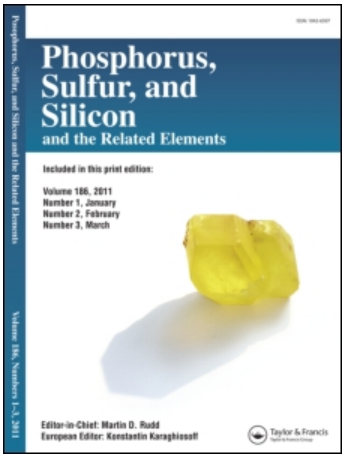

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FLUORINATED CYCLOTHIAPHOSPHAZENES: SYNTHESIS, STRUCTURE AND REACTIVITY

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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 $NPCl_2(NSOX)_2$ (X = Cl, Ph) and $(NPCl_2)_2NSOX$ (X = Cl, F, Ph) with KSO_2F in bulk leads to fluorination at the phosphorus centers. The substitution reaction follows a geminal pattern. Reactions of *trans*-$NPF_2(NSOPh)_2$ with Grignard reagents RMgX (R = Me, ^{t}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*-$NPF_2(NSOPh)_2$ are monoclinic, space group $P2_1/n$, with a = 13.665(7) Å, b = 10.676(1) Å, c = 9.897(3) Å, β = 90.55(3)°, V = 1443.8(9) Å^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) Å.

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 KF/18-crown-6[19] have been applied to convert $(NPCl_2)_3$ (**1**) into compounds $N_3P_3F_{6-n}Cl_n$ (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*-$NPCl_2(NSOCl)_2$ (**2**) with AgF_2 or SbF_3 and $(NPCl_2)_2NSOCl$ (**3**) with AgF_2 yielded *cis* and *trans*-$NPCl_2(NSOF)_2$ (**4**, **5**) and $(NPCl_2)_2NSOF$ (**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 $NPCl_2(NSOX)_2$ or $(NPCl_2)_2NSOX$ (X = F, Cl or Ph) with NaF or KF/18-crown-6 in MeCN only gave traces of fluorinated derivatives (X = Ph), whereas hydrolysis phenomena were observed for X = F or Cl.[24]

In the present study we report reactions of compounds $NPCl_2(NSOX)_2$ (X = Cl, Ph) and $(NPCl_2)_2NSOX$ (X = F, Cl, Ph) with KSO_2F as fluorinating agent. Furthermore reactions of *trans*-$NPF_2(NSOPh)_2$ 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*-$NPF_2(NSOPh)_2$ 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*-$NPCl_2(NSOCl)_2$ (**2**),[26] $(NPCl_2)_2NSOCl$ (**3**),[27,28] *cis* and *trans*-$NPCl_2(NSOF)_2$ (**4**, **5**),[20,21] $(NPCl_2)_2NSOF$ (**6**),[22] *cis*- and *trans*-$NPCl_2(NSOPh)_2$ (**7**, **8**),[25] $(NPCl_2)_2NSOPh$ (**9**),[25] and KSO_2F[29] 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] ^{t}BuLi was obtained commercially from Janssen. LiO^iPr was prepared by stirring ^{t}BuLi and ^{i}PrOH 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). ^{31}P and ^{19}F NMR spectra (in $CDCl_3$) were recorded on a Nicolet NT 200 spectrometer operating at 81 MHz (for ^{31}P NMR) or 188.2 MHz (for ^{19}F NMR) using $(NPCl_2)_3$ (19.9 ppm, solution in $CDCl_3$) and $CFCl_3$ (0 ppm, solution in $CDCl_3$), 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* KSO_2F. A mixture of 2.0 g (6.4 mmol) of **2** and 0.94 g of a KSO_2F (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 ^{31}P NMR and mass spectrometry the distillate contained (1α,3α,5α)-NPClF$(NSOCl)_2$ (**10**), (1α,3α,5β)-NPClF$(NSOCl)_2$ (**11**), and *cis*-$NPF_2(NSOCl)_2$ (**12**) [for nomenclature see Reference 31]. Efforts to separate the reaction products were not successful.

Preparation of cis-$NPF_2(NSOCl)_2$ (**12**). A mixture of 2.0 g (6.4 mmol) of **2** and 1.88 g of a KSO_2F (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 $N_3PS_2F_2Cl_2O_2$: N, 15.11; S, 23.06; Cl, 25.50; found: 14.94; S, 23.26; Cl, 24.93. Mass spectrum: m/e 242 (M^+ ^{35}Cl – ^{35}Cl, 100%).

When the same reaction procedure was carried out at 170°C, the distillate also contained *trans*-$NPF_2(NSOCl)_2$ (**13**) (based on ^{31}P NMR).

