Reactivity of a Cyclothiaphosphazene towards Grignard Reagents. Crystal Structure of the 1:1 Adduct of the Bi(cyclothiaphosphazene)$[NPMe(NSOPh)_2]_2$ and Benzene†

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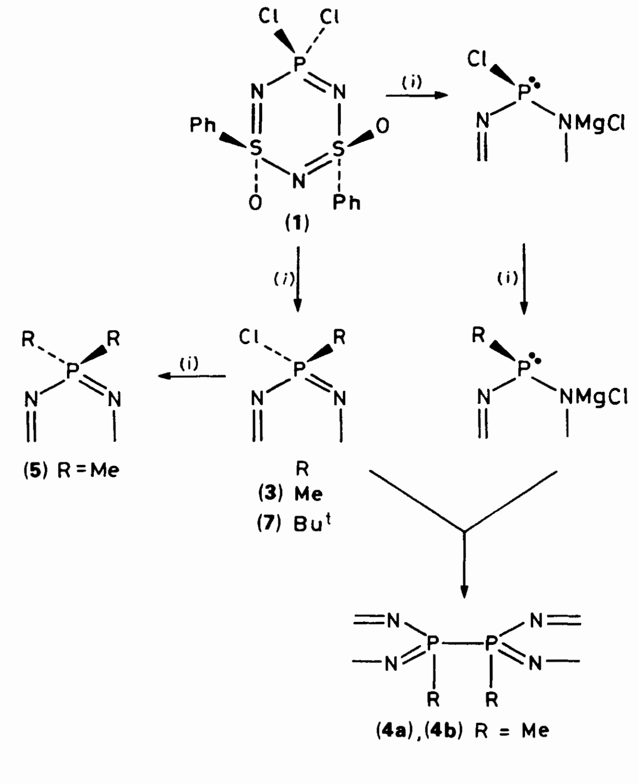
Reactions of the ring system *trans*-$NPCl_2(NSOPh)_2$ (**1**) with MgMeCl and an excess of propan-2-ol in tetrahydrofuran show that chlorine substitution occurs both along a nucleophilic substitution pattern and a metal–halogen exchange process, the latter giving rise to the formation of bicyclic compounds. For reactions of this ring system with $MgBu^tCl$ or the organosilyl Grignard reagents $Mg(CH_2SiMe_3)Cl$ and $Mg[CH(SiMe_3)_2]Cl$ nucleophilic substitution appears to be the preferential process. Application of the copper-assisted Grignard reagents $MgRCl–[\{CuI(PBu^n{}_3)\}_4]$ (R = alkyl) and alkyl iodides, allyl bromide, or propan-2-ol leads to the formation of dialkyl, alkylallyl, or alkylhydrido derivatives, according to an initial metal–halogen exchange process. The crystal and molecular structure of the bicyclic compound $[NPMe(NSOPh)_2]_2{\cdot}C_6H_6$ has been determined. Crystals are triclinic, space group $P\bar{1}$, $a = 8.063(1)$, $b = 8.979(1)$, $c = 12.712(3)$ Å, $\alpha = 71.38(1)$, $\beta = 74.13(1)$, $\gamma = 86.57(1)°$, and $Z = 1$. The basic structure consists of two six-membered N_3PS_2 rings coupled by a P–P bond [2.211 6(9) Å] with the methyl groups in *trans* position. Mean bond lengths‡ are N–P 1.614(2), N–S 1.565(5), 1.585(1), S–O 1.436(1), S–C 1.768(1), and C–C (phenyl) 1.388(1) Å. The endocyclic angles at P and S are 114.6(1) and 113.3(4)° (average), respectively, and those at N range from 121.3(1) to 124.8(1)°.

Two different pathways can be discerned for reactions of the ring systems $(NPCl_2)_n(NSOPh)_{3-n}[n = 1$, (**1**), or 2] and $(NPCl_2)_3$ (**2**) with Grignard or organolithium reagents and an excess of propan-2-ol in tetrahydrofuran: (*i*) metal–halogen exchange and (*ii*) nucleophilic substitution.[1–4] The former process is assumed to proceed *via* a metallophosphazene intermediate in which a halogenomagnesium residue (MgX) or lithium is co-ordinated to a nitrogen together with a neighbouring trivalent phosphorus atom (see Scheme 1). Hydrido derivatives and bicyclic compounds are characteristic reaction products. Nucleophilic substitution results in a direct replacement of one or two chlorine atoms by organic groups. In the reaction of alkyl lithium reagents with compound (**2**) the metal–halogen exchange process predominates;[2] in the case of sulphur-containing rings, however, nucleophilic substitution also plays an important role and is supposed to induce ring cleavage and therefore lower yields.[3] Reactions of (**2**) with alkyl or phenyl Grignard reagents are also assumed to proceed *via* a metal–halogen exchange process, although for secondary and tertiary alkyl Grignard reagents a nucleophilic halogen-replacement mechanism cannot fully be excluded.[1,4] The main reaction products are the monosubstituted trimer $(NPCl_2)_2NPCl(R)$ (R = organic residue) and the bi(cyclophosphazene) $[(NPCl_2)_2\text{-}NPR]_2$. In the reaction of organosilyl Grignards with (**2**) there



