Introduction

Recently, attention has been paid to the aminolysis of (NPCl₂)₂NSOX, with X = Cl or F by cyclic secondary amines [2, 3]. It appeared that the substitution follows a non-geminal pattern, whereas the S-F bond is stable towards aminolysis. From reactions of (NPCl₂)₂NSOX, with X = Cl or F by cyclic secondary amines [2-4] it is known that both the S-F and S-Ph bonds are not severed in the amination reaction.

Studies on the reactions of (NPCl₂)₂ with methyl- and ethylamine revealed that these amines afford mainly non-geminal bis(amino) substitution products. The trans-isomer is formed predominantly. In the reactions of (NPCl₂)₂NSOPh, on the other hand, the cis-isomer is the main product of the non-geminal isomers. Recently, the influence of the solvent on the mode of substitution has been demonstrated in reactions of (NPCl₂)₂ with methylamine and dimethylamine [5], and with i-propylamine [6]. It appears that the ratio of isomers N₂P₂Cl₄Am₂ (Am = amino) depends on the solvent used. A similar observation has been made in the reactions of (NPCl₂)₂NSOPh with methyl- and ethylamine.

Reaction Pattern

(NPCl₂)₂NSOPh (1) reacts with methyl- or ethylamine, molar ratio 1:2, in diethylether as a solvent, to form a monosubstituted product with the amino group attached to a phosphorus atom. No substitution reaction at sulphur is observed. Although only one of the two possible P(amino) isomers could be detected and isolated, the other isomer has also to be present in the product since otherwise the formation of cis-trans-(NPCINHMe₂)₂NSOPh* (5) and cis-trans-(NPCINHEt₂)₂NSOPh* (13) in the 1:4 reactions has to be explained by an isomerization process. Assuming an S₂ type reaction, we expect that for steric reasons in the mono(amino) isomer the amino group and the oxygen atom are in cis-position; the small amount of the trans-isomer escapes detection.

Carrying out the reaction, using four equivalents of amine, all the possible P,P substituted isomers, as depicted below, are formed (derived from ³¹P NMR spectra); again, the phenyl group is not replaced.

Only the cis-cis- and the geminal isomers are formed in sufficiently large amounts to be isolated and characterized. Just as in the ring system

* The first prefix is related to the position of the amino groups which respect to each other, the second prefix is related to the position of the amino groups with respect to the oxygen atom.
The third substitution step also takes place at a phosphorus atom only and both possible trisubstituted isomers are formed.

Again the most abundant isomer is assumed to have a cis-structure.

Even with an excess of amine, no substitution at sulphur is observed and only (NPAm₂)₂NSOPh is formed. The experimental data given above emphasize the stability of the S–Ph bond in (NPCl₂)₂NSOPh in reactions with primary amines. This agrees with the behaviour of trans-NPCl₂-(NSOPh)₂ towards Me₂NH [4].

**NMR Spectra**

As in the ¹H NMR spectra of the methyl- and ethylamino derivatives of cis-NPCl₂(NSOCl)₂, with X = Cl or F [7], the ¹H NMR spectra of the derivatives of (NPCl₂)₂NSOPh show the usual proton-proton couplings and the coupling with the nearest phosphorus atom (Table Ia, b). Moreover, the ¹H NMR spectra are characterized by an additional, small splitting, which does not agree with the ¹H–³¹P-coupling over five bonds (Fig. 1). This feature is due to second-order effects. These effects

Table Ia. NMR data of the methy lamino derivatives of (NPCl₂)₂NSOPh.

