Derivatives of cis-NPCl$_2$(NSOCl)$_2$ and (NPCl$_2$)$_2$NSOCl, Part XII [1]

Triphenylphosphazenyl Derivatives of NPCl$_4$(NSOX)$_2$ and (NPCl$_2$)$_2$NSOX with X = F, Cl or Ph

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Triphenylphosphazenyl Derivatives, Preparation, Characterization

Reaction of the ring systems NPCl$_3$(NSOX)$_2$ and (NPCl$_2$)$_2$NSOX (X = F, Cl, Ph) with HNPPh$_3$ in molar ratio 1:2 gives their mono(triphenylphosphazenyl) derivatives. The compound NPCl(NPPh$_3$)(NSOPh)$_2$ forms a stable 1:1 adduct with acetonitrile. All compounds are characterized by NMR (31P, 19F), IR and mass spectra.

Introduction

It has been shown that in reactions of the cyclic system (NPCl$_2$)$_2$ with the strong nucleophile HNPPh$_3$ the substitution of the chlorine atoms follows a non-geminal pattern. However, it appeared to be impossible to proceed beyond disubstitution [2]. Also the application of the silylation method using (NPFS)$_2$ and Me$_2$SiNPPh$_3$ as reagents did not lead to the introduction of more than two NPPh$_3$ groups [3]. The geminal bis(triphenylphosphazenyl) derivative of (NPCl$_2$)$_2$ can be prepared by a Kirsanov reaction, starting from (NPCl$_2$)$_2$NP(NH$_2$)$_2$ and PCl$_3$Ph$_3$ [4] or by a Grignard reaction of (NPCl$_2$)$_2$NP(NPCl$_2$)$_2$ with PhMgBr [5]. The NPPh$_3$ derivatives exhibit a relatively strong basicity towards HClO$_4$ in nitrobenzene. Both endocyclic protonation (e.g. in (NPCl$_2$)$_2$NP(NPPh$_3$)$_2$ and exocyclic protonation (e.g. in (NPCl$_2$)$_2$NPPh(NPPh$_3$)) has been observed depending on the conformation of the NPPh$_3$ group relative to the mean plane of the NP ring [6–10].

In this paper we report the preparation of the mono(triphenylphosphazenyl) derivatives of the ring systems NPCl$_3$(NSOX)$_2$ and (NPCl$_2$)$_2$NSOX (X = F, Cl or Ph). It will be shown that the product formation is sterically controlled. The $^3$P NMR data reflect the influence of the NPPh$_3$ ligand.

Discussion

The introduction of one NPPh$_3$ group can be achieved at room temperature in moderate to high yields using benzene as a solvent. Exploring reactions to introduce a second NPPh$_3$ group pointed to small yields of disubstituted products. The decreased reactivity can be ascribed both to the electron-donating property and to the bulk of the NPPh$_3$ group already present.

From the NMR data (Table I) it is obvious that the first substitution takes place at a phosphorus atom, since the chemical shift of that atom is changed completely. The phosphazenylation (2 moles ratio of HNPPh$_3$) of cis-NPCl$_2$(NSOF)$_2$ (1) gives two isomers with composition NPCl(NPPh$_3$)(NSOF)$_2$ (2, 3) in ratio of about 4:1. As in previous investigations [11, 12] we assign a cis-arrangement of the NPPh$_3$ group and the oxygen ligands to the isomer formed in the highest yield. The compound cis-NPCl$_2$(NSOCl)$_2$ (4) gives rise to only one isomer on reaction with HNPPh$_3$. Obviously the small intramolecular distances between the chlorine atoms trans to oxygen block a nucleophilic attack at that side of the molecule [13]. The formation of one isomer trans-NPCl(NPPh$_3$)(NSOPh)$_2$ (7) from trans-NPCl$_2$(NSOPh)$_2$ (6) indicates that during the reaction at the phosphorus atom the configurations around the sulphur atoms are retained.

