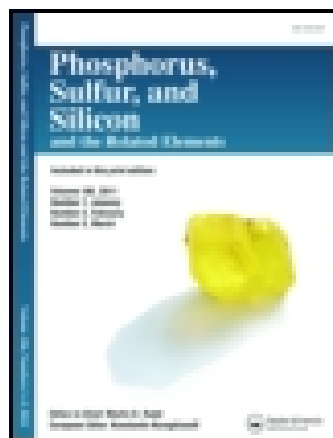




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FLUORINATED CYCLOTHIAPHOSPHAZENES: SYNTHESIS, STRUCTURE AND REACTIVITY

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FLUORINATED CYCLOTHIAPHOSPHAZENES: SYNTHESIS, STRUCTURE AND REACTIVITY

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Dedicated to Professor John G. Verkade on the occasion of his 60th birthday

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Reaction of chlorocyclothiaphosphazenes $\text{NPCl}_2(\text{NSOX})_2$ ($\text{X} = \text{Cl}, \text{Ph}$) and $(\text{NPCl}_2)_2\text{NSOX}$ ($\text{X} = \text{Cl}, \text{F}, \text{Ph}$) with KSO_2F in bulk leads to fluorination at the phosphorus centers. The substitution reaction follows a geminal pattern. Reactions of *trans*- $\text{NPF}_2(\text{NSOPh})_2$ with Grignard reagents RMgX ($\text{R} = \text{Me}, \text{'Bu}$) show substitution of fluorine by alkyl groups to be a slow process. The more reactive PhMgBr gives an acceptable reaction rate and good yields. Organolithium reagents offer organo-substituted cyclothiaphosphazenes in low to moderate yields, depending on the reagent used. Crystals of *cis*- $\text{NPF}_2(\text{NSOPh})_2$ are monoclinic, space group $\text{P2}_1/\text{n}$, with $a = 13.665(7) \text{ \AA}$, $b = 10.676(1) \text{ \AA}$, $c = 9.897(3) \text{ \AA}$, $\beta = 90.55(3)^\circ$, $V = 1443.8(9) \text{ \AA}^3$, and $Z = 4$. The final R and wR values are 0.034 and 0.043, respectively. The PN and SN bond lengths vary from 1.571(2) to 1.590(2) $\text{ \AA}$.

Key words: Cyclothiaphosphazenes, fluorination.

INTRODUCTION

A variety of reagents, PbF_2 ,^{1–3} KSO_2F ,^{4–10} AgF ,^{1,2,11} AgF_2 ,¹² SbF_3 ,^{9,13–15} NaF ,^{8,12,16–18} and $\text{KF}/18\text{-crown-6}$ ¹⁹ have been applied to convert $(\text{NPCl}_2)_3$ (**1**) into compounds $\text{N}_3\text{P}_3\text{F}_{6-n}\text{Cl}_n$ ($n = 1–6$). Fluorination of **1** proceeds via a geminal substitution pattern.^{6–8} Several of these aforementioned reagents have also been tested in the case of chlorocyclothiaphosphazenes. Reactions of *cis*- $\text{NPCl}_2(\text{NSOCl})_2$ (**2**) with AgF_2 or SbF_3 and $(\text{NPCl}_2)_2\text{NSOCl}$ (**3**) with AgF_2 yielded *cis* and *trans*- $\text{NPCl}_2(\text{NSOF})_2$ (**4**, **5**) and $(\text{NPCl}_2)_2\text{NSOF}$ (**6**), respectively.^{20–22} In all cases metathetical replacement of chlorine ligands is restricted to the sulfur centers, which can be explained by an initial coordination of the fluorinating reagents at the sulfur-bonded oxygen atoms.²³ Reactions of $\text{NPCl}_2(\text{NSOX})_2$ or $(\text{NPCl}_2)_2\text{NSOX}$ ($\text{X} = \text{F}, \text{Cl}$ or Ph) with NaF or $\text{KF}/18\text{-crown-6}$ in MeCN only gave traces of fluorinated derivatives ($\text{X} = \text{Ph}$), whereas hydrolysis phenomena were observed for $\text{X} = \text{F}$ or Cl .²⁴

In the present study we report reactions of compounds $\text{NPCl}_2(\text{NSOX})_2$ ($\text{X} = \text{Cl}, \text{Ph}$) and $(\text{NPCl}_2)_2\text{NSOX}$ ($\text{X} = \text{F}, \text{Cl}, \text{Ph}$) with KSO_2F as fluorinating agent. Furthermore reactions of *trans*- $\text{NPF}_2(\text{NSOPh})_2$ towards Grignard and organolithium reagents have been investigated in order to get some insight in the reactivity of

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perfluorocyclothiaphosphazenes. The structure of *cis*-NPF₂(NSO₂Ph)₂ will be described.

