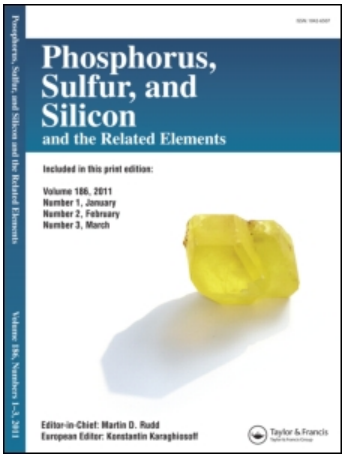


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# Derivatives Of $Npcl_2$ $(Nsocl)_2$ And $(Npcl_2)_2$ Nsocl, Part Xxiv.[1] Friedelcraftdreaction Of $(Npcl_2)_2$ Nsocl And *Cis*-$Npcl_2$ $(Nsocl)_2$ With A Series Of Monosubstituted Benzenes. The Structure Of $Npcl_2$ Nso-*O*-$C_6H_4$ Cinso-*P*-$C_6H_4Cl$

F. J. Viersen[a]; E. Bosma[a]; B. De Ruiter[a]; K. S. Dhathathreyan[a]; J. C. van de Grampel[a]; F. Van Bolhuis[b]
[a] Department of Inorganic Chemistry, University of Groningen, Nijenborgh 16, AG Groningen, The Netherlands [b] Department of Chemistry, University of Groningen, Nijenborgh 16, AG Groningen, The Netherlands

**To cite this Article** Viersen, F. J. , Bosma, E. , De Ruiter, B. , Dhathathreyan, K. S. , van de Grampel, J. C. and Van Bolhuis, F.(1986) 'Derivatives Of $Npcl_2$ $(Nsocl)_2$ And $(Npcl_2)_2$ Nsocl, Part Xxiv.[1] Friedelcraftdreaction Of $(Npcl_2)_2$ Nsocl And *Cis*-$Npcl_2$ $(Nsocl)_2$ With A Series Of Monosubstituted Benzenes. The Structure Of $Npcl_2$ Nso-*O*-$C_6H_4$ Cinso-*P*-$C_6H_4Cl$', Phosphorus, Sulfur, and Silicon and the Related Elements, 26: 3, 285 — 292
**To link to this Article: DOI:** 10.1080/03086648608084582
**URL:** http://dx.doi.org/10.1080/03086648608084582

*Phosphorus and Sulfur*, 1986, Vol. 26, pp. 285–292
0308-664X/86/2603–0285/$15.00/0



# DERIVATIVES OF $NPCl_2(NSOCl)_2$ AND $(NPCl_2)_2NSOCl$, PART XXIV.[1] FRIEDEL-CRAFTS REACTION OF $(NPCl_2)_2NSOCl$ AND *CIS*-$NPCl_2(NSOCl)_2$ WITH A SERIES OF MONOSUBSTITUTED BENZENES. THE STRUCTURE OF $NPCl_2NSO$-*o*-$C_6H_4ClNSO$-*p*-$C_6H_4Cl$

F. J. VIERSEN, E. BOSMA, B. DE RUITER, K. S. DHATHATHREYAN and J. C. VAN DE GRAMPEL

*Department of Inorganic Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands.*

F. VAN BOLHUIS

*Department of Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands.*

(*Received August 29, 1985*)

Friedel-Crafts reactions of $(NPCl_2)_2NSOCl$ with a series of monosubstituted benzenes $C_6H_5R$ (R = Me, OMe, Et, $^i$Pr, Cl, Br and I) provide the sulfur substituted products $(NPCl_2)_2NSOC_6H_4R$ in 40–90% yield. When R = Me or OMe, *ortho*- and *para*-isomers are formed. With the other benzenes, only the *para* substituted derivative is formed. From the reaction of *cis*-$NPCl_2(NSOCl)_2$ with chlorobenzene, five of the six possible isomers of $NPCl_2(NSOC_6H_4Cl)_2$ have been isolated and characterized. Structure assignments are based on $^{31}P$ and $^1H$ NMR data and are confirmed by the X-ray structure data of the *trans-ortho-para* isomer.