The results of the phosphazenylation of (NPCl$_2$)$_2$NSOCl again show the influence of steric hindrance. For X = F and Cl two isomers of the mono (NPPh$_3$) derivative are formed, while the reaction with (NPCl$_2$)$_2$NSOPh (15) leads to one isomer only. The relatively large phenyl group obviously favours a nucleophilic attack at one side of the ring, which is expected to result in a trans-configuration of NPCl$_2$NPCl(NPPh$_3$)(NSOPh) (16). It is worth mentioning that the reaction with (NPCl$_2$)$_2$NSOCl (12) is less affected by steric hindrance than that with cis-NPCl$_2$(NSOCl)$_2$ (4), since
Table I. $^{31}$P and $^{19}$F NMR data of the mono(triphenylphosphazenyl) derivatives of NPCl$_3$NSOCl$_2$ and (NPCl$_3$)$_2$NS0X.

|                  | $^{31}$P [ppm] | $^{19}$F [ppm] | $|J_{P-F}|$ [Hz] | $|J_{A-B}|$ [Hz] | $|J_{B-C}|$ [Hz] | $|J_{A-C}|$ [Hz] |
|------------------|----------------|---------------|-----------------|---------------|----------------|---------------|
| cis-NPCl$_3$(NSOF)$_2$ | (1) 30.9 | 73.2 | 1.0 |
| NPCl(NPPh$_3$)(NSOF)$_2$ | (2) 20.3 | 33.1 | 30.6 74.5 | 3.1 |
| NPCl(NPPh$_3$)(NSOF)$_2$ | (3) 18.9 | 31.4 | not determined |
| cis-NPCl$_3$(NSOCl)$_2$ | (4) 27.6 | not determined |
| NPCl(NPPh$_3$)(NSOCl)$_2$ | (5) 20.2 | 30.7 |
| trans-NPCl$_3$(NSOPh)$_2$ | (6) 22.1 |
| trans-NPCI(NPPh$_3$)(NSOPh)$_2$ | (7) 16.1 | 31.4 |
| NPCl(NPPh$_3$)(NSOPh)$_2$ MeCN | (8) 16.2 | 30.9 |
| NPCl$_2$NPCl(NPPh$_3$)NSOF | (9) 26.1 |
| NPCl$_2$NPCl(NPPh$_3$)NSOF | (10) 17.4 | 31.3 | 74.5 | 3.1 |
| NPCl$_2$NPCl(NPPh$_3$)NSOCl | (11) 16.7 | 30.6 74.4 | 3.8 |
| NPCl$_2$NPCl(NPPh$_3$)NSOCl | (12) 26.3 |
| NPCl$_2$NPCl(NPPh$_3$)NSOCl | (13) 17.5 | 30.0 73.4 | 1.7 |
| NPCl$_2$NPCl(NPPh$_3$)NSOCl | (14) 16.6 | 30.1 70.6 | 3.8 |
| NPCl$_2$NPCl(NPPh$_3$)NSOCl | (15) 20.7 |
| NPCl$_2$NPCl(NPPh$_3$)NSOCl | (16) 16.0 | 29.1 | 63.8 | 3.4 |

$A = $ NPPh$_3$, $B = $ PCl(NPPh$_3$), $C = $ PCl$_3$.

in the latter case only one isomer viz. 5 is formed. This observation agrees very well with the difference in molecular structure of both ring systems [13, 14].

The interaction of 7 and acetonitrile leads to formation of a stable adduct of composition NPCl(NPPh$_3$)(NSOPh)$_2$ MeCN (8). D.T.A. experiments gave two endothermic effects; at 88°C (evolution of MeCN) and at 171°C (melting point of 7). Compared to MeCN the methyl $^1$H resonance signal is shifted to higher field (2.01 to 1.92 ppm). Also a small upfield shift (—3.1 to —3.5 ppm) is observed for the $^3$P signal of the endocyclic phosphorus atom (Table I). The frequency of the CN stretching band of the adduct is about equal to that of MeCN (in 8 ν(CN) = 2255 cm$^{-1}$, in MeCN ν(CN) = 2260 cm$^{-1}$). It is clear that these data do not allow a structure assignment for adduct 8.