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ³¹P [ppm]</th>
<th>δ¹H [ppm]¹</th>
<th>δ¹Jph [Hz]²</th>
<th>δ¹J*ph [Hz] ²</th>
<th>δ¹JNH[Hz] ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NPCl₂)₂NSOPh (1)</td>
<td>20.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>cis-NPCINHMeNPCl₂NSOPh (2)</td>
<td>22.5</td>
<td>20.0</td>
<td>60.8</td>
<td>2.76</td>
<td>3.9</td>
</tr>
<tr>
<td>cis-cis-(NPCINHMe)₂NSOPh (3)</td>
<td>23.1</td>
<td></td>
<td>2.78</td>
<td>3.5</td>
<td>18.3</td>
</tr>
<tr>
<td>trans-(NPCINHMe)₂NSOPh (4)</td>
<td>23.3, 23.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-trans-(NPCINHMe)₂NSOPh (5)</td>
<td>23.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NP(NHMe)₂NPCl₂NSOPh (6)</td>
<td>23.5</td>
<td></td>
<td>12.3, 52.9</td>
<td>2.49, 2.65</td>
<td>4.6</td>
</tr>
<tr>
<td>cis-NP(NHMe)₂NPCINHMeNSOPh (7)</td>
<td>26.9</td>
<td>15.2</td>
<td>50.4</td>
<td>2.54, 2.66</td>
<td>3.4</td>
</tr>
<tr>
<td>trans-NP(NHMe)₂NPCINHMeNSOPh (8)</td>
<td>26.7</td>
<td>14.8</td>
<td>47.9</td>
<td>2.42, 2.56</td>
<td>2.8</td>
</tr>
<tr>
<td>(NP(NHMe)₂)₂NSOPh (9)</td>
<td>17.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹ The phenyl group gives two multiplets centered on 7.3–7.6 and 7.9–8.1 ppm respectively; the value for NH reflects the centre of a broad band; in some cases NH bands are hidden by carbon-bonded H signals;
² ³J*ph = ³Jph + ³Jph ≈ 3Jph;
³ two inner lines of an AB pattern, the outer ones are not visible.
Table Ib. NMR data of the ethylamino derivatives of (NPCl₂)₂NSOCl.

| Compound | δ¹³P [ppm] | δ¹H [ppm] | | | |
|----------|------------|-----------|-------|-------|
| cis-NPCINH₂NPCl₂NSOCl (10) | 22.4 | 17.7 | 61.1 | 1.25 | 3.20 | 4.0 | 14.1 | 6.7 | 1.0 |
| cis-cis-(NPCINH₂)₂NSOCl (11) | 20.8 | | 1.22 | | 3.16 | | 3.6 | 14.0 | 6.3 | not obsd. |
| trans-(NPCINH₂)₂NSOCl (12) | 21.4, 21.2⁹ | | | | | | | |
| cis-trans-(NPCINH₂)₂NSOCl (13) | 21.7 | | | | | | | |
| NP(NH₂)₂NPCl₂NSOCl (14) | 23.3 | 8.5 | 53.9 | 1.03, 1.19 | 2.88, 3.06 | 11.0, 11.9 | not obsd. | 0.9, 0.8 |
| cis-NP(NH₂)₂NPCINH₂NSOCl (15) | 24.3 | 11.1 | 50.0 | 1.02, 1.16, multiplet | 4.0 | not detd. | not detd. | 1.1, 0.9, 1.2 |
| trans-NP(NH₂)₂NPCINH₂NSOCl (16) | 24.6 | 11.5 | 46.7 | | | | |
| (NP(NH₂)₂)₂NSOCl (17) | | 13.5 | | | | | | |

| | | | | | |
| | | | | | |

Note: See Table Ia; a ⁴J*PH = ⁴JPH + 6JPH ≈ ⁴JPH; |³JCHCH| varies from 6.9–7.3 Hz.

have also been found in the proton spectra of the amino derivatives of (NPCl₂)₂ [10].

To demonstrate that this additional splitting does arise from second-order effects, the ¹H NMR spectrum of cis-NPCINHMeNPCl₂NSOCl (2) was simulated. To make an estimation of the necessary parameters a number of double resonance experiments were carried out.

The ³¹P(¹H) spectrum shows an AB spectrum, which provided the values of vₓ, vᵧ and |Jₓᵧ|. The selective decoupled spectra, ³¹P(CH₃) and ³¹P(NH) gave |Jₓₓ|, |Jₓᵧ| and |Jᵧᵧ|, respectively. From the ¹H(³¹P) spectrum the values of vₓ, vᵧ and |Jₓᵧ| could be obtained. By a slight adjustment of the parameters, taking Jₓₓ ≠ 0 and all J’s positive, the simulated spectrum shows very good agreement with the experimental one (Fig. 1).