## INTRODUCTION

Hexachlorocyclotriphosphazene, $(NPCl_2)_3$ reacts with benzene in the presence of $AlCl_3$ to yield $(NPPh_2)_n(NPCl_2)_{3-n}$ ($n = 1, 2, 3$). Only geminal reaction products have been identified.[2,3,4] Under identical reaction conditions $(NSOCl)_3$ decomposes yielding considerable amounts of $SOPh_2$.[5] $(NSOPh)_3$ is obtained from the Friedel-Crafts reaction of *cis*-$(NSOF)_3$ with benzene in the presence of $AlCl_3$.[6] Reaction of the mixed ring systems $(NPCl_2)_2NSOCl$ and *cis*-$NPCl_2(NSOCl)_2$ with benzene under Friedel-Crafts reaction conditions yield the sulfur substituted products, $(NPCl_2)_2NSOPh$ and *cis*- and *trans*-$NPCl_2(NSOPh)_2$, respectively. There is no evidence for reaction at phosphorus even after prolonged reaction time and using an excess of $AlCl_3$.[7] The P-bonded chlorine atoms can be replaced when electron-donating ligands are present.[8] It is known that $(NPCl_2)_3$ reacts with monosubstituted benzenes to a number of substituted products, but the reactions are usually complicated and the yields of products low.[3] Because Friedel-Crafts reactions of $(NPCl_2)_2NSOCl$ and $NPCl_2(NSOCl)_2$ could lead to products with new functional groups which in principle should be useful for linking the inorganic ring to other

molecular fragments through an aromatic spacer group, we investigated the behaviour of these ring systems towards a series of monosubstituted benzenes under Friedel-Crafts conditions.

## RESULTS AND DISCUSSION

### *Friedel-Crafts reactions*

Reaction of **1** with the monosubstituted benzenes, $C_6H_5R$ (R = Me, OMe, Et, $^i$Pr, Cl, Br and I) proceeds smoothly to give the sulfur substituted products $(NPCl_2)_2NSOC_6H_4R$ (**3** to **9**) in 40–90% yields. All the reactions were carried out in an identical manner using a 1 : 1 ratio of **1** and $AlCl_3$ in a large excess of the arene which acts also as the solvent. A reaction temperature of 80–90°C was used. The reactions with toluene and anisole were complete within 24 h. With the other arenes 48 h heating time was required, as found for the reaction of **1** with benzene.[7]

It is known that alkyl, alkoxy groups and halogens direct the second substitution to the *ortho-* and/or *para*-positions. Consequently, one would expect two isomers of $(NPCl_2)_2NSOC_6H_4R$ in these reactions. Surprisingly, most of the reactions led selectively to the *para*-substituted isomers. *Ortho*-substituted isomers were found only for R = Me (*para*:*ortho* = 4 : 1) and R = OMe (*para*:*ortho* = 3 : 2). In the latter case extensive resin formation suppressed the yield to 40%. The high *para*-selectivity of the reactions is probably of steric origin.

The derivatives **3A**, **5**, **6**, **8** and **9** are useful starting materials for the synthesis of a number of interesting compounds some of which being potential polymer intermediates. These results will be a part of a future publication.

The Friedel-Crafts reaction of *cis*-$NPCl_2(NSOCl)_2$ **2** (now using a molar ratio 2: $AlCl_3$ = 1 : 2) with mono substituted benzenes is much more complex. Besides *ortho-* and *para-* isomers, *cis-* and *trans-* isomers have to be considered as has been shown earlier[7] when benzene is the reagent. So the reaction of **2** with monosubstituted benzenes can give six disubstituted isomers (Figure 1) (assuming that no substitution will occur on the phosphorus atom). We have studied the reaction of **2** with the arenes $C_6H_5R$ (R = OMe, Me, Cl and Br) in order to find whether it is possible to isolate all six isomers and if not which isomer(s) is (are) formed predominantly. The reaction mixtures were analyzed using HPLC techniques and $^{31}$P NMR spectroscopy.

The reaction of **2** with anisole led to extensive degradation of the inorganic ring and no pure aryl derivatives of **2** could be isolated. The reaction with toluene gave a complex mixture of about ten products ($^{31}$P NMR; spectral area 20–26 ppm). Attempts to separate these compounds by HPLC were not successful.

