Derivatives of NPC<sub>1</sub>(NS0C<sub>1</sub>)<sub>2</sub> and (NPC<sub>1</sub>)<sub>2</sub>NS0C<sub>1</sub>, Part XXIII [1] Reactivity in Aminolysis Reactions by NH<sub>3</sub>

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Phosphorus-Sulfur-Nitrogen Heterocycles, Aminolysis Reactions

Reactions of the cyclic systems (NPC<sub>1</sub><sub>2</sub>)<sub>2</sub>NSOX and NPC<sub>1</sub><sub>2</sub>(NS0X)<sub>2</sub> (X = F, Cl, Ph) with NH<sub>3</sub> in diethyl ether or acetonitrile at low temperature provide convincing evidence that the P-bonded chlorine atoms are replaced by NH<sub>3</sub> groups along a geminal pathway. No disruption of the S-F and S-Ph bonds occurs. Aminolysis of NPC<sub>1</sub><sub>2</sub>(NS0C<sub>1</sub>) proceeds to NP(NH<sub>3</sub>)<sub>2</sub>(NS0C<sub>1</sub>)<sub>2</sub>, followed by decomposition, (NPC<sub>1</sub>)<sub>2</sub>NS0C<sub>1</sub> can be transformed to NPC<sub>1</sub>NH<sub>2</sub>NP(NH<sub>3</sub>)<sub>2</sub>NS0C<sub>1</sub> without cleavage of the ring skeleton.

Recently we reported about the mechanistic behaviour of the small sized secondary amine aziridine (ethylene-imine) in reactions with N, S and/or P ring systems. It was found that aziridine reacts both along a geminal and a non-geminal pathway [2]. Up to now aziridine can be considered as the only secondary amine capable of geminal substitution. Within the class of primary amines geminal substitution patterns are more common. Mixed geminal and non-geminal patterns have been observed in reactions of RNH<sub>2</sub> with (NPC<sub>1</sub>)<sub>2</sub> [3] or (NPC<sub>1</sub>)<sub>2</sub>NSOX (X = Cl, Ph) [4, 5]. An exclusively geminal pathway has been reported for the aminolysis of (NPC<sub>1</sub>)<sub>2</sub> with NH<sub>3</sub> [6] and BuNH<sub>2</sub> [7].

In this paper we deal with the reactivity of the cyclic systems (NPC<sub>1</sub>)<sub>2</sub>NSOX and NPC<sub>1</sub>(NS0X)<sub>2</sub> (X = F, Cl, Ph) towards NH<sub>3</sub> in diethyl ether or acetonitrile as solvents. The degree of substitution appeared to be dependent on the nature of the solvent. In general, compounds with an even number of NH<sub>3</sub> groups could be obtained in reasonable high yields. The compounds NPC<sub>1</sub>NH<sub>2</sub> and NPC<sub>1</sub>(NS0X) were described earlier [8, 9]; the preparation of cis- and trans-NP(NH<sub>3</sub>)<sub>2</sub>(NS0P)<sub>2</sub> has been reported by us very recently [10].

Experimental

All experiments were carried out under dry nitrogen. Solvents were purified and dried by conventional methods. NH<sub>3</sub> gas was dried over KOH pellets. A solution of NH<sub>3</sub> in Et<sub>2</sub>O or MeCN was obtained by bubbling NH<sub>3</sub> through the solvent concerned. The concentration of NH<sub>3</sub> was determined by titration. The starting materials (NPC<sub>1</sub>)<sub>2</sub>NSOF (I), (NPC<sub>1</sub>)<sub>2</sub>NSOCl (II), (NPC<sub>1</sub>)<sub>2</sub>NSOPh (III), cis-NPC<sub>1</sub>(NS0F)<sub>2</sub> (4), cis-NPC<sub>1</sub>(NS0Cl)<sub>2</sub> (5), cis- and trans-NPC<sub>1</sub>(NS0Ph)<sub>2</sub> (6), (7) were prepared according to the literature [4]. AIO<sub>2</sub> (Merek) was used without purification. The NMR spectra (proton noise decoupled) were recorded at 37 °C on a Varian XL-100 FT spectrometer at 40.5 MHz (31P) and at 94.1 MHz (19F). Chemical shifts were determined relative to the external standards 85% H<sub>3</sub>P0<sub>4</sub> and CFC<sub>3</sub> and defined as positive in low-field direction (Table I). Mass spectra were taken on an AEI MS 9 spectrometer at 70 eV with an accelerating voltage of 8 kV.