EXPERIMENTAL

General. All experiments were carried out under dry oxygen-free nitrogen. Hexane, dichloromethane and chloroform were dried and purified according conventional methods. Tetrahydrofuran, pentane and diethyl ether were distilled from a sodium-potassium-benzophenone mixture. The compounds *cis*-NPCI₂(NSOCl)₂ (2),²⁶ (NPCI₂)₂NSOCl (3),^{27,28} *cis* and *trans*-NPCI₂(NSOF)₂ (4, 5),^{20,21} (NPCI₂)₂NSOF (6),²² *cis*- and *trans*-NPCI₂(NSO₂Ph)₂ (7, 8),²⁵ (NPCI₂)₂NSO₂Ph (9),²⁵ and KSO₂F²⁹ were prepared according published procedures. Grignard reagents were prepared in THF from the appropriate halide and magnesium. MeLi and PhLi were prepared in ether from methylchloride and phenylbromide as described elsewhere.³⁰ ^tBuLi was obtained commercially from Janssen. LiO^tPr was prepared by stirring ^tBuLi and ^tPrOH in diethyl ether for one hour (at room temperature). The HPLC experiments were carried out using a Waters HPLC system consisting of two 6000A pumps, combined with a R401 RI detector. Separations were performed on Lichrosorb Si 60/10 columns (outside diameter 22 mm, length 30 cm). ³¹P and ¹⁹F NMR spectra (in CDCl₃) were recorded on a Nicolet NT 200 spectrometer operating at 81 MHz (for ³¹P NMR) or 188.2 MHz (for ¹⁹F NMR) using (NPCI₂)₃ (19.9 ppm, solution in CDCl₃) and CFCI₃ (0 ppm, solution in CDCl₃), respectively, as external references. Chemical shifts to low fields are taken positive. ¹H NMR spectra were recorded with a Jeol C60-HL spectrometer, using TMS as an internal standard. The NMR data of the compounds prepared are given in Table I. Mass spectra were obtained with an AEI MS 9 spectrometer. Microanalytical information was supplied by the Microanalytical Department of this University.

Preparation. The preparation of compounds 10–18 took place without the use of solvent during reaction. Care must be taken that the reaction mixture is thoroughly stirred and that the components are well-ground before use.

Reaction of 2 with 1 equivalent of KSO₂F. A mixture of 2.0 g (6.4 mmol) of 2 and 0.94 g of a KSO₂F (6.4 mmol)/KF (2.7 mmol)^{29a} mixture was heated at 120°C for 0.5 h. Vacuum distillation afforded 0.2 g of a colorless oil (bp 80–85°C at 0.1 mm Hg), which solidified in the receiver as white crystals. According to ³¹P NMR and mass spectrometry the distillate contained (1α,3α,5α)-NPCIF(NSOCl)₂ (10), (1α,3α,5β)-NPCIF(NSOCl)₂ (11), and *cis*-NPF₂(NSOCl)₂ (12) [for nomenclature see Reference 31]. Efforts to separate the reaction products were not successful.

Preparation of *cis*-NPF₂(NSOCl)₂ (12). A mixture of 2.0 g (6.4 mmol) of 2 and 1.88 g of a KSO₂F (12.8 mmol)/KF (5.5 mmol)^{29a} mixture was heated at 120°C for 2 h. Vacuum distillation afforded 0.4 g of a colorless oil (bp 46–49°C at 0.15 mm Hg) which solidified in the receiver as white crystals with mp 49–51°C. Yield 0.4 g of 12 (1.4 mmol, 22%). Anal. calc. for N₃P₂F₂Cl₂O₂: N, 15.11; S, 23.06; Cl, 25.50; found: N, 14.94; S, 23.26; Cl, 24.93. Mass spectrum: m/e 242 (M⁺ ³⁵Cl – ³⁵Cl, 100%).

When the same reaction procedure was carried out at 170°C, the distillate also contained *trans*-NPF₂(NSOCl)₂ (13) (based on ³¹P NMR).

Attempted preparation of NPF₂(NSOF)₂. A mixture of 1.0 g (3.6 mmol) of 4 and 1.6 g of a KSO₂F (10.8 mmol)/KF (4.6 mmol)^{29a} mixture was heated at 60°C for 0.5 h. Neither distillation nor extraction gave any cyclic products.

Preparation of (NPF₂)₂NSOCl (14). A mixture of 2.0 g (6.1 mmol) of 3 and 3.5 g of a KSO₂F (27.8 mmol)/KF (1.8 mmol) mixture^{29b} was heated at 100°C for 1 h. Vacuum distillation afforded 0.72 g (2.7 mmol, 44%) of a colourless liquid (bp 42–44°C at 15 mm Hg. Anal. calc. for N₃P₂SF₄ClO: N, 15.95; S, 12.17; Cl, 13.45; found: N, 15.99; S, 12.08; Cl, 13.34. Mass spectrum: m/e 228 (M⁺ ³⁵Cl – ³⁵Cl, 100%).