Scheme 1. (*i*) MgRCl

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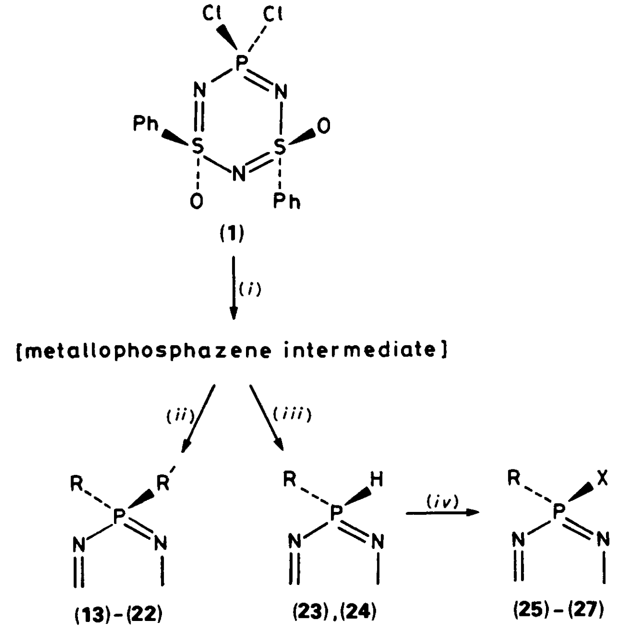
† 5,5′-Bi[5-methyl-1,3-dioxo-1,3-diphenylcyclo($5\lambda^5$-phospha-2,4,6-triaza-$1\lambda^6$,$3\lambda^6$-dithiene)]-benzene (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

‡ Throughout this paper the mean values and their standard errors have been calculated using the formulae given by A. Domenicano, A. Vaciago, and C. A. Coulson, *Acta Crystallogr., Sect. B*, 1975, **31**, 221.



Scheme 2. (*i*) MgRCl, $[\{CuI(PBu^n_3)\}_4]$; (*ii*) R′I or allyl bromide; (*iii*) Pr^iOH; (*iv*) $X_2 = Cl_2, Br_2$, or I_2

is strong evidence that chlorine substitution proceeds *via* a nucleophilic mechanism.[5] Copper-assisted Grignard reagents $MgRCl-[\{CuI(PBu^n_3)\}_4]$ also give rise to metallophosphazene intermediates,[4,6] the structure of which is still controversial. A phosphazenic anion with a copper–nitrogen linkage has been proposed by Allcock and Harris;[6] recently we described a cationic structure containing copper–phosphorus and magnesium–nitrogen linkages.[7]

As part of our investigations concerning the reactivity of cyclothiaphosphazenes $(NPCl_2)_n(NSOX)_{3-n}$ (X = F, Cl, or Ph) towards organometallic reagents we examined reactions with *trans*-$NPCl_2(NSOPh)_2$ (**1**) and Grignard reagents or copper-assisted Grignard reagents $MgRCl-[\{CuI(PBu^n_3)\}_4]$ in tetrahydrofuran as a solvent. A phenyl derivative was chosen in our studies in order to restrict reactions to the phosphorus centre, allowing a direct comparison with $(NPCl_2)_3$.

In addition to the discussion about the reaction pathways, this paper includes a crystal-structure determination of the first example of a phosphorus–phosphorus coupled bi(cyclothiaphosphazene).

Results and Discussion

In order to compare the results of reactions of compound (**1**) with Grignard reagents with those obtained for (**2**), tetrahydrofuran was chosen as a solvent. Most of the experiments were carried out at low temperature in order to avoid degradation of the ring system, thus obtaining maximum yields of cyclic products. As described before,[2,3] some reaction mixtures were analyzed for their composition by n.m.r. spectroscopy (see Experimental section).

(*a*) *Reactions of Compound* (**1**) *with* MgMeCl *in Molar Ratios* 1:1, 1:2, *and* 1:4; *Subsequent Treatment with Propan-2-ol* (*Table* 2, *Scheme* 1).—The data in Table 2 with respect to reactions with MgMeCl clearly show that substitution increases with an increasing amount of Grignard reagent. Five compounds (total yield 70%) were observed (n.m.r. spectroscopic analysis) for the 1:2 reaction of compound (**1**) with MgMeCl and propan-2-ol. Besides some starting material (**1**) (5%) and traces of (1α,3β,5α)-$NPH(OPr^i)(NSOPh)_2$ (**6**),* the mixture contained (1α,3β,5α)-$NPCl(Me)(NSOPh)_2$ (**3**) (35%), two diastereomers (**a**) and (**b**) of the bi(cyclothiaphosphazene) $[NPMe(NSOPh)_2]_2$ (**4**) (20%), and *trans*-$NPMe_2(NSOPh)_2$ (**5**) (10%). The mixture was separated by means of h.p.l.c.; compounds (**3**)—(**5**) were fully characterized (see Experimental section). Recrystallization of an equimolar mixture of (**4a**) and (**4b**) from benzene afforded a pure sample of (**4a**) as a benzene adduct.

The reaction with 4 equivalents of MgMeCl showed a clear preference for the formation of dimethyl derivative (**5**).

(*b*) *Reactions of Compound* (**1**) *with* $MgBu^tCl$ *and Propan-2-ol* (*Table* 2).—Apart from an n.m.r. analysis no further experiments were carried out. The products (1α,3β,5α)-$NPCl(Bu^t)(NSOPh)_2$ (**7**) and (1α,3β,5α)-$NPH(Bu^t)(NSOPh)_2$ (**8**) have been described already for reactions of (**1**) with $LiBu^t$.[3]

(*c*) *Reactions of Compound* (**1**) *with* $Mg[CH_{3-n}(SiMe_3)_n]Cl$ (*n* = 1 *or* 2) *in Molar Ratio* 1:1.2; *Subsequent Treatment with Propan-2-ol* (*Table* 3).—Reaction of compound (**1**) with $Mg(CH_2SiMe_3)Cl$ in molar ratio 1:1.2 and propan-2-ol gave (1α,3β,5α)-$NPCl(CH_2SiMe_3)(NSOPh)_2$ (**9**) as major product (80%) with traces of *trans*-$NP(CH_2SiMe_3)_2(NSOPh)_2$ (**10**). Using 3 equivalents of the Grignard reagent, compound (**10**) was the only reaction product (yield 55%). An analogous result was obtained for disilyl Grignard $Mg[CH(SiMe_3)_2]Cl$. In a 1:1.2 molar ratio reaction (1α,3β,5α)-$NPCl[CH(SiMe_3)_2](NSOPh)_2$ (**11**) was formed in a yield of 70%. The crystal structure of (**11**) has been described elsewhere.[8]