The $^{31}$P NMR spectrum of the crude product from the reaction of **2** with chlorobenzene showed five peaks (Figure 2a) implying the presence of five compounds (ratio 10 : 4 : 3 : 2 : 1). These compounds could be separated by HPLC. Elemental analyses and mass spectra indicated these compounds (**10A**–**10E**) to be isomers of $NPCl_2(NSOC_6H_4Cl)_2$.

$^1$H NMR spectra provided information on the *ortho-para* substitution. The most predominant isomer **10A** and the isomer **10D** showed AA'BB' spin patterns for the

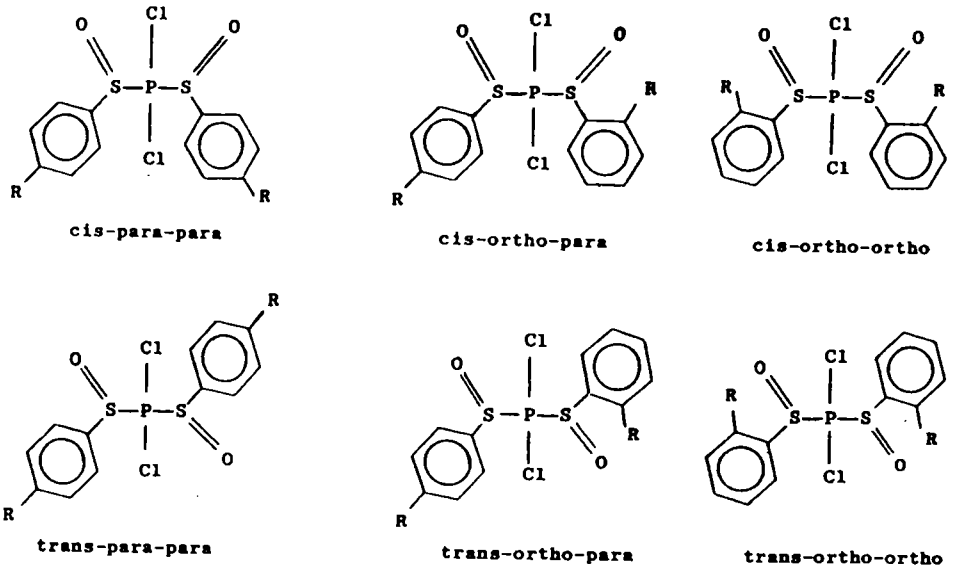


FIGURE 1 Possible isomers $NPCl_2(NSOC_6H_4R)_2$ in side-view representation. Nitrogen atoms are not shown.

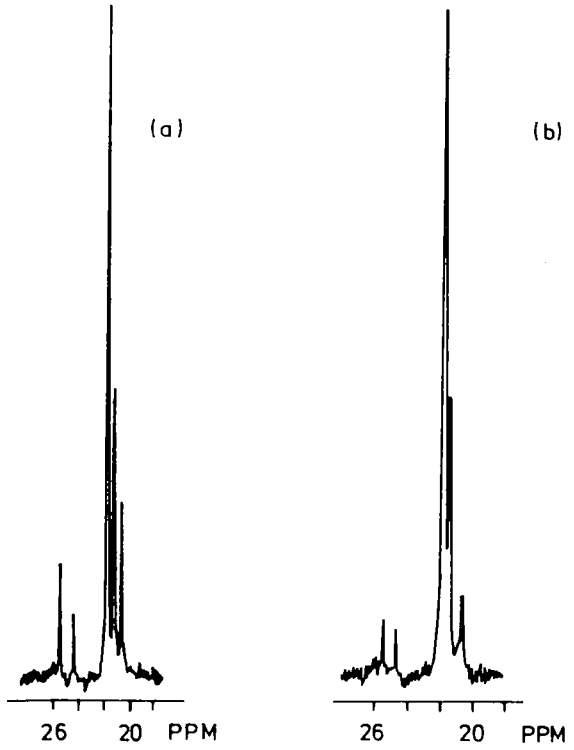


FIGURE 2 $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture of *cis*-$NPCl_2(NSOCl)_2$ (2) and $C_6H_5Cl$ (a) and $C_6H_5Br$ (b).

