Derivatives of *cis*- $\text{NPCl}_2(\text{NSOCl})_2$ and $(\text{NPCl}_2)_2\text{NSOCl}$, V¹

Preparation of $\text{NPCl}_2(\text{NSOPh})_2$ and $(\text{NPCl}_2)_2\text{NSOPh}$.

Reactions of $\text{NPCl}_2(\text{NSOPh})_2$ with Dimethylamine

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Dioxo-dichloro-diphenyl-dithiatriazaphosphorine,
Oxo-tetrachloro-phenyl-thiatriazadiphosphorine, Synthesis, Characterization

Reaction of $(\text{NPCl}_2)_2\text{NSOCl}$ or $(\text{NPCl}_2)_2\text{NSOF}$ with benzene in the presence of AlCl_3 yields $(\text{NPCl}_2)_2\text{NSOPh}$. By the same procedure two isomeric forms of $\text{NPCl}_2(\text{NSOPh})_2$ can be obtained from *cis*- $\text{NPCl}_2(\text{NSOCl})_2$. The phenylated products were characterized by IR, mass and ^{31}P NMR spectra.

Reactions of one of the isomers of $\text{NPCl}_2(\text{NSOPh})_2$ with $(\text{CH}_3)_2\text{NH}$ yield $\text{NPClN}(\text{CH}_3)_2(\text{NSOPh})_2$ (molar ratio 1:2) and $\text{NP}[\text{N}(\text{CH}_3)_2]_2(\text{NSOPh})_2$ (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 $(\text{NPCl}_2)_3$ reacts with boiling benzene in the presence of AlCl_3 to yield $(\text{NPhPh})_n(\text{NPCl}_2)_{3-n}$ ($n=1, 2, 3$). Only geminal reaction products have been detected²⁻⁴. Under identical reaction conditions $(\text{NSOCl})_3$ decomposes, yielding considerable amounts of SOPh_2 ⁵. $(\text{NSOPh})_3$ is formed by the reaction of *cis*-(NSOF)₃ with AlCl_3 in boiling benzene⁶. The partly phenylated product $\text{NSOCl}(\text{NSOPh})_2$ can be obtained by treating $(\text{NSOCl})_3$ with Ph_2Hg ⁷. *cis*- $\text{NPCl}_2(\text{NSOCl})_2$ reacts with Ph_2Hg yielding $\text{NPCl}_2\text{NSOClNSOPh}$ ⁸. No other phenylated derivatives of the mixed ring systems $(\text{NPCl}_2)_n(\text{NSOCl})_{3-n}$ ($n=1, 2$) have been described previously. It seemed interesting therefore to investigate the behaviour of these ring systems towards boiling benzene in the presence of AlCl_3 .

Discussion

$(\text{NPCl}_2)_2\text{NSOCl}$ and $(\text{NPCl}_2)_2\text{NSOF}$ yield, under Friedel-Crafts conditions, the same monophenyl derivative, which therefore has to be $(\text{NPCl}_2)_2\text{NSOPh}$. Even after prolonged reaction times, using an

excess of AlCl_3 , no phosphorus substituted products could be detected. The IR spectrum shows a $\nu(\text{S}=\text{O})$ at 1272 cm^{-1} (compared to 1334 cm^{-1} and 1364 cm^{-1} in $(\text{NPCl}_2)_2\text{NSOCl}$ and $(\text{NPCl}_2)_2\text{NSOF}$, respectively), the ^{31}P NMR spectrum shows only one line at -20.7 ppm ($(\text{NPCl}_2)_2\text{NSOCl}$ and $(\text{NPCl}_2)_2\text{NSOF}$ resonate at -26.3 and -26.1 ppm , respectively).

cis- $\text{NPCl}_2(\text{NSOCl})_2$ 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 $\nu(\text{S}=\text{O})$ at 1263 cm^{-1} (1334 cm^{-1} in *cis*- $\text{NPCl}_2(\text{NSOCl})_2$ and 1368 cm^{-1} in *cis*- $\text{NPCl}_2(\text{NSOF})_2$) which is consistent with the formula $\text{NPCl}_2(\text{NSOPh})_2$ ⁸. This structure assignment is confirmed by ^{31}P NMR measurements: the signal is found at -22.1 ppm (*cis*- $\text{NPCl}_2(\text{NSOCl})_2$: -27.6 ppm , *cis*- $\text{NPCl}_2(\text{NSOF})_2$: -30.9 ppm), while no ^{31}P ^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 $\text{NP}[\text{N}(\text{CH}_3)_2]_2(\text{NSOPh})_2$. The ^1H NMR spectrum (Table I) of this product shows only one doublet, indicating the two di-

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Table I. ^{31}P and ^1H NMR data (CDCl_3 -solutions).

Compound	^1H NMR*		^{31}P NMR δ [ppm]
	δ [ppm]	$^3\text{J}_{\text{P-H}}$ [Hz]	
$(\text{NP}(\text{Cl})_2)_2\text{NSOPh}$			—20.7
$\text{NP}(\text{Cl})_2(\text{NSOPh})_2$ is. A			—25.4
$\text{NP}(\text{Cl})_2(\text{NSOPh})_2$ is. B			—22.1
$\text{NPCl}(\text{CH}_3)_2(\text{NSOPh})_2$	2.72	16.9	—22.7
$\text{NP}[\text{N}(\text{CH}_3)_2]_2(\text{NSOPh})_2$	2.52	11.7	—15.1

* CH_3 -protons. Ph-protons resonate at 7.35–8.35 ppm.

methylamino groups to be equivalent. This is possible only, if the two phenyl groups are situated *trans* to each other. It is reasonable to assume that isomer B also possesses a *trans*-configuration, as drawn in Fig. 1. The formation of only one isomer of $\text{NPCl}(\text{CH}_3)_2(\text{NSOPh})_2$ from isomer B strongly supports this view as the *cis*-isomer of $\text{NP}(\text{Cl})_2(\text{NSOPh})_2$ should give two isomeric forms of the mono amino product (compare the reaction of *cis*- $\text{NP}(\text{Cl})_2(\text{NSOCl})_2$ with $(\text{CH}_3)_2\text{NH}$ ⁹).