Preparation of (NPF₂)₂NSOF (15). A mixture of 1.9 g (6.1 mmol) of 6 and 3.6 g of a KSO₂F (24.4 mmol)/KF (10.5 mmol) mixture^{29a} was heated at 90°C for 1 h, after which the reaction mixture was allowed to cool to room temperature. Sublimation (40°C, 15 mm Hg) gave 0.3 g (1.2 mmol, 20%) of colorless crystals of 15, which had to be stored in the refrigerator at 5°C. Mass spectrum: m/e 247 (M⁺, 100%).

Preparation of *cis* and *trans*-NPF₂(NSO₂Ph)₂ (16, 17). A mixture of 7.0 g (17.8 mmol) of 7 (or 8) and

TABLE I
³¹P and ¹⁹F NMR data^a of compounds prepared

	δP(X)	δP(Y)	δF(A)	δF(B)	δF(C)	¹ J _{AX}	¹ J _{BX}	² J _{AB}
(1α,3α,5α)-NPClF(NSOCl) ₂ (10) ^b	18.9					1037		
(1α,3α,5β)-NPClF(NSOCl) ₂ (11) ^b	19.4					1080		
<i>cis</i> -NPF ₂ (NSOCl) ₂ (12)	-1.4		-74.8	-79.9		984	959	95
<i>trans</i> -NPF ₂ (NSOCl) ₂ (13) ^b	0.2					978		
(NPF ₂) ₂ NSOCl (14) ^c	4.2							
(NPF ₂) ₂ NSOF (15) ^d	4.4							
<i>cis</i> -NPF ₂ (NSOPh) ₂ (16)	1.8		-69.4	-76.3		954	931	93
<i>trans</i> -NPF ₂ (NSOPh) ₂ (17)	-1.0		-72.2			940		
(NPF ₂) ₂ NSOPh (18) ^c	3.5							
<i>gem</i> -NPCl ₂ NPF ₂ NSOPh (19)	-2.4	26.5	-69.2	-72.0		938	934	90
(1α,3β,5α)-NPFPh(NSOPh) ₂ (20)	20.9		-54.9			1028		
<i>trans</i> -NPPPh ₂ (NSOPh) ₂ (21)	17.4							
(1α,3β,5α)-NPF ^t Bu(NSOPh) ₂ (22)	41.0		-75.4			1091		

^a Chemical shifts in ppm; coupling constants in Hz.^b Compound not isolated, data restricted to ³¹P NMR.^c AA'BB'XX' spin system with δP(X) = δP(X'), direct analysis of ¹⁹F NMR spectrum not possible.^d AA'BB'CXX' spin system with δP(X) = δP(X'), direct analysis of ¹⁹F NMR spectrum not possible.

4.5 g of a KSO₂F (35.7 mmol)/KF (2.3 mmol) mixture^{29b} was heated at 120°C for 0.5 h, after which the reaction mixture was cooled to room temperature and extracted with diethyl ether. Recrystallization from hexane gave pure **16** or **17**.

Cis-NPF₂(NSOPh)₂ (**16**): yield 5.5 g (15.1 mmol, 85%) of white crystals, mp 81.5–82.0°C. Anal. calc. for N₃PS₂C₁₂H₁₀F₂O₂: C, 39.89; H, 2.79; N, 11.64; S, 17.71; found: C, 40.02; H, 2.75; N, 11.85; S, 17.93. Mass spectrum: *m/e* 361 (M⁺, 100%).

Trans-NPF₂(NSOPh)₂ (**17**): yield 5.8 g (16.1 mmol, 90%) of white crystals mp 77.5–78.5°C. Anal. calc. for N₃PS₂C₁₂H₁₀F₂O₂: C, 39.89; H, 2.79; N, 11.64; S, 17.71; found: C, 39.60; H, 2.74; N, 11.70; S, 17.80. Mass spectrum: *m/e* 361 (M⁺, 100%).

Preparation of (NPF₂)₂NSOPh (18). A mixture of 5.0 g (13.5 mmol) of **9** and 7.0 g of a KSO₂F (55.6 mmol)/KF (3.6 mmol) mixture^{29b} was heated at 120°C for 0.5 h, after which the reaction mixture was cooled to room temperature and extracted with diethyl ether. Sublimation (80°C at 1.0 mm Hg) gave 3.3 g (10.8 mmol, 80%) of white crystals of **18** with mp 85.5–86°C. Anal. calc. for N₃P₂SC₆H₅F₄O: C, 23.62; H, 1.65; N, 13.77; S, 10.51; found: C, 23.46; H, 1.65; N, 13.68; S, 10.50. Mass spectrum: *m/e* 305 (M⁺, 100%).