TABLE I

$^{31}P$ and $^{1}H$ NMR data for the aryl derivatives of $(NPCl_2)_2NSOCl$ and $NPCl_2(NSOCl)_2$ and for the dimethylamino derivatives $NP(NMe_2)_2(NSOC_6H_4Cl)_2$

| Compound No. | Compound | $\delta^{31}P$ (ppm) | $\delta^{1}H$ (ppm) Me | $^{3}J_{PH}$ (Hz |
|---|---|---|---|---|
| **3A** | $(NPCl_2)_2NSO$-*p*-$C_6H_4Me$ | 20.5 | 2.45 | |
| **3B** | $(NPCl_2)_2NSO$-*o*-$C_6H_4Me$ | 20.1 | 2.84 | |
| **4A** | $(NPCl_2)_2NSO$-*p*-$C_6H_4OMe$ | 20.5 | 3.82 | |
| **4B** | $(NPCl_2)_2NSO$-*o*-$C_6H_4OMe$ | 21.1 | 3.90 | |
| **5** | $(NPCl_2)_2NSO$-*p*-$C_6H_4Et$ | 20.6 | 2.46 (2.72 $CH_2$) | |
| **6** | $(NPCl_2)_2NSO$-*p*-$C_6H_4{}^{i}Pr$ | 20.6 | 2.52 (3.02 CH) | |
| **7** | $(NPCl_2)_2NSO$-*p*-$C_6H_4Cl$ | 20.7 | | |
| **8** | $(NPCl_2)_2NSO$-*p*-$C_6H_4Br$ | 20.7 | | |
| **9** | $(NPCl_2)_2NSO$-*p*-$C_6H_4I$ | 20.7 | | |
| **10A** | *trans*-$NPCl_2(NSO$-*p*-$C_6H_4Cl)_2$ | 21.9 | | |
| **10B** | *trans*-$NPCl_2(NSO$-*p*-$C_6H_4Cl)(NSO$-*o*-$C_6H_4Cl)$ | 21.4 | | |
| **10C** | *trans*-$NPCl_2(NSO$-*o*-$C_6H_4Cl)_2$ | 20.7 | | |
| **10D** | *cis*-$NPCl_2(NSO$-*p*-$C_6H_4Cl)_2$ | 25.4 | | |
| **10E** | *cis*-$NPCl_2(NSO$-*p*-$C_6H_4Cl)(NSO$-*o*-$C_6H_4Cl)$ | 24.3 | | |
| **11A** | *trans*-$NP(NMe_2)_2(NSO$-*p*-$C_6H_4Cl)_2(NSO$-*o*-$C_6H_4Cl)$ | 14.7 | 2.50 | 11.3 |
| **11B** | *trans*-$NP(NMe_2)_2(NSO$-*p*-$C_6H_4Cl)$ | 14.1 | 2.47; 2.49 | 11.9; 11.4 |
| **11D** | *cis*-$NP(NMe_2)_2(NSO$-*p*-$C_6H_4Cl)_2$ | 20.6 | 2.73; 2.79 | 11.3; 12.2 |
| **12A** | *trans*-$NPCl_2(NSO$-*p*-$C_6H_4Br)_2$ | 21.8 | | |
| **12B** | *trans*-$NPCl_2(NSO$-*p*-$C_6H_4Br)(NSO$-*o*-$C_6H_4Br)$ | 21.5 | | |
| **12C** | *trans*-$NPCl_2(NSO$-*o*-$C_6H_4Br)_2$ | 20.7 | | |
| **12D** | *cis*-$NPCl_2(NSO$-*p*-$C_6H_4Br)_2$ | 25.4 | | |
| **12E** | *cis*-$NPCl_2(NSO$-*p*-$C_6H_4Br)(NSO$-*o*-$C_6H_4Br)$ | 24.6 | | |

