Derivatives of cis-NPCl₂(NSOCl)₂ and (NPCl₂)₂NSOCl, V
Preparation of NPCL₂(NSOPh)₂ and (NPCL₂)₂NSOPh.
Reactions of NPCL₂(NSOPh)₂ with Dimethylamine

J. B. VAN DEN BERG, B. DE RUITER, AND J. C. VAN DE GRAMPEL
Laboratorium voor Anorganische Chemie, Rijksuniversiteit Groningen, Zernikelaan, Groningen,
The Netherlands
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Dioxo-dichloro-diphenyl-dithia triazaphosphorine,
Oxotetra chloro-phenyl-thia triazadiphosphorine, Synthesis, Characterization

Reaction of (NPCL₂)₂NSOCl or (NPCL₂)₂NSOF with benzene in the presence of AlCl₃
yields (NPCL₂)₂NSOPh. By the same procedure two isomeric forms of NPCL₂(NSOPh)₂
can be obtained from cis-NPCL₂(NSOCl)₂. The phenylated products were characterized by
IR, mass and 31P NMR spectra.
Reactions of one of the isomers of NPCL₂(NSOPh)₂ with (CH₃)₂NH yield
NPCL(CH₃)₂(NSOPh)₂ (molar ratio 1:2) and NP[N(CH₃)₂]₂(NSOPh)₂ (molar ratio 1:6.8).
The structures of the amino substituted derivatives were determined by means of ¹H NMR
measurements.

It is well known that (NPCL₂)₂ reacts with boiling benzene in the presence of AlCl₃ to yield
(NPPh)ₙ(NPCl)ₙ-α (α = 1, 2, 3). Only geminal reaction products have been detected. Under
identical reaction conditions (NSOCl)₃ decomposes, yielding considerable amounts of SOPh₂. (NSOPh)₃
is formed by the reaction of cis-(NSOF)₃ with AlCl₃ in boiling benzene. The partly phenylated product
NSOCl(NSOPh)₂ can be obtained from cis-NPCL₂(NSOPh)₂. The phenylated derivatives of the mixed ring
systems (NPCL₂)ₙ(NSOCl)ₙ-α (α = 1, 2) have been described previously. It seemed interesting therefore
to investigate the behaviour of these ring systems towards boiling benzene in the presence of AlCl₃.

Discussion
(NPCL₂)₂NSOCl and (NPCL₂)₂NSOF yield, under Friedel-Crafts conditions, the same monophenyl
derivative, which therefore has to be (NPCL₂)₂NSOPh. Even after prolonged reaction times, using an
excess of AlCl₃, no phosphorus substituted products could be detected. The IR spectrum shows a
ν(S=O) at 1272 cm⁻¹ (compared to 1334 cm⁻¹ and 1364 cm⁻¹ in (NPCL₂)₂NSOCl and (NPCL₂)₂NSOF,
respectively), the 31P NMR spectrum shows only one line at —20.7 ppm ((NPCL₂)₂NSOCl and
(NPCL₂)₂NSOF resonate at —26.3 and —26.1 ppm, respectively).

 cis-NPCL₂(NSOCl)₂ reacts under the same conditions to a diphenyl derivative, which turned out to
exist in two isomeric forms A and B (ratio 1:4).
Isomer B could be isolated in a pure state. The IR spectrum of this compound shows a ν(S=O) at 1263
cm⁻¹ (1334 cm⁻¹ in cis-NPCL₂(NSOCl)₂ and 1368 cm⁻¹ in cis-NPCL₂(NSOF)₂) which is consistent with the
formula NPCl₂(NSOPh)₂. This structure assignment is confirmed by 31P NMR measurements: the
signal is found at —22.1 ppm (cis-NPCL₂(NSOCl)₂: —27.6 ppm, cis-NPCL₂(NSOF)₂: —30.9 ppm), while
no 31P ¹H coupling is observed. Isomer A resonates at —25.4 ppm.

In order to elucidate its geometrical structure, isomer B was allowed to react with an excess of
dimethylamine, yielding NP[N(CH₃)₂]₂(NSOPh)₂. The ¹H NMR spectrum (Table I) of this product
shows only one doublet, indicating the two di-
Table I. 31P and 1H NMR data (CDCl3-solutions).

<table>
<thead>
<tr>
<th>Compound</th>
<th>31P NMR* δ [ppm]</th>
<th>1H NMR δ [ppm] 3JF-H [Hz] δ [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPCl2(NSOPh)2</td>
<td>-20.7</td>
<td></td>
</tr>
<tr>
<td>NPCl2(NSOPh)2 is. A</td>
<td>-25.4</td>
<td></td>
</tr>
<tr>
<td>NPCl2(NSOPh)2 is. B</td>
<td>-22.1</td>
<td></td>
</tr>
<tr>
<td>NPCIN(CH2)2(NSOPh)2</td>
<td>2.72</td>
<td>16.9 - 22.7</td>
</tr>
<tr>
<td>NP[N(CH2)2(NSOPh)2</td>
<td>2.52</td>
<td>11.7 - 15.1</td>
</tr>
</tbody>
</table>

* CH3-protons. Ph-protons resonate at 7.35–8.35 ppm.