Preparation of gem-NPCl₂NPF₂NSOPh (19). A mixture of 4.0 g (10.8 mmol) of **9** and 3.2 g of a

KSO₂F (21.6 mmol)/KF (9.3 mmol) mixture^{29a} in 50 ml of benzene was stirred at reflux temperature for 5 h, after which the reaction mixture was cooled and filtered. Removal of the solvent by evaporation gave 3.3 g of a thick oil containing **9**, **18** and **19** (according to a ³¹P NMR spectrum). Separation by means of HPLC (hexane was used as eluent) gave three fractions: 1.2 g (3.2 mmol, 30%) of the starting material, 1.0 g (3.2 mmol, 30%) of **18** and 0.6 g (1.8 mmol, 16%) of **19**. Recrystallization of the third fraction from hexane afforded 0.5 g (1.5 mmol, 14%) of pure **19** as white crystals, mp 80.0–81.5°C. Anal. calc. for N₃P₂SC₆H₃F₂Cl₂ O: C, 21.37; H, 1.50; N, 12.47; S, 9.49; Cl, 20.76; found: C, 21.06; H, 1.60; N, 12.68; S, 9.55; Cl 20.80. Mass spectrum: m/e 337 (M⁺ ³⁵Cl, 100%).

Reaction of 17 with one equivalent of PhMgBr. To a solution of 1.5 g (4.2 mmol) of **17** in 75 ml of THF was added 4.7 ml of a 0.9 n solution of PhMgBr in diethyl ether (4.2 mmol). The mixture was stirred at reflux for one week. After removal of the solvent the crude reaction mixture was dissolved in CH₂Cl₂ and filtered through silicagel. HPLC using CH₂Cl₂ as eluent gave 0.32 g (0.9 mmol, 21%) of the starting material, followed by (1 α ,3 β ,5 α)-NPFPh(NSOPh)₂ (**20**). Recrystallization from a 20:1 mixture of hexane and THF gave 0.80 g (1.9 mmol, 46%) of **20** as white crystals, mp 100.0–101.5°C. Anal. calc. for N₃PS₂C₁₈H₁₅FO₂: C, 51.55; H, 3.60; N, 10.02; S, 15.29; found: C, 51.79; H, 3.59; N, 10.17; S, 15.44. Mass spectrum: m/e 419 (M⁺, 100%).

The third HPLC fraction consisted of *trans*-NPPH₂(NSOPh)₂ (**21**). Recrystallization by adding diethyl ether to a solution of **21** in chloroform gave 0.07 g (0.1 mmol, 3%) of **21** as white crystals, mp 162–163.5°C. Anal. calc. for N₃PS₂C₂₄H₂₀O₂: C, 60.36; H, 4.22; N, 8.80; S, 13.43; found: C, 60.02; H, 4.23; N, 8.87; S, 13.36. Mass spectrum: m/e 477 (M⁺, 100%).

Reaction of 17 with 1.5 equivalent of ^tBuLi. A solution of 7.0 mmol of ^tBuLi in 15 ml of pentane was added dropwise to a stirred solution of 1.7 g (4.7 mmol) of **17** in 175 ml of diethyl ether at –90°C. The reaction mixture was allowed to warm to room temperature over a period of 8 h. Stirring was continued for 17 h at room temperature. After filtration the solvent was removed. The remainder was dissolved in 50 ml of CH₂Cl₂ and filtrated over silicagel. Evaporation of the solvent gave the crude reaction mixture, consisting of (1 α ,3 β ,5 α)-NPF^tBu(NSOPh)₂ (**22**) and **17** (ratio 3:2, according to ¹H NMR). Twofold recrystallization from a hexane/THF mixture (5:1) gave 0.22 g (0.6 mmol, 13%) of pure **22** as white needles, mp 157.5–158.0°C. Anal. calc. for N₃PS₂C₁₆H₁₉FO₂: C, 48.11; H, 4.79; N, 10.52; S, 16.05; found: C, 48.06; H, 4.85; N, 10.46; S, 16.03. Mass spectrum: m/e 399 (M⁺, 27%).