TABLE II

Experimental data

| Starting material | Reagent $C_6H_5R$; $Me_2NH$ | Reaction time (h) | Isolation/ Recrystallization | Product, yield (%), m.p. (°C) |
|---|---|---|---|---|
| **1** | R = Me | 24 | a/b | **3A**, 57, 96.0–98.5 |
| | | | c/d | **3B**, 10, 81.5–83.0 |
| **1** | R = OMe | 24 | a/b | **4A**, 32, 97.5–98.5 |
| | | | e/d | **4B**, 13, 196.5–198.0 |
| **1** | R = Et | 48 | a/b | **5** , 65, 92.0–93.0 |
| **1** | R = $^{i}$Pr | 48 | a/b | **6** , 55, 86.0–87.5 |
| **1** | R = Cl | 48 | a/b | **7** , 71, 104.5–106.0 |
| **1** | R = Br | 48 | a/b | **8** , 87, 121.5–122.5 |
| **1** | R = I | 48 | a/b | **9** , 62, 119.0–120.0 |
| **2** | R = Cl | 48 | f/b | **10A**, 63, 89.0–91.5;111.5–113.5* |
| | | | f/b | **10B**, 15, 161–163.5 |
| | | | f/b | **10C**, 3, 163.0–164.5 |
| | | | f/d | **10D**, 3, 178.0–181.0 |
| | | | f/b | **10E**, 3, 181.5–183.5 |
| **10A** | $Me_2NH$ | 20 | e/d | **11A**, 69, 132.5–134.0 |
| **10B** | $Me_2NH$ | 20 | e/d | **11B**, 52, 124.0–125.0 |
| **10D** | $Me_2NH$ | 20 | e/d | **11D**, 52, 194.5–196.5 |

[a] Extraction residue with hot *n*-$C_5H_{12}$.
[b] Recrystallization from *n*-$C_5H_{12}$.
[c] HPLC, silicagel column, eluent *n*-$C_6H_{14}$: $Et_2O$ = 17:1.
[d] Recrystallization from $Et_2O$.
[e] Extraction residue with $Et_2O$.
[f] HPLC, silicagel column, eluent *n*-$C_6H_{14}$:$Et_2O$:MeCN = 1000:105:1.
*Two crystalline forms.

aryl protons in their $^1H$ NMR spectra. This suggests that these two isomers have *para-para* substitution. In order to determine the *cis-* and *trans-* structure, these two isomers were treated with an excess of dimethylamine to substitute the chlorine atoms on the phosphorus and to get the derivatives $NP(NMe_2)_2(NSOC_6H_4Cl)_2$ **11A** and **11D**, respectively. The $^1H$ NMR spectrum of **11A** showed only one doublet (at 2.50 ppm) implying that the dimethylamino groups are equivalent. Thus, the major product (**10A**) obtained from the reaction of **2** with chlorobenzene has the *trans-para-para* structure. This means that the isomer **10D** should have the *cis-para-para* structure. The $^{31}P$ chemical shift for these two derivatives (Table I) are in conformity with those reported for *trans-* and *cis-* $NPCl_2(NSOPh)_2$.[7]

Further support for this assignment comes from the $^1H$ NMR spectrum of **11D** which shows two doublets (at 2.73 and 2.79 ppm) as expected for a *cis*-derivative. The isomer **10A** exists in two crystalline modifications whose authenticities have been confirmed by elemental analyses and mass spectra.

The isomers **10B** and **10E** have similar $^1H$ NMR spectra. In order to find out the geometrical position of the chlorine atoms on the phenyl rings (*ortho* and *para*) and to determine the *cis-* or *trans-* configuration of the aromatic rings, a single crystal X-ray structure determination was carried out on **10B**. The results are given in Figure 3 and Tables III–V. As can be seen from Figure 3, the two aromatic rings are in the *trans-* position. The chlorine atom is in the *para*-position on one of the phenyl rings and in the *ortho* position on the other phenyl ring. The $^1H$ NMR spectrum of **11B** reflects this configuration. Two doublets (2.47, 2.49 ppm) are seen for the dimethylamino protons showing the slight inequivalence.

The similar nature of the $^1H$ NMR spectra of **10B** and **10E** suggests that the latter should have the *cis- ortho-para* structure. The $^{31}P$ chemical shift for **10E** (24.3 ppm) supports the assignment of a *cis*-structure. The isomer **10C** then should have the *trans-ortho-ortho* structure. This assignment follows from the $^{31}P$ chemical shift (see Figure 2), which falls in the range of the other two *trans*-isomers.