(*d*) *Reactions of Compound* (**1**) *with Copper-assisted Grignard Reagents* MgRCl (R = Pr^n *or* Pr^i) *and Subsequent Treatment with* R′I (R′ = Me, Et, Pr^n, *or* Bu^n), *Allyl Bromide, or* Pr^iOH (*Scheme* 2).—Reactions of compound (**1**) were carried out with 0.5 equivalents of $[\{CuI(PBu^n_3)\}_4]$ and 3.5 equivalents (slight excess) of MgRCl (R = Pr^n or Pr^i) in tetrahydrofuran. Treatment of the reaction mixtures with various primary alkyl iodides or allyl bromide gave compounds (1α,3β,5α)-$NPR(R')(NSOPh)_2$ (**13**)—(**22**) as the only reaction products. Addition of propan-2-ol instead of R′I or allyl bromide resulted in the formation of compounds (1α,3β,5α)-$NPH(R)(NSOPh)_2$ [R = Pr^n, (**23**); or Pr^i (**24**)]. Compound (**24**) could easily be converted into (1α,3β,5α)-$NPX(Pr^i)(NSOPh)_2$ [X = Cl, (**25**); Br, (**26**); or I, (**27**)] by reactions with chlorine, bromine, or iodine (Scheme 2). Crystal structures of compounds (**20**) (R = Pr^n, R′ = Pr^i) and (**27**) have been published elsewhere.[9,10]

(*e*) *Reaction Routes and Mechanism.*—From the results for MgMeCl, as given in Table 1, it follows that at least 2 equivalents of Grignard reagent are needed for a complete consumption of the starting material. This requirement in combination with the nature of the products formed [bicyclic derivatives (**4a**) and (**4b**)] indicates that both nucleophilic substitution and metal halogen exchange must be operative. The corresponding reaction sequences are given in Scheme 1.

Nucleophilic substitution gives successively $NPCl(Me)(NSOPh)_2$ (**3**) and the disubstituted product $NPMe_2(NSOPh)_2$ (**5**). Metal–halogen exchange (1 equivalent of MgMeCl needed) followed by a second reaction with MgMeCl leads to the formation of $N(MgCl)PMe(NSOPh)_2$. Ring coupling reaction of this intermediate with (**3**) yields the bicyclic species $[NPMe(NSOPh)_2]_2$ (**4a**) and (**4b**). The latter process can be suppressed completely by applying 4 equivalents of MgMeCl, which results in compound (**5**) being the only reaction product. Apparently, nucleophilic substitution of (**3**) is a faster process

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* For use of the α and β prefixes see B. de Ruiter and J. C. van de Grampel, *J. Chem. Soc., Dalton Trans.*, 1982, 1773.

Table 1. Analytical and physical data for the compounds

Compound		M.p. (°C)	Yield (%)	m/z [a]	Analysis [b]/% C	H	N	S	^{31}P-{^{1}H} N.m.r. δ/Hz
(3)	$(1\alpha,3\beta,5\alpha)$-NPCl(Me)(NSOPh)$_2$	134—136	31	373 (63), 205 (100)	42.15 (41.75)	3.50 (3.50)	11.15 (11.25)	17.00 (17.15)	35.9
(4a), **(4b)**	[NPMe(NSOPh)$_2$]$_2$		19	676 (1), 338 (60)	45.90 (46.15)	3.90 (3.85)	12.10 (12.25)		22.8 (**4a**) 23.0 (**4b**)
(4a)	As C_6H_6 adduct	224—226							
(5)	*trans*-NPMe$_2$(NSOPh)$_2$	171—173	8	353 (50), 185 (100)	47.45 (47.60)	4.70 (4.55)	11.75 (11.90)	18.00 (18.15)	33.0
(9)	$(1\alpha,3\beta,5\alpha)$-NPCl(CH$_2$SiMe$_3$)(NSOPh)$_2$	114—116	80	445 (82), 430 (100)	43.00 (43.10)	4.75 (4.75)	9.40 (9.35)	14.40 (14.40)	37.8
(10)	*trans*-NP(CH$_2$SiMe$_3$)(NSOPh)$_2$	131—132	50	497 (100), 482 (87)	48.25 (48.25)	6.55 (6.50)	8.40 (8.45)	12.80 (12.90)	36.6
(11)	$(1\alpha,3\beta,5\alpha)$-NPCl[CH(SiMe$_3$)$_2$](NSOPh)$_2$	119—120	65	517 (25), 502 (100)	43.90 (44.05)	5.75 (5.65)	8.15 (8.15)	12.35 (12.35)	38.3
(12)	(NPCl)$_2$NPCl[CH(SiMe$_3$)$_2$]	94—95	81	469 (6), 456 (100)	18.10 (17.85)	4.10 (4.05)	8.80 (8.90)		19.4 (PCl$_2$), 41.9 ^3J(PP) < 1 Hz
(13)	$(1\alpha,3\beta,5\alpha)$-NPMe(Pr^n)(NSOPh)$_2$	Oil	35	381 (25), 339 (100), 324 (42)	50.15 (50.35)	5.40 (5.30)	11.15 (11.00)	16.80 (16.80)	35.7
(14)	$(1\alpha,3\beta,5\alpha)$-NPEt(Pr^n)(NSOPh)$_2$	85—87	66	395 (20), 353 (51), 329 (100)	51.65 (51.60)	5.60 (5.60)	10.45 (10.65)	16.20 (16.20)	40.2
(15)	$(1\alpha,3\beta,5\alpha)$-NPPr$^n{}_2$(NSOPh)$_2$	126—128	57	409 (14), 367 (67), 324 (100)	52.60 (52.80)	5.85 (5.90)	10.25 (10.25)	15.70 (15.65)	38.1
(16)	$(1\alpha,3\beta,5\alpha)$-NPBu^n(Pr^n)(NSOPh)$_2$	90—92	42	423 (18), 381 (26), 367 (37), 324 (100)	53.55 (53.85)	6.20 (6.20)	9.95 (9.90)	15.10 (15.15)	38.6
(17)	$(1\alpha,3\beta,5\alpha)$-NP(C$_3$H$_5$)Pr^n(NSOPh)$_2$	85—87	38	407 (26), 366 (79), 365 (58), 324 (41)	52.90 (53.05)	5.50 (5.45)	10.40 (10.30)	15.65 (15.75)	35.0
(18)	$(1\alpha,3\beta,5\alpha)$-NPMe(Pr^i)(NSOPh)$_2$	98—100	42	381 (44), 339 (99), 324 (59)	50.15 (50.35)	5.30 (5.30)	11.00 (11.00)	16.75 (16.80)	40.9
(19)	$(1\alpha,3\beta,5\alpha)$-NPEt(Pr^i)(NSOPh)$_2$	111—112	48	395 (19), 367 (15), 353 (33), 324 (57)	51.25 (51.60)	5.55 (5.60)	10.55 (10.65)	15.90 (16.20)	45.7
(20)	$(1\alpha,3\beta,5\alpha)$-NPPr^n(Pr^i)(NSOPh)$_2$	113—114	50	409 (49), 367 (39), 324 (100)	52.60 (52.80)	5.90 (5.90)	10.25 (10.25)	15.80 (15.65)	43.4
(21)	$(1\alpha,3\beta,5\alpha)$-NPBu^n(Pr^i)(NSOPh)$_2$	99—100	36	423 (60), 324 (100)	53.95 (53.85)	6.15 (6.20)	9.95 (9.90)	15.15 (15.15)	44.0
(22)	$(1\alpha,3\beta,5\alpha)$-NP(C$_3$H$_5$)Pr^i(NSOPh)$_2$	90—91	27	407 (2), 365 (21), 360 (14), 324 (15)	52.85 (53.05)	5.55 (5.45)	10.35 (10.30)	15.55 (15.75)	40.3
(25)	$(1\alpha,3\beta,5\alpha)$-NPCl(Pr^i)(NSOPh)$_2$	116—117	34	401 (100), 359 (27), 324 (52)	44.70 (44.85)	4.25 (4.25)	10.50 (10.45)	15.85 (15.95)	47.0
(26)	$(1\alpha,3\beta,5\alpha)$-NPBr(Pr^i)(NSOPh)$_2$	118—119	26	445 (27), 366 (100), 324 (68)	40.30 (40.35)	3.80 (3.85)	9.40 (9.40)	14.25 (14.35)	39.3
(27)	$(1\alpha,3\beta,5\alpha)$-NPI(Pr^i)(NSOPh)$_2$	143—145	16	366 (100)	36.50 (36.50)	3.45 (3.50)	8.55 (8.50)	13.25 (13.00)	13.5