I. Aminolysis of (NPC<sub>1</sub>)<sub>2</sub>NSOX (X = F, Cl, Ph)

a. Using a molar ratio ring compound/NH<sub>3</sub> = 0.50 mono-substituted compounds could be isolated; in all cases mixtures of the starting material and bis(amine) derivatives were found (31P NMR spectroscopic evidence).

b. At —17 °C a solution of 0.012 mole of NH<sub>3</sub> in about 5 ml of Et<sub>2</sub>O was stirred into a stirred solution of 0.003 mole of (NPC<sub>1</sub>)<sub>2</sub>NSOX (I) or (2) in 50 ml of Et<sub>2</sub>O. A white precipitate was formed immediately. Stirring was continued for 1 h at —17 °C and 2 h at room temperature. After filtration the solution was evaporated to dryness.

X = F

Recrystallization of the crude reaction product from CHCl<sub>3</sub> afforded white needles of NPC<sub>1</sub>NH<sub>2</sub>(NS0F)<sub>2</sub> (8), m. p. 89.5–90.5 °C. Yield 55%.

Analysis

Caled H 1.47 N 25.56 S 11.70 Cl 25.88
Found H 1.53 N 25.63 S 11.77 Cl 25.66,

m/e: 273 M<sup>+</sup>Cl<sup>+</sup> 100%.
Table I. \(^{31}\)P and \(^{19}\)F NMR data, solvent CD\(_2\)CN.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\delta (\text{PCl}_2)) (ppm)</th>
<th>(\delta (\text{PClNH}_2)) (ppm)</th>
<th>(\delta (\text{P(NH}_2)) (ppm)</th>
<th>(3J(\text{PP})) (Hz)</th>
<th>(3J(\text{PF})) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NPCl(_2))(_2)NSOF</td>
<td>(1)</td>
<td>26.6</td>
<td>75.4</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>NPCl(_2)NP(NH(_2))(_2)NSOF</td>
<td>(8)</td>
<td>25.1</td>
<td>10.6</td>
<td>75.5</td>
<td>4.0</td>
</tr>
<tr>
<td>(NP(NH(_2))(_2))(_2)NSOF</td>
<td>(11)(^a)</td>
<td>14.2</td>
<td>79.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NPCl(_2))(_2)NSOCl</td>
<td>(2)</td>
<td>26.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPCl(_2)NP(NH(_2))(_2)NSOCl</td>
<td>(9)</td>
<td>25.8</td>
<td>10.3</td>
<td>71.6</td>
<td>4.6</td>
</tr>
<tr>
<td>NPClNH(_2)NP(NH(_2))(_2)NSOCl</td>
<td>(12)(^b)</td>
<td>21.5</td>
<td>10.6</td>
<td>64.9</td>
<td></td>
</tr>
<tr>
<td>(NPCl(_2))(_2)NSOPh</td>
<td>(3)</td>
<td>20.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPCl(_2)NP(NH(_2))(_2)NSOPh</td>
<td>(10)</td>
<td>21.3</td>
<td>8.1</td>
<td>60.6</td>
<td></td>
</tr>
<tr>
<td>(NP(NH(_2))(_2))(_2)NSOPh</td>
<td>(13)(^a)</td>
<td>12.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{cis-NPCl} (\text{NSOF}))(_2)</td>
<td>(4)</td>
<td>31.9</td>
<td>73.2</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>(\text{cis-NP(NH}2))(_2) (\text{NSOF})(_2)</td>
<td>(15)</td>
<td></td>
<td>71.6</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>(\text{cis-NPCl} (\text{NSOCl}))(_2)</td>
<td>(5)</td>
<td>28.6</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(\left(1a,3a,5a\right)-\text{NPClNH}_2) (\text{NSOCl})(_2)</td>
<td>(14)</td>
<td>16.6(^b)</td>
<td></td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td>(\text{cis-NP(NH}_2))(_2) (\text{NSOCl})(_2)</td>
<td>(16)</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(\text{cis-NPCl} (\text{NSOPh}))(_2)</td>
<td>(6)</td>
<td>25.7</td>
<td></td>
<td></td>
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<tr>
<td>(\text{cis-NP(NH}_2))(_2) (\text{NSOPh})(_2)</td>
<td>(13)(^a)</td>
<td>12.0(^c)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>(\text{trans-NPCl} (\text{NSOPh}))(_2)</td>
<td>(7)</td>
<td>22.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\left(1a,3\sigma,5\sigma\right)-\text{NPClNH}_2) (\text{NSOPh})(_2)</td>
<td>(17)</td>
<td>17.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{trans-NP(NH}_2))(_2) (\text{NSOPh})(_2)</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