In the simulation, the XY part was placed as far as possible (10,000 Hz = maximum range of computer) from the AB part.

The NH proton signals of a PClAm and a PAm₂ group are found at 3.4–4.0 ppm and 2.5–3.0 ppm, respectively. For the CH₂- and CH₃-proton signals of a PAm₂ group a similar up-field shift is observed. This agrees with the observations made previously for the amino derivatives of (NPCl₂)₃ [6, 8] and of cis-NPCl₂(NSOX)₂, with X = Cl or F [7] and reflects the electron-donating character of the amino group (in PAm₂) compared with the electronegative chlorine atom (in PClAm). Two different signals are
found if two amino groups are attached to the same phosphorus atom. Since a phenyl group is the most shielding, we assume that the signal at the highest field belongs to the amino group in cis-position with respect to the phenyl group.

Considering the \(|J_{NHCH}|\) and \(|J_{PH*}|\) values found for the derivatives of \((NPCl_2)_2NSOPh\) we notice that \(|J_{NHCH}| (MeNH) < |J_{NHCH}| (EtNH), |J_{PH*}| (MeNH) > |J_{PH*}| (EtNH)\) and \(|J_{PH*}| (mono) > |J_{PH*}| (bis)\). This has also been observed in the derivatives of \(cis-NPCl_2(NSOX)_2\), with \(X = Cl\) or \(F\) [7]. From the \(^1\)H chemical shift assignment to the \(PAm_2\) group, given above, it appears that the \(|J_{PH*}|\) value of the amino group \(cis\) to oxygen is the largest one.

As expected, the \(\delta_{31P}\) resonance shifts to higher field on geminal substitution. Comparative examination of the \(\delta_{31P}\) values of the methyl- and ethyl-amino derivatives reveals that \(\delta_{PClNHMe} - \delta_{PClNHEt} \approx 2.3\) ppm and \(\delta_{P(NHMe)_2} - \delta_{P(NHET)_2} \approx 4.0\) ppm.

Analogous differences are found in the spectra of the methyl- and ethylamino derivatives of \(cis-NPCl_2(NSOX)_2\) \((X = Cl, F)\) [7]. As already stated before [7], it is obvious that the difference in basicity between the two amino ligands is the cause of these differences.

Using the same parameters as for the simulation of the proton spectrum, we computed the \(^{31P}\) NMR spectrum of \(cis-NPClNHMeNPCl_2NSOPh\) (2). Fig. 2 shows the resemblance of the experimental and the calculated coupled \(^{31P}\) spectrum.

As shown in Fig. 3 there exists a linear correlation between \(\delta_{PClAm}\) and the degree of substitution at the other phosphorus atom \((n)\). The same correlation has already been found for some secondary amino derivatives of \((NPCl_2)_3\), \((NPCl_2)_2NSCl\) and \(cis-NPCl_2(NSOCl)_2\) [11, 12].

![Fig. 2. Comparison of the experimental and simulated \(^{31P}\) NMR spectrum of \(cis-NPClNHMeNPCl_2NSOPh\).
Inside the parameters (in Hz) used for simulation.](image)

![Fig. 3. Graphical representation of the \(^{31P}\) NMR chemical shift (in ppm) of \(PClAm\) group (Am \(cis\) to = 0) versus the degree of substitution \((n)\).](image)