The $^3$P NMR spectra of the mono(NPPh$_3$) derivatives can be interpreted on the basis of an AB or ABC type pattern, in which A, B and C represent NPPh$_3$, PCl(NPPh$_3$) and PCl$_3$, respectively. As may be seen from Table I the replacement of a Cl atom by a NPPh$_3$ group causes a large upfield shift of the resonance of the endocyclic phosphorus atom involved (22—36 ppm). The tendency of the P(Cl$_2$) signal to shift upfield on substitution at the other phosphorus atom (cf. compounds 10 and 11; 13 and 14) is rather unexpected, since in all derivatives of (NPCl$_2$)$_2$NSOCl ($X = $ F, Cl, Ph) known up to now, the P(Cl$_2$) signal shifts to lower field, if an electron-donating group (amino group) is introduced at the other phosphorus atom [15, 16]. To explain this behaviour we have suggested that the presence of such groups decreases the overall π-electron density in the ring and thus the electron shielding of the phosphorus centers. For the amino-substituted phosphorus atom this deshielding effect, however, is overruled by the electron input of the amino group [15]. In the case of the NPPh$_3$ derivatives of 9 and 12 an analogous explanation may apply: for a phosphazenyl substituent the deshielding effect evidently is overruled by the electron input, even for the remote phosphorus atom.

The values of the exocyclic and endocyclic P-P coupling constants differ markedly which is undoubtedly caused both by the difference of the angle at nitrogen in the two PNP segments and by the nature of the substituents at phosphorus. The values of $|J_{A-C}|$ correspond with those of the phosphazenyl derivatives of (NPCl$_3$)$_2$ in which endocyclic protonation has been observed; compare endocyclic protonation (NPCl$_3$)$_2$NPCl(NPPh$_3$) and NPCl$_2$NPCl(NPPh$_3$) |$J_{A-C}| = 3.4$ and 5.5 Hz, respectively; exocyclic protonation (NPCl$_3$)$_2$NPCl(NPPh$_3$), (NPCl$_3$)$_2$NPOEt(NPPh$_3$) and (NPCl$_3$)$_2$NPMe$_2$(NPPh$_3$) |$J_{A-C}| = 0.4$, 0.9 and <0.1 Hz, respectively [6, 17].
Experimental

All experiments were carried out under dry nitrogen. Solvents were purified and dried by conventional methods. The compounds NPCl(NSOX)₂ and (NPCl₃)₂NSOX (X = F, Cl, Ph) were prepared according to published methods [18-20]. HNPPh₃ was synthesized from Me₃SiNPPh₃ [21], following the procedure of Birkofe et al. [22]. Elemental analyses were carried out at the Microanalytical Department of this University under supervision of Mr. A. F. Hamminga. Infrared spectra were recorded on a Hitachi EPI-G spectrophotometer of Mr. A. F. Hamminga. Infrared spectra were recorded directly by a conventional inlet system. The ³¹P and ¹³C NMR spectra were recorded by Mr. R. H. Fokkens (NMR Department, University of Amsterdam) on a Varian XL-100 FT spectrometer, operating at 40.5 MHz and 94.1 MHz, respectively; chemical shifts (positive in low-field direction) were determined relative to the external standards 85% H₃PO₄ and CFCl₃ at 37 °C. The deuterium resonance of the solvent (CDCl₃) was used for field-frequency lock. The ¹H NMR spectra were recorded at 35 °C on a Varian A-60 spectrometer using TMS as internal reference. For the D.T.A. experiments the samples were heated in glass ampoules at a rate of 2-3 °C min⁻¹. The temperature effect ΔT was measured as a function of the temperature of the sample-holder block.

1. Reaction of NPCl₂(NSOX) with HNPPh₃ (molar ratio 1:2)

At room temperature a solution of 6.0 mmoles of HNPPh₃ in 30 ml of benzene was added slowly to a stirred solution of 3.0 mmoles of NPCl₂(NSOX)₂ in 30 ml of benzene. The reaction mixture was kept at room temperature during 24 h under continuous stirring. After decanting the solvent the residue was extracted twice with 30 ml of benzene. The reaction mixture contained one isomer. Yield 82%.

NPCl(NPPPh₃)(NSOF)₂ (2) m.p. 140-142 °C

Analysis


IR (cm⁻¹) 1480 m, 1440 s, 1332 vs, 1215 vs, 1152 s, 797 m, 763 m, 747 s, 720 s, 688 s, 630 m, 572 vs, 508 vs, 452 m.