[a] Abundance (%) in parentheses. [b] Calculated values in parentheses.

than the coupling reaction or even than the formation of the magnesium intermediates. This conclusion corresponds with the results obtained for reactions with MgBu^{t}Cl. The bulky Bu^t group prevents formation of a bicyclic compound and ring coupling is no longer a driving force for the metal–halogen exchange process.

For the reaction of compound **(1)** with organosilyl Grignards only slightly more than 1 equivalent of Grignard reagent is needed for the formation of the monosubstituted products **(9)** and **(11)**, whereas no hydrido derivatives could be detected in the reaction mixtures (Table 2). These observations clearly point to an exclusive nucleophilic substitution, which is in agreement with the reactions of **(2)** with organosilyl Grignards (ref. 5; this paper Experimental section).

It is noteworthy that reactions between compound **(2)** and Grignard reagents result in moderate to high yields of cyclic substitution products, despite the fact that nucleophilic substitution is one of the reaction pathways. In that respect Grignard reagents differ from alkyl-lithium compounds, where nucleophilic substitution leads to ring degradation.[3]

As for **(2)**, the product formation in reactions of compound **(1)** with copper-assisted Grignards can be understood by assuming a metal–halogen exchange process (Scheme 2).

(*f*) *Crystal and Molecular Structure of Compound* **(4a)**·C_6H_6.—The coupling of the two chiral cyclic units NPMe(NSOPh)$_2$ *via* a P–P bond can lead to the formation of three stereoisomers in which the methyl groups are *trans* positioned, *viz.* a *meso* compound and two enantiomers (Figure 1). This is in agreement with the number of isomers, **(4a)** and **(4b)**, observed by ^{31}P n.m.r. spectroscopy.

Isolation of **(4a)** as a benzene adduct appeared to be possible. Moreover, the stability of the crystals appeared to be good enough to allow a structure determination by *X*-ray diffraction. The molecular geometry (PLUTO drawing) and the numbering scheme adopted are given in Figure 2. Selected data on the geometry are given in Table 4. The structure consists of discrete molecules of **(4a)** and benzene, separated by normal van der Waals distances. Both molecules have a crystallographically imposed inversion centre. This means that the bicyclic derivative **(4a)** is the *meso* compound with the methyl groups in *trans* position. An analogous *trans* conformation has been reported

Table 2. Absolute yields (mol %) of reactions of *trans*-$NPCl_2(NSOPh)_2$ (1) (500 mg) with MgRCl (R = Me or Bu^t) and propan-2-ol at −20 °C.[a] Total yields (in mg) are given in parentheses

		1:1[b]	1:2[b]	1:4[b]			1:1[c]	1:2[c]	1:4[c]
≡PCl_2	**(1)**	45	5		≡PCl_2	**(1)**	50	5	
≡PCl(Me)	**(3)**	20	35		≡PCl(Bu^t)[d]	**(7)**	40	85	85
$(≡PMe)_2$	**(4a)**, **(4b)**	10	20		≡PH(Bu^t)[d]	**(8)**	<1	<1	5
≡PMe_2	**(5)**	5	10	70	≡PH(OPr^i)[d]	**(6)**	<1	<1	
≡PH(OPr^i)[d]	**(6)**	<1	<1						
		80 (400)	70 (380)	70 (350)			90 (480)	90 (480)	90 (490)

[a] See Experimental section. [b] Molar ratio of ring: MgMeCl. [c] Molar ratio of ring: MgBu^{t}Cl. [d] Assignment based on data in ref. 3.