Attempted preparation of $NPF_2(NSOF)_2$. A mixture of 1.0 g (3.6 mmol) of **4** and 1.6 g of a KSO_2F (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 $(NPF_2)_2NSOCl$ (**14**). A mixture of 2.0 g (6.1 mmol) of **3** and 3.5 g of a KSO_2F (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 $N_3P_2SF_4ClO$: 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^+ ^{35}Cl – ^{35}Cl, 100%).

Preparation of $(NPF_2)_2NSOF$ (**15**). A mixture of 1.9 g (6.1 mmol) of **6** and 3.6 g of a KSO_2F (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-$NPF_2(NSOPh)_2$ (**16**, **17**). A mixture of 7.0 g (17.8 mmol) of **7** (or **8**) and

TABLE I

^{31}P and ^{19}F NMR data[a] of compounds prepared

	δP(X)	δP(Y)	δF(A)	δF(B)	δF(C)	$^1J_{AX}$	$^1J_{BX}$	$^2J_{AB}$
(1α,3α,5α)-$NPClF(NSOCl)_2$ (**10**)[b]	18.9					1037		
(1α,3α,5β)-$NPClF(NSOCl)_2$ (**11**)[b]	19.4					1080		
cis-$NPF_2(NSOCl)_2$ (**12**)	-1.4		-74.8	-79.9		984	959	95
trans-$NPF_2(NSOCl)_2$ (**13**)[b]	0.2					978		
$(NPF_2)_2NSOCl$ (**14**)[c]	4.2							
$(NPF_2)_2NSOF$ (**15**)[d]	4.4							
cis-$NPF_2(NSOPh)_2$ (**16**)	1.8		-69.4	-76.3		954	931	93
trans-$NPF_2(NSOPh)_2$ (**17**)	-1.0		-72.2			940		
$(NPF_2)_2NSOPh$ (**18**)[c]	3.5							
gem-$NPCl_2NPF_2NSOPh$ (**19**)	-2.4	26.5	-69.2	-72.0		938	934	90
(1α,3β,5α)-$NPFPh(NSOPh)_2$ (**20**)	20.9		-54.9			1028		
trans-$NPPh_2(NSOPh)_2$ (**21**)	17.4							
(1α,3β,5α)-$NPF^tBu(NSOPh)_2$ (**22**)	41.0		-75.4			1091		

[a] Chemical shifts in ppm; coupling constants in Hz.

[b] Compound not isolated, data restricted to ^{31}P NMR.

[c] AA'BB'XX' spin system with δP(X) = δP(X'), direct analysis of ^{19}F NMR spectrum not possible.

[d] AA'BB'CXX' spin system with δP(X) = δP(X'), direct analysis of ^{19}F NMR spectrum not possible.

4.5 g of a KSO_2F (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-$NPF_2(NSOPh)_2$ (**16**): yield 5.5 g (15.1 mmol, 85%) of white crystals, mp 81.5–82.0°C. Anal. calc. for $N_3PS_2C_{12}H_{10}F_2O_2$: 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-$NPF_2(NSOPh)_2$ (**17**): yield 5.8 g (16.1 mmol, 90%) of white crystals mp 77.5–78.5°C. Anal. calc. for $N_3PS_2C_{12}H_{10}F_2O_2$: 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 $(NPF_2)_2$ NSOPh (**18**). A mixture of 5.0 g (13.5 mmol) of **9** and 7.0 g of a KSO_2F (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 $N_3P_2SC_6H_5F_4O$: 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-$NPCl_2NPF_2NSOPh$ (**19**). A mixture of 4.0 g (10.8 mmol) of **9** and 3.2 g of a

KSO_2F (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 ^{31}P 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 $N_3P_2SC_6H_5F_2Cl_2O$: 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^+ ^{35}Cl, 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 CH_2Cl_2 and filtered through silicagel. HPLC using CH_2Cl_2 as eluent gave 0.32 g (0.9 mmol, 21%) of the starting material, followed by (1α,3β,5α)-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 $N_3PS_2C_{18}H_{15}FO_2$: 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*-$NPPh_2(NSOPh)_2$ (**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 $N_3PS_2C_{24}H_{20}O_2$: 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 'BuLi.* A solution of 7.0 mmol of 'BuLi 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 CH_2Cl_2 and filtrated over silicagel. Evaporation of the solvent gave the crude reaction mixture, consisting of (1α,3β,5α)-NPF'Bu$(NSOPh)_2$ (**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 $N_3PS_2C_{16}H_{19}FO_2$: 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 $8.18° < \theta < 13.69°$. 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 factors[35] 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] EUCLID[37] 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 plot[39] have been deposited with the Cambridge Crystallographic Data Centre.