**Experimental**

All experiments were carried out under dry nitrogen. \((NPCl_2)_2NSOPh\) was synthesized as described elsewhere [4]. Solutions of methyl- or ethylamine in diethylether or acetonitrile were obtained by distilling the amine via a KOH column into a vessel containing the solvent. Amine concentrations were 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 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 $^1$H NMR spectra were recorded on a Varian A60 spectrometer at 35 °C from freshly prepared solutions in CDCl$_3$ and standardized towards internal TMS. $^3$P—$^{31}$P double resonance experiments were carried out at 100.1 MHz on a Varian XL-100 under high power noise decoupling conditions (bandwidth 3000 Hz). The $^{31}$P NMR spectra were recorded by Mr. R. H. Fokkens (NMR Department, University of Amsterdam) on a Varian XL-100 FT spectrometer in 5 mm tubes at 37 °C and 40.5 MHz with proton noise decoupling. Chemical shifts were determined relative to the external standard 85% H$_3$PO$_4$ and defined as positive in low-field direction. The $^3$H resonance of the solvent CDCl$_3$ was used for field-frequency lock. Selective $^3$H decoupled spectra were obtained by low power coherent decoupling conditions (gyrocode setting = 99 dB). Spectral simulation was performed by the spin-simulation program SIMEQ.

Both the purified products and the crude reaction mixtures were subjected to $^1$H and $^{31}$P NMR measurements. The ratio of products, as given in the experimental part, were estimated from the $^{31}$P NMR spectra of the crude reaction mixtures.

**General method of preparation**

At low temperature, a solution of the appropriate amount of amine in 40 ml of diethyl ether or acetonitrile was added dropwise to a stirred solution of 5 mmoles of (NPCl$_2$)$_2$NSOPh (1) in 40 ml of diethyl ether 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 that temperature under stirring. The solution was filtered off and the residue extracted with diethyl ether or acetonitrile, over a period of about 30 min. The reaction mixture was allowed to warm up to room temperature and was kept for about 100 h at that temperature under stirring. The solution was filtered off and the residue extracted with diethyl ether or acetonitrile. After evaporation of the solvent, the crude reaction product was obtained and purified by recrystallization from a suitable solvent.

1. **Reaction of (NPCl$_2$)$_2$NSOPh with MeNH$_2$ (molar ratio 1:2) in Et$_2$O**

   The reaction was carried out at —20 °C. The crude reaction mixture was recrystallized from n-C$_6$H$_{14}$. Yield: 50.9% of NPClNHEtNPClNSOPh (2), m.p. 76–82 °C.

   **Analysis**

   Caled C 23.00 H 2.48 N 15.33 S 8.77 Cl 29.10.
   Found C 23.20 H 2.56 N 15.33 S 8.91 Cl 29.22.
   m/e: 364 M$^{35}$Cl+ 100%.

2. **Reaction of (NPCl$_2$)$_2$NSOPh with MeNH$_2$ (molar ratio 1:4) in Et$_2$O**

   The reaction was carried out at —30 °C. The crude reaction product consisted of a 20:6:1:1:3 mixture of the compounds 2, 3, 4, 5 and 6. No attempts were made to isolate the products.

3. **Reaction of (NPCl$_2$)$_2$NSOPh with MeNH$_2$ (molar ratio 1:4) in MeCN**

   The reaction was carried out at —30 °C. The crude product, consisting of a 5:1:7 mixture of the compounds 3, 5 and 6, was recrystallized from Et$_2$O. Yield 8.9% of (NPCINHMe)$_2$NSOPh (3), m.p. 155 to 156 °C.

   **Analysis**

   Caled C 26.68 H 3.64 N 19.45 P 17.20 Cl 19.69.
   Found C 26.51 H 3.73 N 19.66 P 17.02 Cl 19.85.
   m/e: 359 M$^{35}$Cl+ 38.5%, 330 (M$^{35}$Cl—NCH$_3$) — 100%.

   Compound 6 could not be obtained in an analytically pure state.

4. **Reaction of (NPCl$_2$)$_2$NSOPh with MeNH$_2$ (molar ratio 1:6) in MeCN**

   The reaction was carried out at —40 °C. The crude reaction product, consisting of a 1:1:4:18:2 mixture of the compounds 3, 5, 6, 7 and 8, was recrystallized from a mixture of CHCl$_3$ and Et$_2$O. Yield: 6.6% of NP(NHMe)$_2$NPClNHMeNSOPh (7), m.p. 142–147 °C.