Table 3. Absolute yields (mol %) of reactions of *trans*-$NPCl_2(NSOPh)_2$ (1) (500 mg) with $Mg[CH_{3-n}(SiMe_3)_n]Cl$[a] (*n* = 1 or 2) and propan-2-ol. Total yields (in mg) are given in parentheses

		n = 1 1:1.2[b]	*n* = 1 1:3[b]	*n* = 2 1:1.2[c]
≡PCl_2	**(1)**			
≡$PCl[CH_{3-n}(SiMe_3)_n]$	**(9)**	80		**(11)** 70
≡$P[CH_{3-n}(SiMe_3)_n]_2$	**(10)**	5	**(10)** 55	
		85 (480)	55 (360)	70 (450)

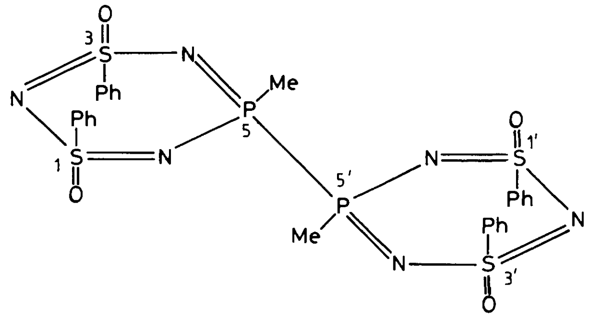
[a] See Experimental section. [b] Molar ratio of ring: $Mg(CH_2SiMe_3)Cl$. [c] Molar ratio of ring: $Mg[CH(SiMe_3)_2]Cl$.

for $(N_3P_3Cl_4Ph)_2$,[11] $(N_3P_3MePh_4)_2$,[12] and $(N_3P_3Cl_4Me)_2$.[13] It is noteworthy that for $(N_4P_4Cl_6Me)_2$, a bicyclic compound consisting of two eight-membered rings, a *cis* conformation is observed.[14] The conformation of the PNS ring in **(4a)**·C_6H_6 approaches that of a boat[15] with torsion angles ranging from −26.1(2) to 27.5(2)° and a lowest asymmetry parameter value C_s equal to 2.0(2)° for P(1) and N(2).[16] Puckering parameters are Q = 0.354(1) Å, θ = 89.7(2)°, and φ = 116.9(2)°.[17] The phenyl rings C(1)—C(6) and C(7)—C(12) display normal geometry with a mean C–C bond length 1.388(1) Å. In the benzene ring the average C–C bond length is 1.385(2) Å. The phenyl substituents are in *trans* position with respect to the PNS ring. The torsion angles show that the phenyl ring C(1)—C(6) is almost perpendicular to the adjacent S–O bond [C(2)–C(1)–S(1)–O(1) −86.2(2)°], whereas the other phenyl group is almost coplanar with S(2)–O(2) [C(8)–C(7)–S(2)–O(2) −156.4(2)°]. Phosphorus and sulphur show a distorted tetrahedral geometry. The variations in the P–N and S–N bond lengths are similar to those observed in related compounds.[18] The P–P bond length [2.211 6(9) Å] may be compared with those reported for other bicyclophosphazenes.[11–14] A short intermolecular C–H···O distance is observed: H(131)···O(1) (1 − *x*, −*y*, 1 − *z*) 2.33(2) Å [sum of the van der Waals radii is 2.72 Å (ref. 19)]; the corresponding angle C–H–O is 152(2)°.

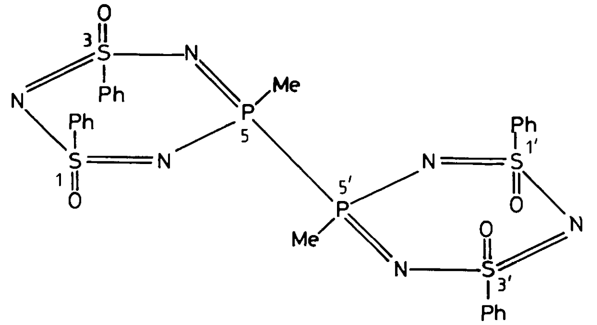
Experimental

All experiments were carried out in an atmosphere of dry, oxygen-free nitrogen, applying gas-vacuum techniques in combination with Schlenk-type glassware. Liquids were transferred with syringes.

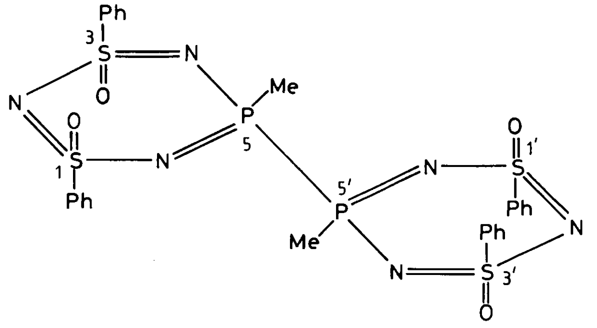
Tetrahydrofuran was distilled prior to use under nitrogen from sodium potassium benzophenone. All other solvents were purified and dried by conventional methods. Solutions of Grignard reagents MgRCl (R = Me, Pr^n, Pr^i, or Bu^t) in tetrahydrofuran were obtained commercially (Alfa). Concentrations were checked regularly by titration. The compounds $Mg(CH_2SiMe_3)Cl$ and $Mg[CH(SiMe_3)_2]Cl$ were prepared by standard methods from Mg and Me_3SiCH_2Cl (Janssen) and $(Me_3Si)_2CHCl$, respectively; $(Me_3Si)_2CHCl$ was synthesized according to a literature method.[20] Alkyl iodides R′I (R′ = Me, Et, Pr^n, or Bu^n) (Janssen) were purified by distillation from P_2O_5; allyl bromide (Janssen) was used as received. Propan-