TABLE II
Crystal data and details of the structure determination

Chemical Formula	$C_{12}H_{10}F_2N_3O_2PS_2$
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)
ß, 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 ($I > 2.5\ \sigma(I)$)	2220
number of refined parameters	230
final agreement factors	
$R = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.034
$wR = [\Sigma w(\|F_o\| - \|F_c\|)^2 / \Sigma\|wF_o\|^2]^{1/2}$	0.043
weighting scheme	$1/\sigma^2(F)$

RESULTS AND DISCUSSION

Fluorination

The general reaction procedure for fluorination involves heating of a well-ground mixture of the ring system $NPCl_2(NSOX)_2$ or $(NPCl_2)_2NSOX$ (X = F, Cl or Ph) and an appropriate amount of KSO_2F above the melting temperature of the ring system concerned in an atmosphere of dry nitrogen until the evolution of SO_2 ceases. The products can be isolated from the reaction mixture by distillation (X = F, Cl) or extraction (X = Ph).

By heating *cis*-$NPCl_2(NSOCl)_2$ (**2**) with one equivalent of KSO_2F 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*-$NPF_2(NSOCl)_2$ (**12**). In accordance with a preferential attack at the oxygen side of the ring plane[23] 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}* (Å)
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)

* $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$

equivalents of KSO_2F in a yield of 22%. Attempts to improve the conversion by applying an excess of KSO_2F failed. A higher reaction temperature (170°C) led to the formation of both *cis*- and *trans*-$NPF_2(NSOCl)_2$ (**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*-$NPCl_2(NSOF)_2$ (**4**) decomposed during reaction with KSO_2F. Heating $(NPCl_2)_2NSOCl$ (**3**) or $(NPCl_2)_2NSOF$ (**6**) with four equivalents of KSO_2F afforded $(NPF_2)_2NSOCl$ (**14**) and $(NPF_2)_2NSOF$ (**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 ^{31}P NMR data. Reactions of *cis*- and *trans*-$NPCl_2(NSOPh)_2$ (**7**, **8**) with two equivalents of KSO_2F 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 KSO_2F. 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)		
$(C\text{-}C)_{\text{mean value}}$	1.390(1)		

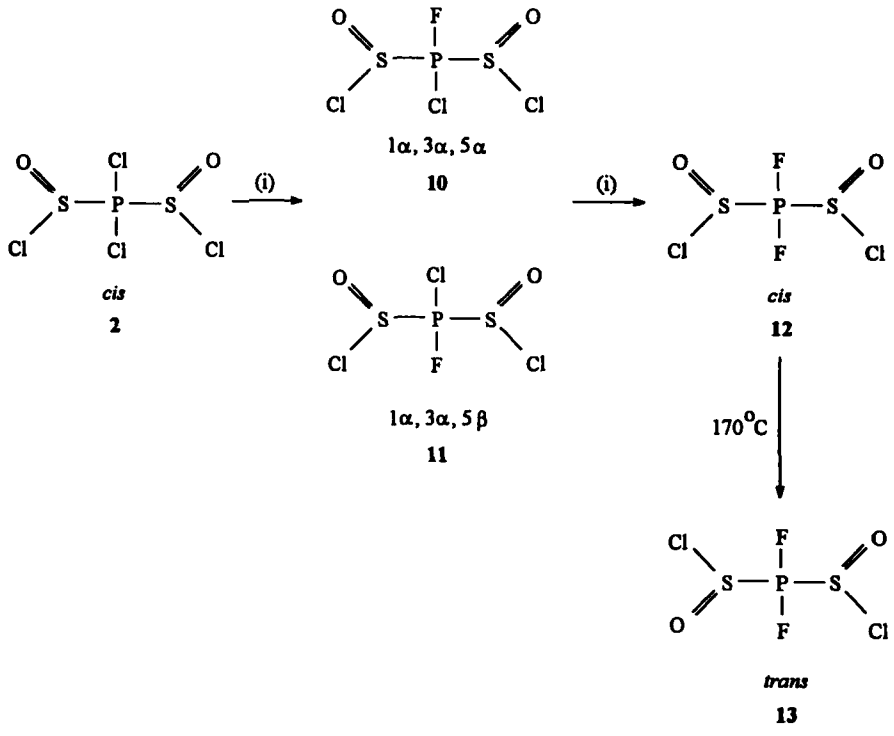
$(NPCl_2)_2NSOPh$ (**9**) proved to give a high yield of $(NPF_2)_2NSOPh$ (**15**) when treated with KSO_2F. Reaction of **9** with two equivalents of KSO_2F in benzene at reflux temperature afforded *gem*-$NPCl_2NPF_2NSOPh$ (**19**), which could be isolated from the reaction mixture by means of HPLC.

