viz. the phosphorus atom, the NH proton and the CH$_3$ protons. The NH proton is recognizable as a broad band, which shifts to lower field after prolonged standing of the solution (in CDCl$_3$), probably due to decomposition. The NH resonance and the coupling with the NH proton disappear by shaking a freshly prepared solution with D$_2$O.

As shown in Table I the NH proton resonance is found in the mono (amino) derivatives at 3.9 to 4.0 ppm and in the bis(amino) derivatives at 3.0–3.2 ppm. This is consistent with the results obtained for the ethyl- and i-propylamino derivatives of (NPC$_2$)$_2$ [9, 10]. A similar up-field shift is observed for the methyl and methylene protons, which points to the electron-donating capacity of the amino groups.

Considering the $|^{3}J_{PH}|$ and $|^{3}J_{NHCH}|$ values, we notice that they are not very sensitive for variation of the substituent X. They depend more on the amine used and on the degree of substitution: $|^{3}J_{PH}| (\text{MeNH}) > |^{3}J_{PH}| (\text{EtNH})$ and $|^{3}J_{PH}| (\text{mon}) > |^{3}J_{PH}| (\text{di})$; $|^{3}J_{NHCH}| (\text{MeNH}) < |^{3}J_{NHCH}| (\text{EtNH})$ and $|^{3}J_{NHCH}| (\text{mon}) > |^{3}J_{NHCH}| (\text{di})$. With regard to the $|^{3}J_{PH}|$ values of the two isomers of cis-NPCl Am (NSOX)$_2$, it appears that $|^{3}J_{PH}| (\text{cis}) < |^{3}J_{PH}| (\text{trans})$. This corresponds with the observations made by De Ruijter for the dimethylamino derivatives of cis-NPC$_2$(NSOCl)$_2$ [2].
For the compounds cis-NPAm{(NSO)X}2 the two different amino groups can be distinguished in the \( ^1H \) NMR spectra. Regarding the \( |J_{PH}| \) values of the two groups and comparing these values with those of the cis- and trans-isomers of NPCAm{(NSO)X}2, we assume that the signal with the smallest \( |J_{PH}| \) belongs to the amino group in cis-position with respect to the oxygen atoms.

**Experimental**

All experiments were carried out under dry nitrogen. cis-NPCl2{(NSOCl)2} and cis-NPCl2{(NSOF)2} were synthesized as described elsewhere \[11, 12\]. A solution of methyl- or ethylamine in diethylether or acetonitrile was obtained by distilling the amine via a KOH column into a vessel containing diethylether or acetonitrile. The concentration was determined by titration. Solvents were purified and dried by conventional methods. The element analyses were carried out at the Microanalytical Department of this University under supervision of Mr. A. F. Hamminga. The infrared spectra were recorded on a Hitachi EPI-G spectrophotometer using Nujol mulls between KBr discs. Calibration was carried out by means of polystyrene film bands. The mass spectra were taken by Mr. A. Kiewiet (Department of Organic Chemistry of this University) on an AEI MS9 mass spectrometer at 70 eV, using an accelerating voltage of 8 kV. The samples were introduced directly by a conventional inlet system. The \( ^1H \) NMR spectra were taken on a Varian A 60 spectrometer at 35 °C from a freshly prepared solution in CDCl3 and standardized towards internal TMS. The \( ^31P \)-NMR and \( ^19F \)-NMR spectra were recorded by Mr. R. H. Fokkens and Mr. C. Kruk (NMR Department, University of Amsterdam) on a Varian XL-100 FT spectrometer at 37 °C, operating at 40.5 MHz and 94.1 MHz, respectively. Chemical shifts were determined relative to the external standards \( 85\% \) H3PO4(\( ^31P \)) and CFCl3(\( ^19F \)) and defined as positive in low-field direction. The \( ^1H \) resonance of the solvent CDCl3 was used for field-frequency lock.

**General method of preparation**

At —20 °C, a solution of \( n \) mmoles of amine in 40 ml of diethylether or acetonitrile was added dropwise to a stirred solution of \( m \) mmoles of ring compound in 40 ml of diethylether or acetonitrile, over a period of about 30 min. The reaction mixture was allowed to warm up slowly to room temperature and was kept for about 20 h at room temperature under stirring. The solution was filtered off and the residue extracted with diethylether or acetonitrile. After evaporation of the solvent, the crude reaction product was obtained and purified by recrystallization from a suitable solvent.

**1. Reaction of cis-NPCl2{(NSOCl)2} with MeNH2 (molar ratio 1:2) in Et2O**

The crude reaction product, consisting of a 5:1 mixture of the compounds 3 and 4, was recrystallized from CCl4. Yield: 28.5\% of cis-cis-NPCINHMe{(NSOCl)2} (3), m.p. 105—108 °C.

**Analysis**

Calcd C3.95 H1.35 18.56 20.98 34.89.

Found C3.95 H1.35 18.56 20.98 34.89.

**IR (cm\(^{-1}\))**

3390 s, 3360 s, 1330 vs, 1278 vs, 1190 vs, 1116 vs, 1093 vs, 1016 vs, 909 m, 888 s, 823 s, 792 s, 703 s, 629 vs, 535 vs, 516 s, 499 s, 427 m.