X-ray analysis of 16. Suitable crystals were obtained by recrystallization from a mixture of hexane and THF. A transparent colorless, block shaped crystal, 0.05 × 0.10 × 0.20 mm, was glued on a top of a glass fiber and mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a Micro VAX-2000 computer. Unit cell dimensions and their standard deviations were derived from the angular settings of 21 reflections in the range 8.18° < θ < 13.69°. The unit cell was identified as monoclinic. Reduced cell calculations did not indicate any higher lattice symmetry.³² The intensities of the three standard reflections, monitored every 2 h of X-ray exposure time, showed no greater fluctuations during data collection than those expected from Poisson statistics. Intensity data were corrected for Lorentz and polarization effects and scale variation. Correction for absorption was judged to be not necessary in view of the observed small intensity variation for a 360 ψ -scan of reflection (310) close to axial. Variance $\sigma^2(I)$ was calculated based on counting statistics and the term (P^2I^2) where P (=0.040) is the instability constant as derived from the excess variance in the reference reflections.³³ Equivalent reflections were averaged and stated observed if satisfying the $I > 2.5 \sigma(I)$ criterion of observability. Pertinent numerical data on the structure determination are given in Table II.

The structure was solved by direct methods (GENTAN).³⁴ Refinement on F was carried out by block-diagonal least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map. Final refinement on F was carried out by full matrix least-squares techniques with anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic thermal displacement parameters for the hydrogen atoms. Convergence was reached at R = 0.034. A final difference Fourier map did not show any significant residual features. Final fractional atomic coordinates and equivalent isotropic thermal displacement parameters for the non-hydrogen atoms are given in Table III. Molecular geometry data are collected in Table IV. Neutral atom scattering factors³⁵ were used with anomalous dispersion factors,³⁶ being applied to the non-hydrogen atoms. All calculations were performed on the CDC-Cyber 170/760 computer at the University of Groningen with the program packages XTAL,³⁴ EUCLID³⁷ and a locally modified version of the program PLUTO.³⁸ Tables of hydrogen atom positions, thermal displacement parameters, comprehensive lists of bond distances and angles, Tables of F_o, F_c and $\sigma(F)$ and ORTEP plot³⁹ have been deposited with the Cambridge Crystallographic Data Centre.

TABLE II
Crystal data and details of the structure
determination

Chemical Formula	C ₁₂ H ₁₀ F ₂ N ₃ O ₂ PS ₂
Formula weight, g.mol	361.32
Space group	P2 ₁ /n
a, Å	13.665(7)
b, Å	10.676(1)
c, Å	9.897(3)
β, deg	90.55(3)
V, Å ³	1443.8(9)
Z	4
T, K	130
λ, Å	0.71073
D _{calc} , g.cm ⁻³	1.662
F(000), electrons	736
μ(MoKα), cm ⁻¹	4.9
number of reflections	
total, unique	3093, 2809
observed (I > 2.5 σ(I))	2220
number of refined parameters	230
final agreement factors	
R = Σ(F _o - F _c)/Σ F _o	0.034
wR = [Σw(F _o - F _c) ² /Σw F _o ²] ^{1/2}	0.043
weighting scheme	1/σ ² (F)

RESULTS AND DISCUSSION

Fluorination

The general reaction procedure for fluorination involves heating of a well-ground mixture of the ring system NPCl₂(NSOX)₂ or (NPCl₂)₂NSOX (X = F, Cl or Ph) and an appropriate amount of KSO₂F above the melting temperature of the ring system concerned in an atmosphere of dry nitrogen until the evolution of SO₂ ceases. The products can be isolated from the reaction mixture by distillation (X = F, Cl) or extraction (X = Ph).

By heating *cis*-NPCl₂(NSOCl)₂ (**2**) with one equivalent of KSO₂F a mixture of two isomers of NPFCl(NSOCl)₂ (**10**, **11**, ratio 3:1) was obtained together with the starting material and the difluoro derivative *cis*-NPF₂(NSOCl)₂ (**12**). In accordance with a preferential attack at the oxygen side of the ring plane²³ the 1α,3α,5α-configuration (Scheme 1) is tentatively ascribed to the most abundant isomer. The moisture sensitivity of the fluoro compounds prohibited separation of the compounds by HPLC. Compound **12** could be isolated from the reaction mixture of **2** and two

TABLE III

Final fractional atomic coordinates and equivalent thermal displacement parameters for non-H atoms with their estimated standard deviations in parentheses