Fig. 1. Geometrical structure of $\text{NP}(\text{Cl})_2(\text{NSOPh})_2$ isomer B.

Experimental

All experiments were carried out under dry nitrogen. $\text{NP}(\text{Cl})_2(\text{NSOCl})_2$, $(\text{NP}(\text{Cl})_2)_2\text{NSOCl}$ and $(\text{NP}(\text{Cl})_2)_2\text{NSOF}$ were synthesized as described elsewhere^{10–12}. 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 Micro-analytical 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. ^{31}P NMR spectra were taken by Mr. R. H. FOKKENS (NMR Department; University of Amsterdam) on a Varian XL 100 FT spectrometer, operating at 40.5 MHz. Chemical shifts were determined relative to the external standard 85% H_3PO_4 . 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 $(\text{NP}(\text{Cl})_2)_n(\text{NSOX})_{3-n}$ ($n = 1, 2$; $\text{X} = \text{F}, \text{Cl}$), AlCl_3 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 CaCl_2 and evaporated to dryness under reduced pressure. The products were purified by recrystallization from diethylether [$\text{NP}(\text{Cl})_2(\text{NSOPh})_2$] or *n*-pentane [$(\text{NP}(\text{Cl})_2)_2\text{NSOPh}$]. The best results were obtained using the following molar ratios of the ring compound and AlCl_3 :

Ring compound	Molar ratio	Yield [%]		Product
		Crude	Purified	
$(\text{NP}(\text{Cl})_2)_2\text{NSOF}$	1:1	82	70	$(\text{NP}(\text{Cl})_2)_2\text{NSOPh}$
$(\text{NP}(\text{Cl})_2)_2\text{NSOCl}$	1:1	95	85	$(\text{NP}(\text{Cl})_2)_2\text{NSOPh}$
$\text{NP}(\text{Cl})_2(\text{NSOCl})_2$	1:2	80	70	$\text{NP}(\text{Cl})_2(\text{NSOPh})_2$

$\text{NP}(\text{Cl})_2(\text{NSOPh})_2$ was formed in two isomeric forms (A and B; ratio 1:4), one of which (B) could be isolated after careful recrystallization from diethylether.

1-Oxo-3,3,5,5-tetrachloro-1-phenyl-1,2,4,6,3,5-thia-triazadiphosphorine

$(\text{NP}(\text{Cl})_2)_2\text{NSOPh}$ (M.W. 370.95) m.p. 91.5–92 °C.

Anal.

Calcd C 19.43 H 1.36 N 11.33 P 16.70 S 8.64 Cl 38.23,

Found C 19.43 H 1.38 N 11.33 P 16.35 S 8.70 Cl 38.07,

C 19.33 H 1.36 N 11.44 P 16.54 S 8.79 Cl 38.13.

IR (cm^{-1}) 470 m, 535 s, 555 s, 602 s, 615 sh, 670 m, 685 m, 695 m, 755 s, 770 m, 835 s, 870 m, 1000 w, 1024 w, 1100 s, 1187 vs br, 1240 sh, 1272 s.

m/e 369 (M^{35}Cl)⁺ 70% 28 N_2^+ 100%.

1,3-Dioxo-5,5-dichloro-1,3-diphenyl-1,3,2,4,6,5-dithia-triazadiphosphorine

$\text{NP}(\text{Cl})_2(\text{NSOPh})_2$ (isomer B) (M.W. = 394.24) m.p. 124.5–126 °C.

Anal.

Calcd C 35.56 H 2.56 N 10.66 S 16.27 Cl 17.99,

Found C 35.55 H 2.48 N 10.71 S 16.43 Cl 17.99,

C 35.56 H 2.49 N 10.82 S 16.35 Cl 18.05.

IR (cm^{-1}) 453 w, 473 w, 493 w, 506 w, 555 vs, 598 s, 613 sh, 662 m, 680 m, 686 m, 713 s, 740 s, 742 s, 830 s, 835 sh, 840 sh, 995 s, 1021 m, 1050 s, 1091 m, 1151 vs, 1159 vs, 1180 vs, 1263 vs, 1273 sh.

m/e 393 (M^{35}Cl)⁺ 100%.

B. Reactions of $\text{NP}(\text{Cl})_2(\text{NSOPh})_2$

(m.p. 124.5–126 °C) with dimethylamine

1. A solution of 2.54 mmole of $\text{NP}(\text{Cl})_2(\text{NSOPh})_2$ 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 $\text{NP}(\text{NMe}_2)_2(\text{NSOPh})_2$.

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

1,3-Dioxo-5,5-bis(dimethylamino)-1,3-diphenyl-1,3,2,4,6,5-dithiatriazaphosphorine
 $\text{NP}(\text{NMe}_2)_2(\text{NSOPh})_2$ (M.W. 411.49)
 m. p. 170–171 $^\circ\text{C}$.

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 w, 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
 $\text{NPCINMe}_2(\text{NSOPh})_2$ (M.W. 402.86)

m. p. 115.5–116.5 $^\circ\text{C}$.

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 14.00 S 15.97 Cl 8.77,

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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