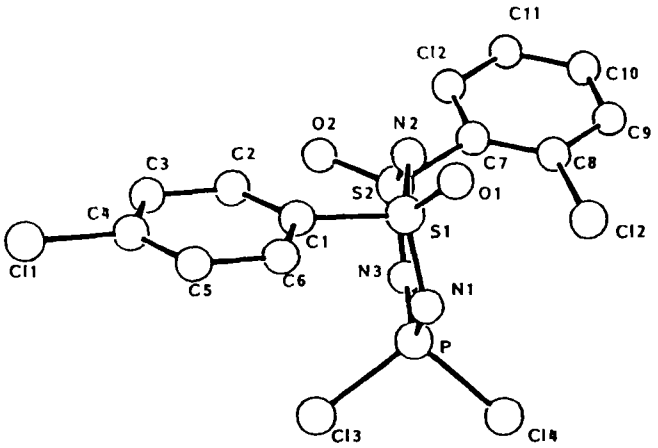


FIGURE 3 Molecular structure and adopted numbering scheme of isomer $NPCl_2(NSOC_6H_4Cl)_2$ (**10B**).

The observed ratio of product formation is the logical result of a preference of formation of *trans*-products over *cis*-products, and of products with *para*- substituted ligands over those with *ortho*-substituted ones. The fact that reactions with **1** are apparently more selective with respect to the formation of *para*-isomers than those with **2** is probably due to steric requirements.

The $^{31}P$ NMR spectrum of the crude reaction mixture of **2** with bromobenzene exhibited an analogous pattern as that of the reaction with chlorobenzene. Five resonance signals (ratio 14 : 5 : 2 : 1 : 1) could be discerned belonging to three *trans*-isomers (20–22 ppm) and two *cis*- isomers (24–25.5 ppm). Although no attempts were made to separate the individual compounds, structures can be assigned according to the structure-yield relationship found for the chlorobenzene-**2** system (Table I, compounds **12A–12E**). Compared with chlorobenzene there is a stronger tendency to form the *trans-para-para* isomer in the case of bromobenzene, which can be explained from a larger steric hindrance of the bromophenyl group.

### *Structure of* $NPCl_2(NSOC_6H_4Cl)_2$ **10B**

The molecular structure including the atomic numbering scheme is given in Figure 3. Atomic coordinates and some selected intramolecular bond distances and angles are compiled in Tables III and IV, respectively. The inorganic ring skeleton is not completely planar as can be concluded from the data given in Table V. The P—N and S—N bond lengths can be considered as equal within the experimental error. This observation corresponds with the values of endocyclic bond lengths found in *cis*-$NPCl_2(NSOPh)_2$ and can be traced back to the small difference in electronegativity between the phosphorus and sulfur centres.[9] The values of the endocyclic bond angles fall in the range found for similar compounds *cis*-$NPCl_2(NSOX)_2$ (X = Ph[9], Cl[10], F[11]) suggesting a $sp^3$ type hybridization at P, S and a $sp^2$ one at nitrogen. The differences of the bonding parameters in the organic rings border to significance, mean values are: C—C = 1.384(7) Å, C—C—C = 120(1)° for *p*-$C_6H_4Cl$, and C—C = 1.386(5) Å, C—C—C = 120.1(4)° for *o*-$C_6H_4Cl$.

TABLE III

Positional parameters for nonhydrogen atoms with e.s.d. in parentheses

| Atom | x | y | z | atom | x | y | z |
|---|---|---|---|---|---|---|---|
| P | −0.0770(2) | −1.0567(2) | 0.2298(1) | C1 | 0.1958(7) | −0.8199(5) | 0.2343(5) |
| S1 | 0.1622(2) | −0.9636(1) | 0.3321(1) | C2 | 0.3034(8) | −0.8518(7) | 0.1464(5) |
| S2 | 0.2817(2) | −1.2212(1) | 0.2359(1) | C3 | 0.3187(9) | −0.7329(7) | 0.0679(5) |
| N1 | −0.0339(6) | −0.9585(5) | 0.3082(4) | C4 | 0.2259(8) | −0.5901(6) | 0.0838(5) |
| N2 | 0.3065(6) | −1.1150(5) | 0.3151(4) | C5 | 0.1186(9) | −0.5572(6) | 0.1705(5) |
| N3 | 0.0832(6) | −1.1939(5) | 0.2022(4) | C6 | 0.1026(8) | −0.6757(6) | 0.2488(5) |
| Cl1 | 0.2455(3) | −0.4422(2) | −0.0114(2) | C7 | 0.3591(7) | −1.4030(6) | 0.3130(5) |
| Cl2 | 0.1027(2) | −1.3242(2) | 0.4634(1) | C8 | 0.2813(8) | −1.4482(6) | 0.4078(5) |
| Cl3 | −0.1881(2) | −0.9308(2) | 0.0894(1) | C9 | 0.3438(9) | −1.5945(7) | 0.4615(6) |
| Cl4 | −0.2773(2) | −1.1233(2) | 0.2898(2) | C10 | 0.486(1) | −1.6946(7) | 0.4201(6) |
| 01 | 0.1860(6) | −0.9308(5) | 0.4376(3) | C11 | 0.567(1) | −1.6518(7) | 0.3268(6) |
| 02 | 0.3926(6) | −1.2217(5) | 0.1430(3) | Cl3 | 0.5038(9) | −1.5034(7) | 0.2715(5) |