\(^a\) Solvent (CD\(_3\)SO); \(^b\) the value \(\delta (\text{PClNH}_2) = -2.1\) as reported for 14 in ref. [8] does not correspond with analogous shifts in this Table; \(^c\) from ref. [10].

**X = Cl**

Recrystallization of the reaction product from CH\(_2\)Cl\(_2\) gave white, hygroscopic needles of NPCl\(_2\)NP(NH\(_2\))\(_2\)NSOCl (9), decomp. 50 °C. Yield 37%.

Analysis
Caled H 1.39 N 11.04 Cl 36.62.
Found H 1.44 N 11.06 Cl 36.59.
No reliable mass spectrometric data could be obtained.

c. At —17 °C NH\(_3\) was bubbled through a stirred solution of 0.003 mole of 3 in 50 ml of Et\(_2\)O for 1 h. A white precipitate appeared immediately. Stirring was continued for 2 h at room temperature. After filtration the solution was evaporated to dryness. The reaction product was recrystallized from CH\(_2\)Cl\(_2\), affording colourless crystals of NPCl\(_2\)NP(NH\(_2\))\(_2\)NSOPh (10); m.p. 148.0-149.5 °C. Yield 63%.

Analysis
Caled C 21.70 H 2.73 N 9.65 Cl 21.35.

**X = F**

Recrystallization of the reaction product from MeCN afforded white crystals of [NP(NH\(_2\))\(_2\)]\(_2\)NSOF (11); m.p. 228-230 °C. Yield 83%.

Analysis
Caled H 3.43 N 41.70 S 13.64.
Found H 3.45 N 40.90 S 13.64.
\(m/e = 235 \text{ M}^+ 100\%\).

**X = Cl**

Recrystallization of the reaction product from MeCN gave white crystals of one of the isomers (probably \(\text{cis}\)) of NPClNH\(_2\)NP(NH\(_2\))\(_2\)NSOCl (12), decomp. 200 °C. Yield 66%.

Analysis
Caled H 2.33 N 31.01 S 11.83 Cl 26.16.
Found H 2.23 N 31.33 S 11.76 Cl 26.00.
\(m/e = 270 \text{ M}^+ 29\%, 254 (\text{M}^+ - \text{Cl} - \text{NH}_2)^+ 100\%\).

e. Starting from 3 the same procedure was followed as described under 1c, using MeCN instead of Et\(_2\)O as a solvent.