(1α, 3β, 5α) - (1′β, 3′α,5′β)



(1α, 3β, 5α)-(1′α, 3′β,5′β)



(1β, 3α,5α) - (1′β,3′α,5′β)

Figure 1. Schematic drawings of the stereoisomers of $[NPMe(NSOPh)_2]_2$

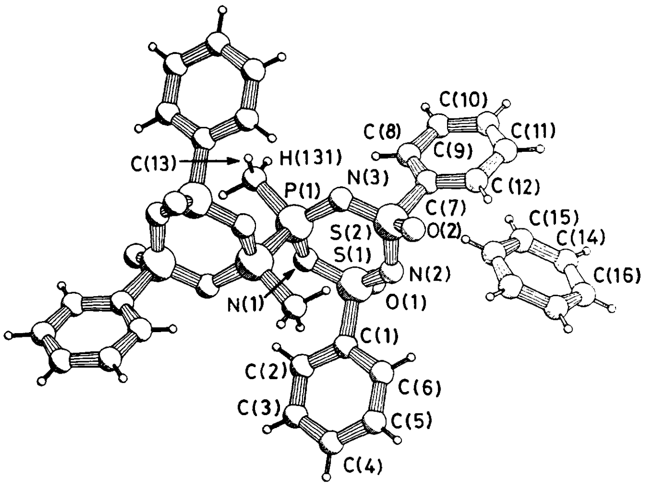


Figure 2. PLUTO drawing of the molecule (**4a**)·C_6H_6 illustrating the puckering and the numbering scheme adopted

Table 4. Selected data (distances in Å, angles in °) on the geometry of compound (**4a**)·C_6H_6

Residue 1			
S(1)–N(1)	1.568(1)	S(1)–O(1)	1.437(2)
S(1)–N(2)	1.585(2)	S(2)–O(2)	1.435(2)
S(2)–N(2)	1.585(2)	S(1)–C(1)	1.769(2)
S(2)–N(3)	1.555(2)	S(2)–C(7)	1.767(2)
P(1)–N(1)	1.615(2)	P(1)–C(13)	1.774(2)
P(1)–N(3)	1.612(2)	P(1)–P(1A)	2.211 6(9)
	C–C	1.388(1) (mean)	
N(1)–S(1)–N(2)	113.6(1)	C(13)–P(1)–P(1A)	104.65(6)
N(2)–S(2)–N(3)	112.9(1)	S(1)–N(1)–P(1)	121.3(1)
N(1)–P(1)–N(3)	114.6(1)	S(1)–N(2)–S(2)	124.8(1)
O(1)–S(1)–C(1)	107.51(9)	S(2)–N(3)–P(1)	122.7(1)
O(2)–S(2)–C(7)	107.4(1)		
	C–C–C	120.0(3) (mean)	
Residue 2			
C–C	1.385(2) (mean)	C–C–C	120.0(2) (mean)

2-ol (Merck) was dried on molecular sieves. The compounds *trans*-$NPCl_2(NSOPh)_2$ (**1**)[21] and $[\{CuI(PBu^n_3)\}_4]$[22] were prepared according to published methods, and $(NPCl_2)_3$ (**2**) was obtained from Shin Nisso Kaku and used without purification.

Purification by h.p.l.c. was carried out using a Waters system, consisting of two 6000 A pumps, combined with a R401 refractive index detector. Separations were performed on a Polygosil 60-10 CN silica gel column (internal diameter 10 mm, length 25 cm).

Proton n.m.r. (60 MHz, $CDCl_3$ solution) spectra were recorded on a Perkin-Elmer R-24B instrument using $SiMe_4$ as internal reference, ^{31}P n.m.r. spectra ($CDCl_3$ solution) on a Nicolet NT 200 spectrometer, operating at 81 MHz. The compound $(NPCl_2)_3$ (**2**) was used as external reference (19.9 p.p.m. with respect to 85% H_3PO_4 solution in $CDCl_3$). In all cases the ^2H resonance line of the solvent was used for field-frequency lock. Chemical shifts are positive to low field. Mass spectra were obtained with an AEI MS9 mass spectrometer (Mr. A. Kiewiet, Department of Organic Chemistry, University of Groningen).

Elemental analyses were carried out at the Microanalytical Department under the supervision of Mr. A. F. Hamminga. Analytical and some physical data of the compounds prepared are given in Table 1. The ^1H n.m.r. data are as expected and are therefore not tabulated.

Analysis of the Crude Reaction Mixtures by N.M.R. Methods.—Reactions of compound (**1**) (0.5 g, 1.3 mmol) with MgRCl in molar ratio 1:1, 1:2, or 1:4 (R = Me or Bu^t) and 1:1.2 or 1:3 [R = Me_3SiCH_2 or $(Me_3Si)_2CH$] in tetrahydrofuran (50 cm^3) and propan-2-ol (0.49 cm^3, 6.5 mmol) were carried out under standard reaction conditions (for a typical reaction procedure see below). After the reaction the solvent was removed *in vacuo*. The reaction products were dissolved in dichloromethane and filtered through a silica gel column to remove salts and polymeric substances. The reaction mixtures thus obtained could be completely dissolved in $CDCl_3$ (2.5 cm^3). The composition of each reaction mixture was analyzed by ^{31}P and ^1H n.m.r. spectroscopy,. Results are given in Tables 2 and 3.

Reactions of trans-$NPCl_2(NSOPh)_2$ (**1**).—(*a*) *With* MgMeCl *in molar ratio* 1:2, *and propan-2-ol.* A solution of MgMeCl (10.4 mmol) in tetrahydrofuran (15 cm^3) was added dropwise to a stirred solution of compound (**1**) (2.1 g, 5.3 mmol) in tetrahydrofuran (200 cm^3) at −78 °C. After stirring for 16 h at −20 °C, propan-2-ol (2 cm^3, 26 mmol) was added dropwise. The reaction was allowed to warm to room temperature within 1.5 h, after which the solvent was removed by evaporation. Filtration of a solution of the remainder in dichloromethane (200 cm^3) through a silica gel column (internal diameter 2.5 cm, length 5 cm) and subsequent evaporation of the solvent afforded a mixture of compounds (1.7 g). This mixture [solution in dichloromethane–tetrahydrofuran (1:1)] was chromatographed by means of h.p.l.c., using a hexane–tetrahydrofuran (2.5:1) eluant. Three fractions were isolated.