Atom	x	y	z	U_{eq}^a (Å ²)
P(1)	0.06631(5)	0.40853(6)	0.34049(6)	0.0164(2)
S(1)	0.01708(4)	0.22218(5)	0.52064(6)	0.0141(2)
S(2)	0.12334(5)	0.16949(6)	0.28926(6)	0.0159(2)
F(1)	0.1436(1)	0.5091(1)	0.3693(2)	0.0255(5)
F(2)	-0.0083(1)	0.4885(1)	0.2637(1)	0.0256(5)
O(1)	-0.0774(1)	0.1864(2)	0.5680(2)	0.0196(5)
O(2)	0.1163(1)	0.0818(2)	0.1802(2)	0.0225(5)
N(1)	0.0227(2)	0.3637(2)	0.4780(2)	0.0166(6)
N(2)	0.0473(2)	0.1305(2)	0.4015(2)	0.0160(6)
N(3)	0.1082(2)	0.3083(2)	0.2401(2)	0.0186(6)
C(1)	0.1026(2)	0.2066(2)	0.6555(2)	0.0153(6)
C(2)	0.0935(2)	0.1016(2)	0.7383(2)	0.0183(6)
C(3)	0.1590(2)	0.0868(2)	0.8451(3)	0.0230(6)
C(4)	0.2320(2)	0.1745(3)	0.8688(3)	0.0240(6)
C(5)	0.2414(2)	0.2769(2)	0.7846(3)	0.0250(6)
C(6)	0.1761(2)	0.2946(2)	0.6773(2)	0.0197(6)
C(7)	0.2406(2)	0.1637(2)	0.3651(2)	0.0163(6)
C(8)	0.3058(2)	0.2632(2)	0.3527(2)	0.0210(6)
C(9)	0.3951(2)	0.2571(3)	0.4192(3)	0.0260(8)
C(10)	0.4195(2)	0.1521(3)	0.4956(3)	0.0263(8)
C(11)	0.3544(2)	0.0531(3)	0.5062(3)	0.0240(6)
C(12)	0.2638(2)	0.0578(2)	0.4412(2)	0.0203(6)

$$^a U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_i \cdot a_j$$

equivalents of KSO₂F in a yield of 22%. Attempts to improve the conversion by applying an excess of KSO₂F failed. A higher reaction temperature (170°C) led to the formation of both *cis*- and *trans*-NPF₂(NSOCl)₂ (**12**, **13**). The *cis-trans* isomerization probably proceeds via a S_N1-like mechanism in the presence of KCl, formed during the fluorinating process. Contrary to its chloro analogue **2** *cis*-NPCl₂(NSOCl)₂ (**4**) decomposed during reaction with KSO₂F. Heating (NPCl₂)₂NSOCl (**3**) or (NPCl₂)₂NSOCl (**6**) with four equivalents of KSO₂F afforded (NPF₂)₂NSOCl (**14**) and (NPF₂)₂NSOCl (**15**), respectively. Again low conversions (<50%) were observed. Compound **15** sublimes at room temperature, which prevents elemental analysis. The structure was derived from mass spectral and ³¹P NMR data. Reactions of *cis*- and *trans*-NPCl₂(NSOCl)₂ (**7**, **8**) with two equivalents of KSO₂F provided the corresponding fluoro analogues **16** and **17** in high yields (80–90%). No mono substituted derivatives were detected, even when using only one equivalent of KSO₂F. Also

TABLE IV

Selected data on the geometry of **16**. Standard deviations in the last decimal place are given in parentheses.

Interatomic Distances (Å)		Bond angles (°)	
S(1) - O(1)	1.430(2)	O(1) - S(1) - C(1)	108.6(1)
S(1) - N(1)	1.571(2)	O(2) - S(2) - C(7)	110.6(1)
S(1) - N(2)	1.590(2)	F(1) - P(1) - F(2)	99.02(8)
S(2) - O(2)	1.431(2)	N(1) - S(1) - N(2)	112.3(1)
S(2) - N(2)	1.584(3)	N(2) - S(2) - N(3)	112.3(1)
S(2) - N(3)	1.573(2)	N(1) - P(1) - N(3)	119.0(1)
P(1) - F(1)	1.531(2)	S(1) - N(1) - P(1)	123.2(1)
P(1) - F(2)	1.527(2)	S(1) - N(2) - S(2)	122.3(1)
P(1) - N(1)	1.566(2)	S(2) - N(3) - P(1)	119.6(1)
P(1) - N(3)	1.572(2)		
(C - C) mean value	1.390(1)		