TABLE IV

Selected bond lengths (Å) and angles (°) with e.s.d. in parentheses

| | | | |
|---|---|---|---|
| P—N1 | 1.568(6) | N1—P—N3 | 117.3(3) |
| P—N3 | 1.579(4) | N1—S1—N2 | 112.9(3) |
| S1—N1 | 1.564(5) | N2—S2—N3 | 114.2(3) |
| S1—N2 | 1.570(4) | P—N1—S1 | 122.1(3) |
| S2—N2 | 1.579(5) | S1—N2—S2 | 125.0(3) |
| S2—N3 | 1.555(5) | P—N3—S2 | 122.8(4) |
| P—Cl3 | 1.984(2) | Cl3—P—Cl4 | 101.0(1) |
| P—Cl4 | 1.976(2) | 01—S1—C1 | 107.5(3) |
| S1—01 | 1.419(5) | 02—S2—C7 | 106.6(2) |
| S2—02 | 1.430(4) | | |
| S1—C1 | 1.765(6) | | |
| S2—C7 | 1.765(5) | | |
| C11—C4 | 1.736(6) | | |
| C12—C8 | 1.735(6) | | |

TABLE V

Distances of atoms to the least-squares plane through P N1 S1 N2 S2 N3. The equation of the plane is $0.3115x' + 0.4423y' - 0.8410z' + 7.6170 = 0$, x', y' and z' being orthogonalized coordinates

| | | | |
|---|---|---|---|
| P | 0.034(2) | 01 | −0.623(4) |
| N1 | −0.100(5) | C1 | 1.841(5) |
| S1 | 0.134(1) | 02 | 1.171(4) |
| N2 | −0.106(5) | C7 | −1.392(6) |
| S2 | 0.038(1) | | |
| N3 | −0.000(5) | | |



## EXPERIMENTAL

*General.* All experiments were carried out under dry nitrogen. $(NPCl_2)_2NSOCl$ **1** and *cis*-$NPCl_2(NSOCl)_2$ **2** were synthesized as described elsewhere.[12,13] Solvents were purified by conventional methods. Toluene, anisole, ethylbenzene, and cumene were distilled over sodium. Chlorobenzene, bromobenzene and iodobenzene were distilled over molecular sieves (4 Å).

$^1H$ NMR spectra were recorded on a Jeol C60-HL instrument using TMS as internal standard. $^{31}P$ NMR spectra (proton-noise decoupled) were recorded on a Nicolet 283A FT spectrometer operating at 80.9 MHz using $(NPCl_2)_3$ solution in $CDCl_3$ ($\delta$ $^{31}P$ = 19.9 ppm) as an external reference. Low field shifts are positive. Mass spectra, which were taken on an AEI MS9 spectrometer at 70 eV with an accelerating voltage of 8 kV, were used for identification purposes only. Elemental analyses on C, H, N, S and Cl were performed in the Micro-analytical Department of this University under supervision of Mr. A. F. Hamminga. All products isolated gave satisfactory analyses.

*Friedel-Crafts reactions.* To 150 ml of the monosubstituted benzene, 10 g (30.4 mmol) of **1** and 4.09 g (30.6 mmol) of $AlCl_3$ were added. The mixture was heated under stirring for 48 h (24 h for toluene and anisole) at 80–90°C. After cooling, the reaction mixture was poured into a mixture of 80 ml of conc. hydrochloric acid and 500 g of crushed ice. The layers were separated and the water layer was washed twice with 200 ml portions of dichloromethane. The combined organic layers were washed once with 200 ml of water and dried over anhydrous $CaCl_2$ until transparent. The solvent was then removed under reduced pressure. The residue thus obtained was treated further (for details see Table II). Reactions with **2** were carried out in a similar fashion but using a molar ratio of **2**: $AlCl_3$ = 1 : 2. Experimental details are also given in Table II. In some cases HPLC on a lichrosorb Si 60/10 column ($\phi$ 22 mm, length 30 cm) was used to separate the mixture of products.