Fraction 1: 0.68 g. Recrystallization from diethyl ether gave white crystals of (1α,3β,5α)-NPCl(Me)$(NSOPh)_2$ (**3**).

Fraction 2: 0.18 g. Recrystallization from dichloromethane–hexane (1:3) gave white crystals of *trans*-$NPMe_2(NSOPh)_2$ (**5**).

Fraction 3: 0.66 g. Recrystallization from dichloromethane–tetrahydrofuran (1:1) gave white crystals of $[NPMe(NSOPh)_2]_2$ (**4a**) and (**4b**), two diastereomers. Recrystallization by slow evaporation from a saturated benzene solution gave 0.1 g of white crystals of [(1α,3β,5α)-NPMe$(NSOPh)_2$][(1β,3α,5β)-NPMe$(NSOPh)_2$]·C_6H_6 (**4a**)·C_6H_6, which appeared to be the centrosymmetric diastereomer, m.p. 224—226 °C.

(*b*) *With* $Mg(CH_2SiMe_3)Cl$ *in molar ratios* 1:1.2 *and* 1:3, *and propan-2-ol.* A solution of $Mg(CH_2SiMe_3)Cl$ (1.5 or 3.8 mmol) in tetrahydrofuran (10 cm^3) was added dropwise to a stirred solution of compound (**1**) (0.5 g, 1.3 mmol) in tetrahydrofuran (20 cm^3) at 20 °C. The reaction mixture was then refluxed at 66 °C for 20 h. Propan-2-ol (0.5 cm^3, 6.5 mmol) was added and the reaction mixture was allowed to cool to room temperature after which the solvent was removed by evaporation. Extraction of the remainder with five 40-cm^3 portions of pentane afforded the crude products (0.48, 0.36 g). Recrystallization from diethyl ether gave the pure compounds: in the case of the 1:1.2 reaction, white crystals of (1α,3β,5α)-$NPCl(CH_2SiMe_3)(NSOPh)_2$ (**9**); in the case of the 1:3 reaction, white crystals of *trans*-$NP(CH_2SiMe_3)_2(NSOPh)_2$ (**10**).

(*c*) *With* $Mg[CH(SiMe_3)_2]Cl$ *in molar ratio* 1:1.2, *and propan-2-ol.* For procedure see under (*b*). Reaction of compound (**1**) (2.5 g, 6.3 mmol) in tetrahydrofuran (50 cm^3) with $Mg[CH(SiMe_3)_2]Cl$ (7.6 mmol) in tetrahydrofuran (20 cm^3) and propan-2-ol (2.4 cm^3, 31.2 mmol) gave the crude product (2.3 g). Recrystallization from pentane–diethyl ether (2:1) afforded pure white crystals of (1α,3β,5α)-$NPCl[CH(SiMe_3)_2]$-$(NSOPh)_2$ (**11**).

(*d*) *With* MgRCl *and* R′I, *or allyl bromide.* A solution of MgRCl (R = Pr^n or Pr^i) (8.8 mmol) in tetrahydrofuran (10 cm^3) was added dropwise to a stirred solution of compound (**1**) (1.0 g, 2.5 mmol) and of $[\{CuI(PBu^n{}_3)\}_4]$ (0.5 g, 1.3 mmol) in tetrahydrofuran (40 cm^3) at −70 °C. Stirring was continued for 17 h at room temperature, after which R′I (R′ = Me, Et, Pr^n, or Bu^n) (12.5 mmol) or allyl bromide (12.5 mmol) was added dropwise at 0 °C. After stirring for an additional period of 48 h at room temperature the solvent was removed by evaporation. A solution of the remainder in benzene (50 cm^3) was washed with 10% hydrochloric acid (50 cm^3) and subsequently dried on anhydrous calcium chloride. Evaporation of the filtered solution, followed by filtration of a solution of the remainder in CH_2Cl_2 (40 cm^3) through neutral alumina and subsequent evaporation of the solvent, gave the crude reaction product. Recrystallization from diethyl ether afforded pure compounds (1α,3β,5α)-NPR(R′)$(NSOPh)_2$ (**14**)–(**22**). Crude (1α,3β,5α)-NPMe(Pr^n)$(NSOPh)_2$ (**13**) was dissolved in boiling diethyl ether. Cooling of the solution gave a colourless oil of pure (**13**).

(1α,3β,5α)-NPH(R)$(NSOPh)_2$ [R = Pr^n, (**23**); *or* Pr^i, (**24**)]. Procedure as above. Instead of the alkyl iodides, propan-2-ol (12.5 mmol) was added dropwise at 0 °C. Stirring was continued for 1 h at room temperature after which the reaction mixture was treated as described above. Compounds (**23**) and (**24**) were obtained as white solids and used without purification in further syntheses: (**23**), yield 63%, $\delta(^1H)$ 7.36 [1 H, d, ^1J(PH) 545, PH], $^{31}P-\{^1H\}$ 14.1 p.p.m.; (**24**), yield 67%, $\delta(^1H)$ 7.14 [1 H, d, ^1J(PH) 539, PH], $^{31}P-\{^1H\}$ 22.0 p.p.m.

Reaction of $(NPCl_2)_3$ (**2**) *with* $Mg[CH(SiMe_3)_2]Cl$ *in Molar Ratio* 1:1.2, *and Propan-2-ol.*—For procedure see under (*b*). Reaction of compound (**2**) (2.0 g, 5.8 mmol) in tetrahydrofuran (50 cm^3) and $Mg[CH(SiMe)_3)_2]Cl$ (8.0 mmol) in tetrahydrofuran (20 cm^3) and propan-2-ol (2.2 cm^3, 29 mmol) yielded 2.4 g of the crude product. Recrystallization from acetonitrile [or sublimation at 110 °C and 0.5 mmHg (*ca.* 67 Pa) pressure] gave white crystals of $(NPCl)_2NPCl[CH(SiMe_3)_2]$ (**12**).