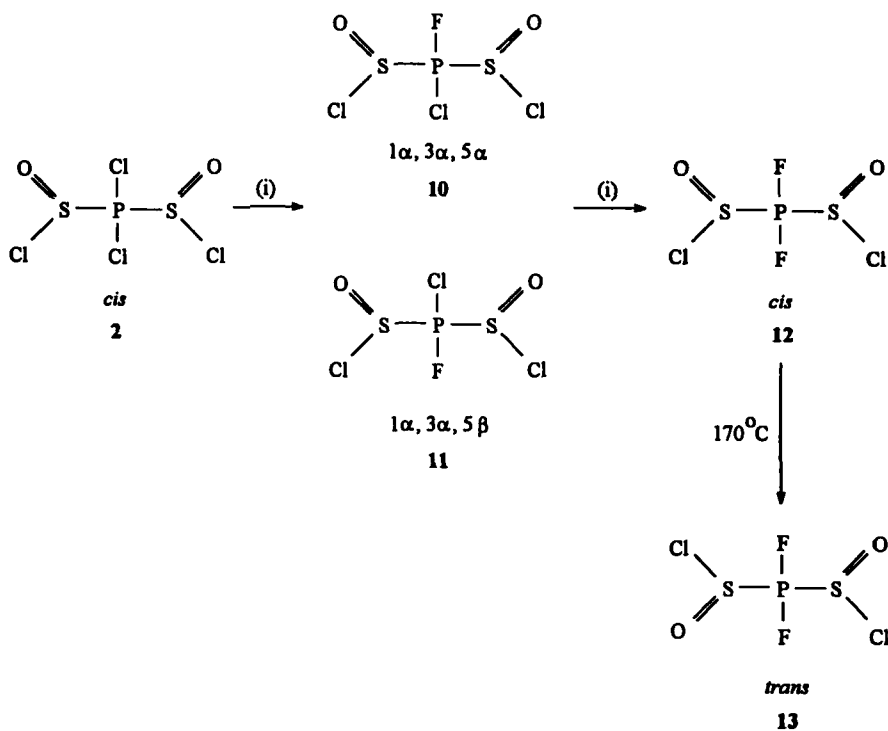
(NPCl₂)₂NSOPh (**9**) proved to give a high yield of (NPF₂)₂NSOPh (**15**) when treated with KSO₂F. Reaction of **9** with two equivalents of KSO₂F in benzene at reflux temperature afforded *gem*-NPCl₂NPF₂NSOPh (**19**), which could be isolated from the reaction mixture by means of HPLC.

According to the results described above fluorination by KSO₂F preferentially leads to fully substituted derivatives via a geminal substitution pattern.

Under the current reaction conditions low conversions are characteristic for the cyclothiaphosphazenes NPCl₂(NSOX)₂ and (NPCl₂)₂NSOX (X = F, Cl), whereas the phenylated systems NPCl₂(NSOX)₂ and (NPCl₂)₂NSOX (X = Ph) show almost complete conversions. This may be explained by the fact that the phenylated systems form homogeneous reaction mixtures with KSO₂F at the appropriate reaction temperature in contradistinction to the halocyclothiaphosphazenes.

*Reactivity of trans-NPF₂(NSOPh)₂ (**17**) Towards Grignard and Organolithium Reagents*

A number of reactions were carried out with **17** in order to get an insight into its reactivity towards RMgX and RLi (R = Me, ^tBu and Ph). The experimental data (compiled in Table V) show that **17** is not very reactive in substitution reactions with Grignard reagents, except for PhMgBr which gives the phenyl substituted derivatives in moderate to good yields. This is in line with the behavior of (NPF₂)₃, viz. substitution reactions with aryl Grignard reagents are successful.^{40,41} Compound **17** seems to be somewhat less reactive than (NPF₂)₃. The latter compound consumes one equivalent of PhMgBr completely in two days,⁴⁰ whereas **17** needs a reaction time of a week. Probably, steric hindrance caused by the phenyl groups is responsible for the low reactivity. Steric hindrance also becomes manifest for the reaction with ^tBuLi. Whereas (NPF₂)₃ is completely consumed by one equivalent of the alkyl-lithium reagent to give N₃P₃F₃^tBu in 60% yield,⁴² **17** yields a mixture containing the starting material and (1 α ,3 β ,5 α)-NPF^tBu(NSOPh)₂ (**22**) (ratio 6:1; total yield of cy-



Scheme 1

clic material 50%) under the same reaction conditions. Conversion is increased on addition of more than one equivalent of $t\text{BuLi}$, but the yield becomes very low. A similar observation was made for $(\text{NPF}_2)_3$.⁴²

With MeLi some monosubstituted material could be detected (^1H , ^{31}P NMR), but ring degradation appears to be the main reaction as a result of formation of carbanions by deprotonation of the methyl group.^{42,43} Treatment of **17** with PhLi gives mono and disubstituted products, but yields are lower than those obtained with PhMgBr . As observed for Grignard reagents compound **17** exhibits a lower reactivity towards PhLi than $(\text{NPF}_2)_3$. In the latter case mono and disubstituted products are obtained in yields of 60–70%.⁴⁴

NMR Spectra

The NMR spectra of most compounds could be interpreted by a first-order treatment, however assignments of chemical shifts and coupling constants were verified by spectrum simulation (Table 1). The spectra of **14**, **15** and **18** did not allow a direct analysis, but were simulated by varying NMR data from "simple cases." Data found by simulation are not included in Table 1.