The reaction product was recrystallized from MeCN, affording white, hygroscopic leaves of [NP(NH\(_2\))\(_2\)]\(_2\)NSOPh (13), m.p. 218-220 °C. Yield 75%.
Analysis

Calcd C 24.58 H 4.47 S 10.93.
Found C 24.68 H 4.97 S 10.81.
m/e = 293 M+ 100%.

2. Aminolysis of NPCl₂(NSOX)₂ (X = F, Cl, Ph)

a. At −70 °C a solution of 0.006 mole of NH₃ in about 5 ml of Et₂O was stirred into a stirred solution of 0.003 mole of NPCl₂(NSOF)₂ (5), (6) or (7) in 50 ml of Et₂O. A white precipitate appeared immediately. Stirring was continued for 1 h at −17 °C and 2 h at room temperature. After filtration the solution was evaporated to dryness.

\[ X = \text{Cl} \ (\text{cis}) \]

Recrystallization of the reaction product from CH₂Cl₂ afforded white, hygroscopic needles of one of the isomers (probably \(1a,3a,5a\) [10]) of NPCINH₂(NSOPh)₂ (14), decomp. 155 °C. Yield 85%.

Analysis

Calcd H 0.69 N 19.22 S 22.00 Cl 36.49.
Found H 0.83 N 19.22 S 22.11 Cl 36.42.

No reliable mass spectroscopic data could be obtained.

\[ X = \text{Ph} \]

The crude reaction mixture consisted of the starting material NPCl₂(NSOPh)₂ and NPC(NH₂)₂(NSOPh)₂ (mass spectroscopic evidence).

b. At −17 °C a solution of 0.012 mole of NH₃ in about 5 ml of Et₂O was added to a solution of 0.003 mole NPCl₂(NSOX)₂ (4) or (5) in 50 ml Et₂O. Further reaction conditions as under 2a.

\[ X = \text{F} \ (\text{cis}) \]

Recrystallization of the reaction product from a 1:50 mixture of MeNO₂ and CH₂Cl₂ gave white needles of cis-NP(NH₂)₂(NSOF)₂ (15), m.p. 154.5–156 °C. Yield 73%.

Analysis

Calcd H 1.68 N 29.28 S 26.81.
Found H 1.75 N 29.17 S 26.82.
m/e 239 M+ 100%.

\[ X = \text{Cl} \ (\text{cis}) \]

Recrystallization of the reaction product from CH₂Cl₂ gave white, hygroscopic needles of cis-NP(NH₂)₂(NSOCl)₂ (16), decomp. 136 °C. Yield 75%.

Analysis

Calcd H 1.49 N 25.74 S 23.57 Cl 26.06.
Found H 1.55 N 26.05 S 23.56 Cl 26.38.

No reliable mass spectroscopic data could be obtained.

3. Friedel-Crafts phenylations

a. A mixture of 0.003 mole of (1a,3a,5a)-NPCINH₂(NSOCl)₂ and 0.006 mole of AlCl₃ in 50 ml of C₆H₆ was stirred under reflux during 48 h. The reaction mixture was poured into a mixture of 20 g crushed ice and 10 ml of concentrated hydrochloric acid. After hydrolysis the benzene layer was separated and the residual solution washed with 2 × 20 ml of C₆H₆. The combined C₆H₆ fractions were washed with water, dried over CaCl₂, and evaporated to dryness. Recrystallization of the crude reaction product from CH₂Cl₂ afforded white needles of (1a,3a,5a)-NPCINH₂(NSOPh)₂ (17), m.p. 184–186 °C. Yield 46%.

Analysis

Calcd C 38.45 H 3.23 N 14.95 S 17.11 Cl 9.46.
Found C 38.35 H 3.31 N 14.93 S 17.12 Cl 9.41.
m/e 374 M+Cl+ 96%, 206 (M+Cl–NPh₂)+ 100%.