**2. Reaction of cis-NPCl2{(NSOCl)2} with MeNH2 (molar ratio 1:4) in Et2O**

The crude reaction product consisted of a 7:1:2 mixture of the compounds 3, 4 and 5. No disubstituted product was isolated.

**3. Reaction of cis-NPCl2{(NSOCl)2} with MeNH2 (molar ratio 1:4) in MeCN**

The crude reaction product was recrystallized from CHCl3. Yield: 9.0\% of cis-NP(NHMe)2{(NSOCl)2} (5), m.p. 83-84.5 °C.

**Analysis**

Calcd C8.03 H2.65 N23.35 21.50 23.78.

Found C8.03 H2.65 N23.35 21.50 23.78.

**IR (cm\(^{-1}\))**

3370 s, 3340 s, 1328 vs, 1301 vs, 1186 vs, 1122 s, 1025 vs, 834 m, 818 m, 718 s, 662 vs, 573 s, 543 s, 527 vs, 434 m.

**4. Reaction of cis-NPCl2{(NSOCl)2} with EtNH2 (molar ratio 1:2) in Et2O**

The crude reaction product, consisting of a 5:1 mixture of the compounds 6 and 7, was recrystallized from a mixture of Et2O and n-C2H6. Yield: 41.9\% of cis-cis-NPCINHEt{(NSOCl)2} (6), m.p. 107–109 °C.

**Analysis**

Calcd C7.80 1.92 17.69 20.31 33.27.

Found C7.80 1.92 17.69 20.31 33.27.

**IR (cm\(^{-1}\))**

3370 s, 3335 s, 1323 vs, 1309 vs, 1291 vs, 1118 vs, 1171 vs, 1117 vs, 1093 vs, 1097 vs, 1084 s, 1028 vs, 829 m, 712 vs, 659 vs, 570 m, 541 m, 527 vs, 434 m.

**m/e**

318 M32Cl 1.1\%, 283 (M32Cl—32Cl)+ 100\%.
5. Reaction of cis-NPCl₂(NSOCl)₂ with EtNH₂ 
(molar ratio 1:4) in a mixture of Et₂O and MeCN 
The reaction was carried out with 5 mmoles of 
cis-NPCl₂(NSOCl)₂ in MeCN and 20.0 mmoles of 
EtNH₂ in a 1:1 mixture of Et₂O and MeCN. The 
crude reaction product was recrystallized from 
CCl₄. Yield: 26.8% of cis-NP(NH₂)₂(NSOCl)₂ (8), m.p. 
89-91 °C. 

Analysis 
Caled C14.64 H3.69 N21.34 S 19.54 C121.61, 
Found C14.58 H3.67 N21.50 S 19.73 C121.57, 

IR (cm⁻¹) 
3370 s, 3350 s, 1420 m, 1314 vs, 1299 vs, 1273 m, 
1199 m, 1138 s, 1122 vs, 1078 m, 1043 s, 
998 m, 974 m, 814 m, 794 m, 778 m, 703 m, 651 m, 
604 m b r, 552 s, 520 m, 472 m.

m/e 
292 (M²Cl⁻³⁵Cl)⁺ 100%.

6. Reaction of cis-NPCl₂(NSOF)₂ with MeNH₂ 
(molar ratio 1:2) in Et₂O 
The crude reaction product, consisting of a 7:3 
mixture of the compounds 9 and 10, was recrystall-
lized from n-C₅H₁₂. Yield: 46.5% of 
cis-cis-NP(NHMe)₂(NSOF)₂ (9), m.p. 62-64 °C. 

Analysis 
Caled C4.41 H1.48 N20.55 S23.52 Cl 13.00, 
Found C4.76 H1.55 N20.52 S23.54 Cl 12.87, 

IR (cm⁻¹) 
3375 s, 1215 vs br, 1161 s, 1110 m, 1071 s, 861 s, 
804 vs, 732 s, 708 m, 638 s, 579 s, 544 m, 523 m.

m/e 
286 M⁻³⁵Cl+ 9.7%, 271 (M⁻³⁵Cl-CH₃)⁺ 100%.

9. Reaction of cis-NPCl₂(NSOF)₂ with EtNH₂ 
(molar ratio 1:3.6) in Et₂O 
The crude reaction product was recrystallized 
from a mixture of CCl₄ and n-C₅H₁₂. Yield: 27.9% 
of cis-NP(NH₂)₂(NSOF)₂ (11), m.p. 44-45 °C. 

Analysis 
Caled C16.27 H4.10 N23.72 S21.72, 
Found C16.48 H3.92 N23.97 S21.93, 

IR (cm⁻¹) 
3365 s, 1360 vs, 1279 s, 1240 vs, 1168 s, 
1112 vs br, 1084 and 1080 vs, 980 m, 850 m, 757 s, 
724 vs, 704 s, 550 m, 520 m, 444 m br.

m/e 
295 M⁻⁺ 60.0%, 260 (M⁻⁻CH₃⁻⁻HF)⁺ 100%.

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forsch. 33b, 959 (1978); H. H. Baalmann and 
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