Experimental

All experiments were carried out under dry nitrogen. NPCl2(NSOCl)2, (NPCl2)2NSOCl and (NPCl2)2NSOF were synthesized as described elsewhere. Dimethylamine was distilled into the reaction vessel via a KOH column. Solvents were purified and dried by conventional methods. The element analyses were carried out in the Microanalytical Department of this University under supervision of Mr. A. F. HAMMINGA. Infrared spectra were recorded on a Hitachi EPI-G spectrophotometer using KBr discs. Spectra were calibrated by means of polystyrene film bands. 1H NMR spectra were taken on a Varian A-60 spectrometer and standardized towards internal TMS. 31P NMR spectra were taken by Mr. R. H. FOKKENS (NMR Department; University of Amsterdam) on a Varian XL100 FT spectrometer, operating at 40.5 MHz. Chemical shifts were determined relative to the external standard 85% H3PO4. Mass spectra were recorded on an AEI M.S.9 mass spectrometer operating at 70 eV, using an accelerating voltage of 8 kV. The sample was introduced directly by a conventional inlet system at 100 °C (Mr. A. Kiewiet, Department of Organic Chemistry, this University).

A. Friedel-Crafts reactions

A mixture of (NPCl2)n(NSOX)3-n (n = 1, 2; X = F, Cl), AlCl3 and benzene (10 ml per mmole of the ring compound) was boiled under reflux and continuous stirring for 48 hours, cooled to room temperature and poured out into a mixture of concentrated hydrochloric acid and crushed ice (volume ratio 1:7). The water layer was extracted twice with 25 ml of benzene and the combined benzene layers were washed with water, dried over CaCl2 and evaporated to dryness under reduced pressure. The products were purified by recrystallization from diethyl ether [NPCl2(NSOPh)2] or n-pentane [(NPCl2)2NSOPh]. The best results were obtained using the following molar ratios of the ring compound and AlCl3:

| Yield [%] | | | |
|-----------|-------------------|-------------------------------|
| Ring compound | Molar ratio | Crude | Purified Product |
| (NPCl2)2NSOF | 1:1              | 82              | 70 (NPCl2)2NSOPh |
| (NPCl2)2NSOCl | 1:1             | 85              | 70 (NPCl2)2NSOPh |
| NPCl2(NSOCl)2 | 1:2             | 80              | 70 NPCl2(NSOPh)2 |

NPCl2(NSOPh)2 was formed in two isomeric forms (A and B; ratio 1:4), one of which (B) could be isolated after careful recrystallization from diethyl ether.


IR (cm−1) 453 w, 473 w, 493 w, 506 w, 555 vs, 598 s, 613 sh, 662 m, 680 m, 713 s, 740 s, 742 s.


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A solution of 2.54 mmole of NPCl2(NSOPh)2 in 30 ml of acetonitrile was added to a stirred solution...
of 17.3 mmole of dimethylamine in 30 ml of acetonitrile at —35 °C. The reaction mixture was stirred for twenty hours at room temperature, the solvent was driven off in vacuo and the residue extracted twice with 40 ml of boiling diethylether. The ether extracts were evacuated until crystals appeared in the solution. Yield 55% of NP(NMe$_2$)$_2$(NSOPh)$_2$.

2. 5.1 mmole of dimethylamine was added to a stirred solution of 2.54 mmole of NPCl$_2$(NSOPh)$_2$ in 40 ml of acetonitrile at —35 °C. Treatment of the reaction mixture was carried out as under 1. Yield 80% of NPClNMe$_2$(NSOPh)$_2$.

1,3-Dioxo-5,5-bis(dimethylamino)-1,3-diphenyl-1,3,2,4,6,5-dithiatriazaphosphorine

NP(NMe$_2$)$_2$(NSOPh)$_2$ (M.W. 411.49) m. p. 170-171 °C.

Anal.
Calcd C 46.70 H 5.39 N 17.02 S 15.58,
Found C 46.90 H 5.38 N 17.07 S 15.75,
C 46.97 H 5.32 N 17.16 S 15.79.

IR (cm$^{-1}$) 464 m, 505 s, 571 vs, 605 w, 688 s, 697 s, 716 s, 751 s, 758 s, 837 s, 847 sh, 989 vs, 1027 m, 1034 m, 1065 m, 1096 sh, 1147 vs br, 1171 vs 1248 vs, 1290 sh br.

m/e 411 M$^+$ 8% 44 NMe$_2^+$ 100%.

1,3-Dioxo-5-chloro-5-(dimethylamino)-1,3-diphenyl-1,3,2,4,6,5-dithiatriazaphosphorine

NPClNMe$_2$(NSOPh)$_2$ (M.W. 402.86) m.p. 115.5-116.5 °C.

Anal.
Calcd C 41.74 H 4.00 N 13.91 S 15.92 Cl 8.80,
Found C 41.94 H 3.97 N 15.07 S 15.77,
C 41.87 H 4.03 N 13.99 S 16.20 Cl 8.80.

IR (cm$^{-1}$) 433 w, 499 w, 514 m, 538 s, 567 vs, 613 w, 631 s, 683 s, 716 s, 747 s, 772 w, 837 s, 852 s, 988 s, 1027 w, 1037 w, 1055 m, 1143 vs, 1170 w, 1185 s, 1252 s, 1270 m.

m/e 402 (M$^{35}$Cl$^+$) 20% 44 NMe$_2^+$ 100%.

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