   **Analysis**

   Found C 30.34 H 4.79 N 23.57 S 9.02 Cl 10.07.
   m/e: 354 M$^{35}$Cl+ 100%.

5. **Reaction of (NPCl$_2$)$_2$NSOPh with MeNH$_2$ (molar ratio 1:13.6) in MeCN**

   The reaction was carried out at —40 °C. The crude reaction product was recrystallized from a mixture of CHCl$_3$ and Et$_2$O. Yield: 4.8% of NP(NHMe)$_2$NPClNHMeNSOPh (9), m.p. 148–150 °C.

   **Analysis**

   Caled C 34.38 H 6.06 N 28.07 S 9.18.
   Found C 34.38 H 6.08 N 27.86 S 9.10.
   m/e: 349 M+ 100%.

6. **Reaction of (NPCl$_2$)$_2$NSOPh with EtNH$_2$ (molar ratio 1:2) in Et$_2$O**

   The reaction was carried out at —70 °C. The crude reaction product was recrystallized from n-C$_6$H$_{14}$. Yield: 6.8% of NPCINH$_2$EtNPCl$_2$NSOPh (10), m.p. 54–56 °C.

   **Analysis**

   Caled C 25.31 H 2.92 N 14.76 S 8.45 Cl 28.02.
   Found C 25.38 H 2.91 N 14.79 S 8.52 Cl 28.04.
   m/e: 378 M$^{35}$Cl+ 99.5%, 301 (M$^{35}$Cl—C$_6$H$_{14}$) 100%.

7. **Reaction of (NPCl$_2$)$_2$NSOPh with EtNH$_2$ (molar ratio 1:4) in Et$_2$O**

   The reaction was carried out at —20 °C. The crude reaction product consisted of a 4:6:1:5 mix-
ture of the compounds 10, 11, 12 and 14. No attempts were made to isolate products.

8. Reaction of (NPCl₂)₂NSOPh with EtNH₂ (molar ratio 1:4) in MeCN

The reaction was carried out at —20 °C. The crude reaction product consisted of a 3:1:4 mixture of the compounds 11, 12 and 14. No attempts were made to isolate products.

9. Reaction of (NPCl₂)₂NSOPh with EtNH₂ (molar ratio 1:4) in a mixture of MeCN and Et₂O

The reaction was carried out with 5 mmoles of (NPCl₂)₂NSOPh in 40 ml of MeCN and 20 mmoles of EtNH₂ in a 1:1 mixture of MeCN and Et₂O at —30 °C. The crude product was fractionally re-crystallized from Et₂O. Yield 2.6% of (NPCINH₂E₆)₂NSOPh (11), m.p. 143.5-145 °C and 4.6% of NP(NH₂E₆)₂NPCl₂NSOPh (14), m.p. 72 to 75 °C.

Analysis
Calcd C 30.94 H 4.41 N 18.04 S 8.26
Found C 31.21 H 4.57 N 17.96 S 8.20
m/e: 387 M35Cl+ 64.6%, 344 (M35Cl-NCH₂CH₃)+ 100%.

10. Reaction of (NPCl₂)₂NSOPh with EtNH₂ (molar ratio 1:6) in MeCN

The reaction was carried out at —20 °C. The crude reaction mixture consisted of a 9:3:1:15:43:19 mixture of the compounds 11, 12, 13, 14, 15 and 16. Despite many efforts it was not possible to obtain compound 15 in an analytically pure state.

11. Reaction of (NPCl₂)₂NSOPh with EtNH₂ (molar ratio 1:13.6) in MeCN

The reaction was carried out at —40 °C. The crude reaction mixture was recrystallized from Et₂O. Yield: 10.7% of {NP(NH₂E₆)}₂NSOPh (17), m.p. 121.5-123 °C.

Analysis
Calcd C 41.47 H 7.21 N 24.18 S 7.91
Found C 41.60 H 7.06 N 23.95 S 7.91
m/e: 405 M+ 100%.

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