*Dimethylaminolysis*[13]. To a solution of 0.926 g (2.0 mmol) of **10** in 30.0 ml of acetonitrile was added dropwise under vigorous stirring a solution of 0.765 g (17.0 mmol) of $Me_2NH$ in 30 ml of acetonitrile at −35°C. After warming up to room temperature the mixture was stirred for 20 h at that temperature, and subsequently evaporated to dryness. The residue thus obtained was extracted carefully with diethyl ether, concentrated and cooled to get crystals of **11**.

*Structure determination of* **10B**. A single crystal of **10B** (size 0.25 × 0.25 × 0.10 mm) was prepared by careful crystallization from pentane. Data collection was performed at 298°K on an Enraf-Nonius CAD4-SDP23M diffractometer, using graphite monochromated MoK$\alpha$ radiation ($\lambda$ = 0.7107 Å). Calculations were carried out on a PDP-11/23, making use of Enraf-Nonius CAD4-SDP programs. Cell parameters were obtained from a least-squares fitting of 18 reflections with $4° \leq \theta \leq 10°$. The intensities of 2469 reflections ($1 \leq \theta \leq 22°$) were measured by the $\omega$-2$\theta$ scan technique, 2386 reflections having $I \geq 3\sigma(I)$. All intensities were corrected for Lorentz-polarization effects, no absorption corrections were applied. The structure was solved by direct methods (Multan 82). Full matrix refinement of positional and anisotropic thermal parameters for the non-hydrogen atoms converged to a final R-value = 0.046, $R_w$ = 0.056 (w = 1) involving 2386 reflections.

*Crystal Data*. $C_{12}H_8N_3O_2PS_2Cl_4$. M = 463.13. Triclinic space group $P\bar{1}$, a = 7.884(1), b = 9.587(1), c = 12.369(1) Å, $\alpha$ = 80.69(2), $\beta$ = 88.86(2), $\tau$ = 71.11(2)°, V = 872.3 Å$^3$, Z = 2, $D_c$ = 1.763 gcm$^{-3}$, $\mu$(MoK$\alpha$) = 10.14 cm$^{-1}$, F(000) = 464.

*Note*. Anisotropic thermal parameters are deposited with the Cambridge Crystallographic Data Centre (CCDC), U.K.



## REFERENCES

1. H. Winter and J. C. van de Grampel, *Z. Naturforsch.*, **38B**, 1652 (1983).
2. C. T. Ford, F. E. Dickson and I. I. Bezman, *Inorg. Chem.*, **3**, 177 (1964).
3. K. G. Acock, R. A. Shaw and F. B. G. Wells, *J. Chem. Soc.*, 121 (1964).
4. E. T. McBee, K. Okuhara and C. J. Morton, *Inorg. Chem.*, **4**, 1672 (1965).
5. T. Moeller, T. Chang, A. Ouchi, A. Vandi and A. Failli, *Inorg. Synth.*, **13**, 9 (1972).
6. T. Moeller and A. Ouchi, *J. Inorg. Nucl. Chem.*, **28**, 2147 (1966).
7. J. B. van den Berg, B. de Ruiter and J. C. van de Grampel, *Z. Naturforsch.*, **31B**, 1216 (1976).
8. J. B. van den Berg and J. C. van de Grampel, *Z. Naturforsch.*, **34B**, 27 (1979).
9. A. Meetsma, A. L. Spek, H. Winter, C. Cnossen-Voswijk, J. C. van de Grampel and J. L. de Boer, *Acta Cryst.*, submitted for publication.
10. J. C. van de Grampel and A. Vos, *Acta Cryst.*, **B25**, 651 (1969).
11. P. A. Tucker and J. C. van de Grampel, *Acta Cryst.*, **B30**, 2795 (1974).
12. D. Suzuki, H. Akagi and K. Matsumura, *Synthesis*, 369 (1983).
13. Procedure described in: B. de Ruiter, Ph.D. Thesis, University of Groningen, 1981.