Derivatives of cis-NPC\(_12\)(NSOCl)\(_2\) and (NPC\(_12\))\(_2\) NSOCl, VI

Pyridinium Derivatives of cis-NPC\(_12\)(NSOF)\(_2\) and cis-NPC\(_12\)(NSOCl)\(_2\)

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Pyridinium Derivatives, Synthesis, Spectral Characteristics

The compounds with composition NPC\(_5\)(NSOF)\(_2\)(C\(_6\)H\(_5\))OH (1) and NPC\(_5\)(NSOCl)\(_2\) (C\(_6\)H\(_5\))OH (2) are prepared by reaction of cis-NPC\(_5\)(NSOX)\(_2\) (X = F, Cl) with pyridine in ether. The pyridinium derivatives are colourless crystalline solids. Tentative structure assignments are given based on NMR data.

By treating (NPC\(_12\))\(_2\) in pyridine solution with ethanol the hexakisethoxy derivative can be prepared. In this reaction triazaphosphorine pyridinium salts are supposed to play an important role as transition states during the substitution. The ion \(N_2P_3Ph_2C_6H_5\)\(^+\) has been postulated for the pyridine-catalyzed hydrolysis of \(N_2P_3ClPh_3\)\(^+\).

In our investigations on ethoxy derivatives of cis-NPC\(_5\)(NSOF)\(_2\) we observed an analogous salt with composition NP(OEt)(NSOF)\(_2\)(C\(_6\)H\(_5\))OH. This prompted us to investigate the reaction between cis-NPC\(_5\)(NSOX)\(_2\) (X = F, Cl) and pyridine in more detail. In this communication we report the preparation and characterization of two pyridinium derivatives, derived from these ring compounds.

Spectra and Structure

Although the IR spectra of 1 and 2 (Experimental Part) are quite complex, some common features can be recognized. In the region 400-850 cm\(^{-1}\) analogous strong absorptions are found, viz. compound 1: 516, 609, 676, 723, 753, 806 cm\(^{-1}\); compound 2: 509, 636, 675, 709, 743, 820 cm\(^{-1}\). Ring absorptions are found between 1100 and 1200 cm\(^{-1}\), while bands between 1300 and 1400 cm\(^{-1}\) can be assigned to SO stretching modes. The SF vibration in 1 is observed at 873 cm\(^{-1}\) (compare 890 in cis-NPC\(_5\)(NSOF)\(_2\) at 885 cm\(^{-1}\)).

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As may be seen from Table I the \(^{31}\)P NMR spectra show a singlet for each of the compounds 1 and 2 at -3.2 and -4.3 ppm respectively. When comparing these values with those of cis-NPC\(_5\)(NSOF)\(_2\) (\(\delta_P = 30.9\) ppm) and cis-NPC\(_5\)(NSOCl)\(_2\) (\(\delta_P = 27.6\) ppm) we see that the signals are shifted to higher field by about 33 ppm. Comparing the \(\delta_P\) values of the pyridinium derivatives with each other, we observe that the presence of the more electronegative NSOF groupings results in a less negative value of the \(^{31}\)P resonance signal.

Table I. Chemical shifts \(\delta\) in the \(^{31}\)P NMR spectra of cis-NPC\(_5\)(NSOF)\(_2\), cis-NPC\(_5\)(NSOCl)\(_2\), 1 and 2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(^{31})P NMR spectra</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-NPC(_5)(NSOF)(_2) (1)</td>
<td>30.9</td>
<td>CDCl(_3)</td>
</tr>
<tr>
<td></td>
<td>-3.2</td>
<td>CD(_2)CN</td>
</tr>
<tr>
<td>cis-NPC(_5)(NSOCl)(_2) (2)</td>
<td>27.6</td>
<td>CDCl(_3)</td>
</tr>
<tr>
<td></td>
<td>-4.3</td>
<td>CD(_2)CN</td>
</tr>
</tbody>
</table>