The ^{31}P NMR spectra of both **12** and **16** (ABX spin systems) consist of two doublets as the fluorine ligands are chemically non-equivalent. The ^{19}F NMR spectra show two doublets for each fluorine atom. *Gem*- $\text{NPCl}_2\text{NPF}_2\text{NSOPh}$ (**19**) represents an ABXY spin system. Its ^{31}P NMR spectrum consists of a doublet (Y-part) and a

TABLE V
Experimental data^a of reactions of **17** with RMgX and RLi

Reagent (number of equivs.)	Solvent	Product Ratio ^b			Total yield (%) of cyclic material
		PF ₂	PFR	PR ₂	
MeMgI (2)	Et ₂ O	100	-	-	100
	THF	90	10	-	80
^t BuMgCl (2)	Et ₂ O	100	-	-	100
	THF	100	-	-	100
PhMgBr (1)	THF	30	65	5	70
	THF	-	85	15	65
	THF	-	30	70	45
MeLi (1)	Et ₂ O	90	10	-	40
^t BuLi (1)	Et ₂ O	60	10	-	50
	Et ₂ O	40	60	-	30
	Et ₂ O	-	100	-	8
PhLi (1)	Et ₂ O	10	90	-	50
	Et ₂ O	-	75	25	40

^a See also Preparation.

^b Estimated from NMR and/or HPLC experiments.

triplet of doublets (X-part). The triplet form of the X-part implicates that $^1J_{AX}$ and $^1J_{BX}$ are almost equal. Spectrum simulation resulted in an optimum fit by taking $^1J_{AX}$ and $^1J_{BX}$ positive and $^2J_{XY}$ negative. (NPF₂)₂NSOPh (**18**) represents an AA'BB'XX' spin system. The chemical shifts (experimental) are given in Table I. Simulation of the ³¹P NMR spectrum was successful, when applying several multiple-bond FF coupling constants. However, simulation of the ¹⁹F NMR spectrum did not lead to a satisfactory result.

Structure of *cis*-NPF₂(NSOPh)₂ (**16**)

The molecular structure and atomic numbering scheme of the molecule of **16** are illustrated in Figure 1, selected bond lengths and angles are given in Table IV. The asymmetric unit contains one independent molecule with no atom setting at special position. The conformation of the inorganic ring resembles that of a half-chair⁴⁵ with torsion angles ranging from -41.2(2) to 30.0(2)° and lowest asymmetry parameter ΔC_s [N(1)] = 13.5(2)°. Puckering parameters⁴⁶ are Q = 0.319(2) Å, θ = 51.9(4)° and φ = 266.1(4)°. The atoms S(2) and N(2) deviate significantly from the least-squares plane through P(1), N(1), S(1), N(2), S(2) and N(3) with distances of 0.209(4) and -0.204(5) Å, respectively. The asymmetric feature of the molecule is also reflected by the position of the phenyl groups, which are positioned under an angle of 17.7(1)° to each other. The differences between the PN and SN bond lengths border to significance, which is in line with the small difference in electronegativity of the SOPh

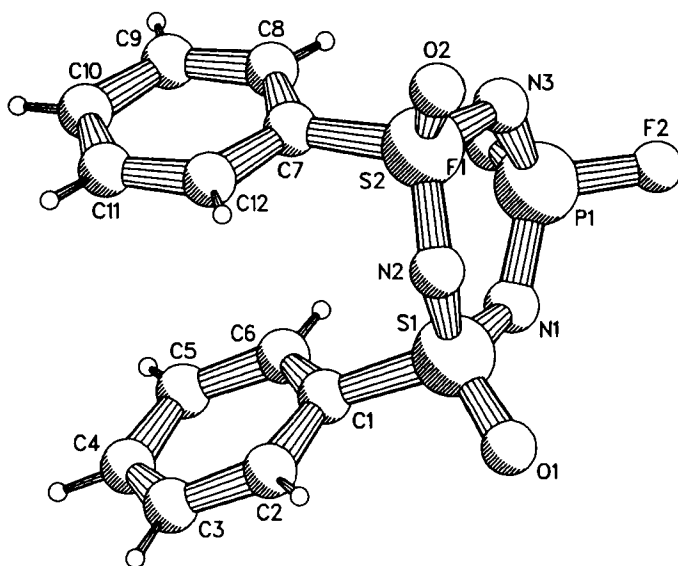


FIGURE 1 Molecular structure (Pluto drawing) and adopted numbering scheme of *cis*-NPF₂(NSOPh)₂ (**16**).

and PF₂ centers.⁴⁷ The CC bond lengths in the phenyl rings are equal within the experimental error with a mean value of 1.390(1) Å. However, three sets of CCC bond angles can be discerned, one for the endocyclic angles at C(1) and C(7) with a mean value of 121.5(2)°, one for the angles at C(2), C(6), C(8) and C(12) with a mean value of 118.7(1)° and one for the angles at C(3), C(4), C(5), C(9), C(10) and C(11) with a mean value of 120.4(1)°.

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