According to the results described above fluorination by KSO_2F preferentially leads to fully substituted derivatives via a geminal substitution pattern.

Under the current reaction conditions low conversions are characteristic for the cyclothiaphosphazenes $NPCl_2(NSOX)_2$ and $(NPCl_2)_2NSOX$ (X = F, Cl), whereas the phenylated systems $NPCl_2(NSOX)_2$ and $(NPCl_2)_2NSOX$ (X = Ph) show almost complete conversions. This may be explained by the fact that the phenylated systems form homogeneous reaction mixtures with KSO_2F at the appropriate reaction temperature in contradistinction to the halocyclothiaphosphazenes.

Reactivity of trans-$NPF_2(NSOPh)_2$ (**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, ^{t}Bu 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 $(NPF_2)_3$, viz. substitution reactions with aryl Grignard reagents are successful.[40,41] Compound **17** seems to be somewhat less reactive than $(NPF_2)_3$. 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 ^{t}BuLi. Whereas $(NPF_2)_3$ is completely consumed by one equivalent of the alkyllithium reagent to give $N_3P_3F_5{}^t$Bu in 60% yield,[42] **17** yields a mixture containing the starting material and (1α,3β,5α)-$NPF^tBu(NSOPh)_2$ (**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 'BuLi, but the yield becomes very low. A similar observation was made for $(NPF_2)_3$.[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 $(NPF_2)_3$. 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*-$NPCl_2NPF_2NSOPh$ (**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] PF_2	PFR	PR_2	Total yield (%) of cyclic material
MeMgI	(2)	Et_2O	100	-	-	100
	(2)	THF	90	10	-	80
^{t}BuMgCl	(2)	Et_2O	100	-	-	100
	(2)	THF	100	-	-	100
PhMgBr	(1)	THF	30	65	5	70
	(2)	THF	-	85	15	65
	(5)	THF	-	30	70	45
MeLi	(1)	Et_2O	90	10	-	40
^{t}BuLi	(1)	Et_2O	60	10	-	50
	(1.5)	Et_2O	40	60	-	30
	(3)	Et_2O	-	100	-	8
PhLi	(1)	Et_2O	10	90	-	50
	(1.5)	Et_2O	-	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. $(NPF_2)_2NSOPh$ (**18**) represents an AA'BB'XX' spin system. The chemical shifts (experimental) are given in Table I. Simulation of the ^{31}P NMR spectrum was successful, when applying several multiple-bond FF coupling constants. However, simulation of the ^{19}F NMR spectrum did not lead to a satisfactory result.

Structure of cis-$NPF_2(NSOPh)_2$ (**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-chair[45] with torsion angles ranging from −41.2(2) to 30.0(2)° and lowest asymmetry parameter ΔC_s [N(1)] = 13.5(2)°. Puckering parameters[46] 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

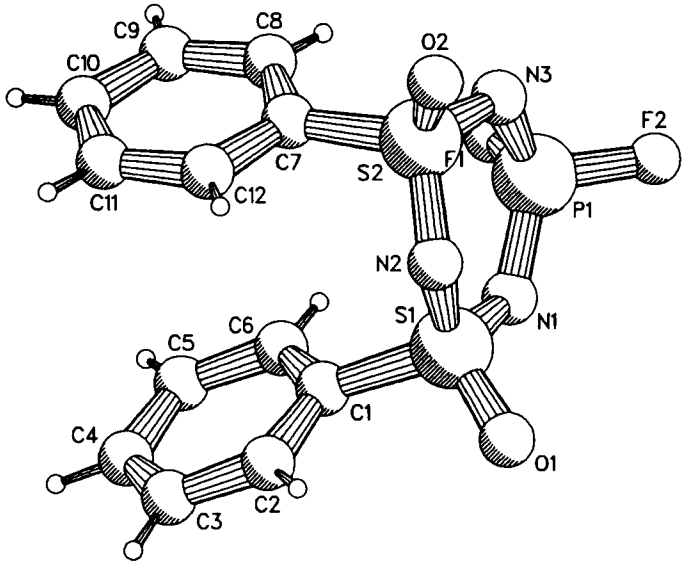


FIGURE 1 Molecular structure (Pluto drawing) and adopted numbering scheme of *cis*-$NPF_2(NSOPh)_2$ (**16**).

and PF_2 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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