The bonding state of the pyridine ring in the compounds 1 and 2 is reflected by the \(^{13}\)C NMR data (Table II). Just as in the \(C_6H_5\)NH\(^+\)-ion the chemical shifts \(\delta_C\) in 1 and 2 show analogous displacements relative to pyridine, viz. \(\delta(C_2,3,4)\) and \(\delta(C_6)\) to lower field, \(\delta(C_5,6)\) to higher field. Moreover, the value of \(J(C_2,3,4)\) becomes much larger. We conclude that in the pyridine derivatives the pyridine system has a positive charge. This conclusion is confirmed by a comparison of the \(^1\)H NMR data (Table III). Both in 1 and 2 in \(C_6H_5\)NH-
Table II. Chemical shifts $\delta$ and coupling constants $^{1}J_{C-H}$ in the $^{13}C$ NMR spectra of pyridine, pyridinium ion, 1 and 2 (solvent CD$_3$CN).

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ [ppm]</th>
<th>$^{1}J_{C-H}$ [Hz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_5$H$_5$N</td>
<td>151.4</td>
<td>125.2</td>
</tr>
<tr>
<td>C$_5$H$_5$NH$^+$</td>
<td>144.7</td>
<td>131.3</td>
</tr>
<tr>
<td>1**</td>
<td>142.1</td>
<td>128.4</td>
</tr>
<tr>
<td>2</td>
<td>142.6</td>
<td>128.8</td>
</tr>
</tbody>
</table>

* From a solution of C$_5$H$_5$N, CF$_3$COOH and H$_2$SO$_4$ in CDCl$_3$ 50;
** recorded at $-13.5$ °C.

Table III. Chemical shifts $\delta$ in the $^1$H NMR spectra of pyridine, pyridinium ion**, 1 and 2 (solvent CD$_3$CN).

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ H (2, 6) [ppm]</th>
<th>$\delta$ H (3, 5) [ppm]</th>
<th>$\delta$ H (4) [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_5$H$_5$N</td>
<td>8.6</td>
<td>7.3</td>
<td>7.6</td>
</tr>
<tr>
<td>C$_5$H$_5$NH$^+$</td>
<td>8.7</td>
<td>7.8</td>
<td>8.3</td>
</tr>
<tr>
<td>1**</td>
<td>8.9</td>
<td>8.1</td>
<td>8.6</td>
</tr>
<tr>
<td>2</td>
<td>8.9</td>
<td>8.1</td>
<td>8.7</td>
</tr>
</tbody>
</table>

* Because of the complexity of the resonance signals approximate values of $\delta_H$ are given;
** from a solution of equimolar quantities of pyridine and CF$_3$COOH in CD$_3$CN.

The resonance signals are shifted to low field relative to pyridine.

From the foregoing analysis of the NMR data some possible structures can be formulated viz. 

$[\text{NP}(\text{C}_5\text{H}_5\text{N})\text{Cl}](\text{NSOCl})_2][\text{OH}]^-$ or $[\text{NP}](\text{O})\text{Cl(NSOCl)}_2][\text{C}_5\text{H}_5\text{NH}]^+$ (X = F, Cl), both having a positive charged pyridine group. No conclusive evidence can be obtained from the IR spectra, as in the region 1800–4000 cm$^{-1}$ only weak or very weak absorptions are observed, Therefore a structure determination by X-rays is necessary to give a definite answer.

**Experimental**

All experiments were carried out under dry nitrogen. Solvents were purified and dried by conventional methods. Pyridine was destilled from KOH. The element analyses were carried out at the Microanalytical Department of this University under supervision of Mr. A. F. HAMMINGA. The IR spectra were recorded on a Hitachi EPI-G spectrophotometer, using Nujol mulls between KBr discs. The spectra were calibrated by means of polystyrene film bands. $^1$H NMR spectra were taken on a Varian A-60 spectrometer and standardized towards internal TMS. The $^{13}C$ NMR spectra of pyridine and compound 2 were recorded on a Varian XL-100 FT spectrometer ($t = 30$ °C) at 25.2 MHz using TMS as internal standard. The $^{13}C$ NMR spectrum of 1 (at $-13.5$ °C) and the $^{31}$P NMR spectra were recorded by Mr. R. H. FOKKENS and Mr. C. KRU (NMR Department, University of Amsterdam) on a Varian XL-100 FT spectrometer operating at 25.2 MHz and 40.5 MHz respectively. The values of $\delta_P$ were determined relative to the external standard $85\%$ H$_2$PO$_4$. For all spectra the $\delta$-values are defined as positive in low-field direction.