Preparation of Compounds (1α,3β,5α)-NPX(Pr^i)$(NSOPh)_2$ [X = Cl, (**25**); Br, (**26**); *or* I, (**27**)].—Chlorine was bubbled through a solution of (1α,3β,5α)-NPH(Pr^i)$(NSOPh)_2$ (**24**) (0.59 g, 1.6 mmol) in tetrachloromethane (25 cm^3) for 4 min at 0 °C. After stirring for 1 h at room temperature chlorine was again bubbled through the reaction mixture for 4 min. For the preparation of the bromo and iodo derivatives a solution of bromine or iodine (4.8 mmol) in tetrachloromethane (20 cm^3) was added dropwise to a solution of (**24**) (0.59 g, 1.6 mmol) in tetrachloromethane (20 cm^3) at 0 °C. Stirring was continued for 17 h at room temperature, after which the solvent was removed by evaporation. Filtration of the remainder in dichloromethane (30 cm^3) through neutral alumina and subsequent evaporation of the solvent gave the crude reaction product. Recrystallization from diethyl ether afforded the pure compounds.

Crystal Structure Determination of Compound (**4a**)·C_6H_6.—A colourless crystal of compound (**4a**)·C_6H_6 was glued on the top of a glass fibre and mounted on an Enraf-Nonius CAD-4F diffractometer. Intensity data for 7 330 reflections were collected at room temperature in the range 1.76 < θ < 27.0 (*h* −9 to 10, *k* −10 to 11, *l* 0 to 16), using graphite-monochromated Mo-$K_{\bar{\alpha}}$ (λ = 0.710 73 Å) radiation and the ω—2θ technique with ω scan width = (0.85 + 0.35 tan θ)°. Three reference reflections measured every 2 h [$\bar{1}$32, root mean square deviation (r.m.s.d.) 1.5; 312, r.m.s.d. 2.0; 014, r.m.s.d. 1.7%] showed no indication of crystal decomposition during the 56.5 h of *X*-ray exposure. The intensities were corrected for scale variation and for Lorentz and polarization effects, but not for absorption. The data set was averaged to 3 665 unique reflections, of which 3 200 satisfied $I \geqslant 2.5\sigma(I)$.

Table 5. Final fractional atomic co-ordinates for non-hydrogen atoms of compound (**4a**)·C_6H_6 with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
S(1)	0.824 01(6)	0.070 97(6)	0.281 38(4)
S(2)	0.855 02(6)	0.332 77(6)	0.351 10(4)
P(1)	0.865 39(6)	0.029 72(6)	0.498 53(4)
O(1)	0.669 7(2)	0.055 2(2)	0.249 5(1)
O(2)	0.984 0(2)	0.456 3(2)	0.310 9(1)
N(1)	0.813 0(2)	−0.036 8(2)	0.407 6(1)
N(2)	0.882 4(2)	0.247 2(2)	0.256 4(2)
N(3)	0.848 0(2)	0.216 9(2)	0.473 1(2)
C(1)	0.997 3(2)	0.007 0(2)	0.187 7(2)
C(2)	1.032 1(3)	−0.152 2(2)	0.216 2(2)
C(3)	1.161 8(3)	−0.204 1(2)	0.139 7(2)
C(4)	1.255 9(3)	−0.098 0(3)	0.037 9(2)
C(5)	1.219 5(3)	0.060 5(3)	0.011 1(2)
C(6)	1.089 0(3)	0.114 6(2)	0.085 2(2)
C(7)	0.652 3(2)	0.421 8(2)	0.360 2(2)
C(8)	0.502 9(3)	0.338 5(2)	0.433 1(2)
C(9)	0.345 5(3)	0.410 1(2)	0.433 6(2)
C(10)	0.339 0(3)	0.563 6(2)	0.362 2(2)
C(11)	0.489 4(3)	0.645 2(2)	0.290 5(2)
C(12)	0.647 8(3)	0.575 1(2)	0.288 3(2)
C(13)	0.740 0(2)	−0.070 4(2)	0.640 0(2)
C(14)	0.343 7(3)	0.527 5(3)	−0.026 8(2)
C(15)	0.349 1(3)	0.433 5(3)	0.082 4(2)
C(16)	0.494 0(3)	0.594 2(3)	−0.109 0(2)

Crystal data. $C_{26}H_{26}N_6O_4P_2S_4{\cdot}C_6H_6$, *M* = 754.82, triclinic, *a* = 8.063(1), *b* = 8.979(1), *c* = 12.712(3) Å, α = 71.38(1), β = 74.13(1), γ = 86.57(1)°, *U* = 838.5(3) $Å^3$ (by least-squares refinement on 22 setting angles in the range 20.16 < θ < 22.79°), space group $P\bar{1}$, *Z* = 1, D_c = 1.495 g cm^{-3}, *F*(000) = 392. Reduced cell calculations did not indicate any higher lattice symmetry.[23] Crystal dimensions 0.18 × 0.18 × 0.15 mm, μ(Mo-$K_{\bar{\alpha}}$) = 4.1 cm^{-1}.

Structure analysis and refinement. The structure was solved by direct methods (GENTAN[24]) and refined on *F* by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms located on a difference Fourier map were included in the final refinement with one overall isotropic thermal parameter. Final *R* and *R′* were 0.033 and 0.044, respectively [$w = 1/\sigma^2(F)$]. The final fractional atomic co-ordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table 5. Scattering factors were taken from Cromer and Mann,[25] anomalous dispersion factors from Cromer and Liberman.[26] All calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program packages XTAL,[24] EUCLID,[27] and a locally modified version of PLUTO.[28]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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