NPCl(NPPPh₃)(NSOCl)₂ (5) m.p. 138-141 °C

Analysis


IR (cm⁻¹) 1480 m, 1445 m, 1440 m, 1340 s, 1246 vs, 1230 vs, 1165 vs, 1155 vs, 1138 vs, 1012 m, 995 m, 850 s, 797 m, 763 m, 747 s, 720 s, 690 s, 630 s, 572 s, 540 s, 530 s, 510 m.

The reaction mixture contained one isomer. Yields after purification 53%.

NPCl(NPPPh₃)(NSOCl)₂ · MeCN (8)

Analysis


IR (cm⁻¹) 2255 vw (MeCN), 1445 m, 1440 m, 1340 m, 1246 vs, 1230 vs, 1165 vs, 1155 vs, 1138 vs, 1012 m, 995 m, 850 s, 797 m, 763 m, 747 s, 720 s, 690 s, 630 m, 572 s, 540 s, 530 s, 510 m.

By heating the adduct during 24 h at 90 °C and 0.2 mm Hg the acetonitrile could be removed quantitatively.

2. Reaction of (NPCl₃)₂NSOX with HNPPh₃ (molar ratio 1:2)

The same procedure was used as outlined under 1.

NPCl(NPPPh₃)(NSOF)₂ (2) m.p. 140-142 °C

Analysis

Caled C56.69 H3.97 N8.82 C15.63 S10.19. Found C56.74 H3.97 N8.82 C15.58 S10.09.

IR (cm⁻¹) 1440 m, 1335 m, 1247 vs, 1165 vs, 1157 vs, 1138 vs, 1037 m, 1020 m, 995 m, 850 s, 835 s, 750 s, 722 s, 709 m, 688 s, 629 m, 562 s, 539 s, 528 s, 485 m.

m/e 634 M₊35Cl⁻ 100%, 557 (M₊35Cl⁻-Ph⁺) 66%.

A crystalline mixture of two isomers 10 and 11 (ratio about 3:1) was obtained, which could not be separated by recrystallization. Yield 34%.
NPCl₂NPCl(NPPh₃)NSOF (10) and (11)  
Analysis  
Calcd C 39.05 H 2.73 N 10.12 Cl 19.21. 
m/e 552 M₃5Cl⁺ 100%, 533 (M₃5Cl-F)+ 48%,  
517 (M₃5Cl-35Cl) 42%. 
X = Cl  

From the mixture of two isomers 13 and 14 (ratio about 4:1) one compound could be obtained  
in a pure state. Yield 56%. 

NPCl₂NPCl(NPPh₃)NSOCl (13) m.p. 143-145 °C  
Analysis  
Calcd C 37.92 H 2.65 N 9.83 Cl 24.87, 
Found C 38.05 H 2.74 N 9.84 Cl 24.47. 
IR (cm⁻¹) 1440 m, 1310 s, 1210 vs b, 1180 m, 1135 s,  
1115 m, 1090s, 1085 m, 865 m, 850 m, 845 m, 798 m, 750 m,  
745 m, 723 s, 690 s, 652 s, 587 s, 540 s, 528 s, 497 m,  
465 m. 
m/e 568 M₃5Cl⁺ 5%, 533 (M₃5Cl-F)+ 100%.  

X = Ph  
The reaction mixture contained one isomer. Yield 58%. 

NPCl₂NPCl(NPPh₃)NSOPh (16) m.p. 164-166 °C  
Analysis  
Calcd C 47.12 H 3.30 N 9.16 Cl 17.39. 
Found C 47.49 H 3.31 N 9.20 Cl 16.90. 
IR (cm⁻¹) 1438 m, 1317 m, 1309 m, 1241 s, 1203 m,  
1176 s, 1169 s, 1155 vs, 1115 m, 838 m, 748 m,  
733 s, 722 s, 690 m, 645 s, 573 s, 540 vs, 525 m,  
490 m. 
m/e 610 M₃5Cl⁺ 100%, 575 (M₃5Cl-35Cl)+ 1%,  
533 (M₃5Cl-Ph)+ 43%.  

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