1. Reaction of cis-NPCl$_2$(NSOCl)$_2$ with pyridine

At room temperature C$_5$H$_5$N (0.59 g = 7.46 mmol) was added to a stirred solution of cis-NPCl(NSOCl)$_2$ (1.00 g = 3.60 mmol) in 25 ml of dry diethylether. After a few minutes a white precipitate was formed. The mixture was stirred during twenty hours and then evaporated to dryness under vacuum. The residue was a yellow oil, which is extremely hygroscopic. An element analysis showed the composition to be NPCL$_2$(C$_5$H$_5$N)(NSOCl)$_2$. By introducing solvents containing traces of moisture this compound was converted to compound 1. The residue was dissolved in 30 ml of dry acetonitrile and the solution partly evaporated until a precipitate appeared. This was filtered off and the remaining solution evaporated to dryness. The resulting yellow oil was dissolved in 30 ml of dry chloroform and evaporated until beginning crystallisation. Cooling at $-20$ °C gave 1 as white crystals. Yield 50.3% (0.61 g = 1.81 mmol).

As the compound is unstable at room temperature no attempts were made for further purification. NPCL(NSOCl)$_2$(C$_5$H$_5$N)OH; m.w. = 338.68; m.p. 120–124.5 °C

Calcd C 17.72 H 1.79 N 16.54 Cl 10.47

Found C 17.72 H 1.79 N 16.54 Cl 10.47

2. Reaction of cis-NPCl$_2$(NSOCl)$_2$ with pyridine

At room temperature C$_5$H$_5$N (2.12 g = 6.80 mmol) was added to a stirred solution of cis-NPCl(NSOCl)$_2$ (1.80 g = 5.79 mmol) in 60 ml of dry diethylether. A few minutes after the addition a white precipitate was formed. The reaction mixture was stirred for an additional twenty hours and then evaporated to dryness under vacuum. The residue consisted of a brown-yellowish oil, which became solid after a few minutes. An element analysis showed the composition to be NPCL$_2$(C$_5$H$_5$N)(NSOCl)$_2$.

The extremely hygroscopic residue was dissolved in 60 ml of dry acetonitrile and then partly evapo-
rated until a precipitate appeared. This was filtered off and the remaining solution evaporated to dryness. The resulting yellow oil was dissolved in 75 ml of dry chloroform and partly evaporated. Cooling at —20 °C gave colourless crystals of 2. Yield 55.8% (1.20 g = 3.23 mmoles).

Attempts to recrystallize the compound failed because of the lack of stability.

NPCl(NSOCl)(C5H5N)OH; m. w. = 371.59; m. p. 118–120 °C

Calcd C 16.16 H 1.63 N 15.08 S 17.26 Cl 28.62,

Found C 15.75 H 1.53 N 14.94 S 16.96 Cl 28.74,

IR (400–4000 cm⁻¹) 509 vs, 518 vw, 532 s, 610 w, 636 vs, 655 m, 675 s, 709 s, 743 s, 820 s, 870 vw, 910 w, 1005 vw, 1030 vs, 1114 s, 1185 vs, 1238 s, 1252 w, 1272 w, 1296 s, 1312 s, 1530 w, 1610 w, 1635 vw, 2716 vw, 3076 vw, 3101 vw, 3146 vw, 3166 vw, 3236 vw.

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6 A. Iedema and J. C. van de Grampel, unpublished results.
10 J. Runsink, private communication.