Discussion

The experimental data clearly show that the successive replacement of chlorine atoms in compounds (NPCl₂)₂NSOX (1), (2) and (3) by NH₃ groupings proceeds according to a geminal pathway. No substitution takes place at an SOF or SOPh centre, whereas in (2) the S-Cl bond is stable, at least up to and including the third step. For reactions of (NPCl₂)₂NSOX with methylamine or ethylamine a similar low reactivity of the sulfur centre has been observed. In contradistinction to reactions with NH₃ the nucleophilic attack at phosphorus in the reaction system (NPCl₂)₂NSOX-methyl-(or ethyl-)amine proceeds both along a geminal and non-geminal route [4, 5].

Monosubstituted compounds NPCl₂NPCINH₂NSOX could not be isolated. In this respect (NPCl₂)₂NSOX behaves like (NPCl₂)₃, where (NPCl₂)₂NPCINH₂ can only be prepared by indirect syntheses starting from (NPCl₂)₂NP(NH₂)₂ [12]. Reactions in diethyl ether always led to disubstituted products (8), (9), (10) even when an excess of NH₃ was used. Substitution to the tetra-kis-(amino) stage was achieved by using acetonitrile as a solvent. Only in the case of 2, the reaction of this compound with NH₃ (molar ratio compound/NH₃ = 0.125) in acetonitrile delivered one (probably the cis-isomer, [4]) of the two possible isomers of the tris(amino) derivative NPCINH₂NP(NH₂)₂NSOCl.

Efforts to prepare [NP(NH₂)₂]₂NSOCl starting from 12 and using an excess of NH₃ in acetonitrile.
failed. Only NH₄Cl and polymeric products were obtained.

For the ring compounds NPC₁₂(NSOX)₃, (4), (5), (6) and (7) again the nucleophilic attack by NH₃ takes place at the PC₁₂ or PC₁NH₂ rather than at the SOX centres. The mono(amino) derivatives of 6 and 7 appeared to be the most reactive substrates. Even in the molar ratio ring compound/NH₃ = 0.5 6 and 7 afforded disubstituted products, whereas under the same conditions 4 and 5 gave monosubstituted products. The compound NPC₁NH₂(NSOF)₂ has been described to appear in two isomeric forms, (1a,3a,5a) and (1a,3a,5p) [9], 14 was obtained as one (probably 1a,3a,5a) isomer [8].

\[
\begin{align*}
\text{cis-NPC₁NH₂NP(NH₂)₂NSOCl} & \\
\end{align*}
\]

\[
\begin{align*}
\text{NPC₁NH₂(NSOF)₂} & \\
\end{align*}
\]

(1a,3a,5α)

The less stereospecific behaviour of 4 as compared with 5 has also been observed for reactions with methylvamine or ethylamine, and can be ascribed to the smaller size of the fluorine atoms, allowing a reaction at the halogen side of the ring system [13]. A Friedel-Crafts reaction with 14 yielded NPC₁NH₂(NSOPh)₂ (17) (one isomer), which on its turn could be converted into trans-NP(NH₂)₂(NSOPh)₂ (identical with NP(NH₂)₂(NSOPh)₂ prepared by direct aminolysis of 7 [10]). Therefore, 17 possesses a structure in which the phenyl groups are in trans position (1a,3β,5α-isomer).

According to this scheme the higher reactivity of 17 as compared with the fluoro and chloro analogues might be explained from the ease by which the chloride ion can be liberated. As the amount of negative charge on chlorine depends on the electronegativity of the SOX centre [16], the lower this electronegativity, the higher the reactivity of the compound concerned. Considering the reactivity of compounds NPC₁₂NPC₁NH₂NSOX a similar reasoning can be applied. Less clear is the situation at the tris(amino) stage. The possibility to isolate 12, while reactive towards further substitution, from a 1:8 molar ratio reaction mixture may result from a rapid, NH₃-consuming, decomposition of higher substitution products. The formation of NH₄Cl and polymeric products, when 12 is treated with an excess of NH₃, supports this view.

\[1\] Part XXII. B. de Ruiter and J. C. van de Grampel, Phosphorus and Sulfur 14, 99 (1982).


