Heteroatom Chemistry
Volume 5, Number 4, 1994

Sulfur Derivatives of 3-Methyl-5-phenyl-1,2,4,3-triazaphosphole

Alfred Schmidpeter,* Franz Steinmüller, and Konstantin Karaghiosoff

Institut für Anorganische Chemie der Universität München Meiserstr. 1, D-80333 München, Germany

Received 17 March 1994; revised 11 May 1994

ABSTRACT

The triazaphosphole **1** *adds sulfur along with HCl or* H_2S *to yield, respectively, the dihydrotriazaphosphole thiochloride* **4** *and sesquisulfide* **5** *(two diastereomers). In pyridine solution,* **1** *adds sulfur alone to yield the trimer of a triazaphosphole monosulfide* **7**. *Its central cyclotriphosphazane trisulfide ring has a trans structure and a boat conformation.*

INTRODUCTION

A characteristic feature of two-coordinate phosphorus as a member of a 6π ring system i.e., of a phosphinine or heterophosphole, is its low nucleophilicity in general and its inertness to chalcogen oxidation in particular [1]. Accordingly, 1,2,4,3-triazaphospholes are reported as being unreactive toward elemental sulfur. A phosphinine's reaction with sulfur has been achieved in boiling benzene with the catalytic help of *N*-methylimidazole [3,4]. The products are dimers of the phosphinine sesquisulfide and disulfide. No oligomer of the transient monosulfide was found. We report here the formation of a trimeric triazaphosphole monosulfide. For the first time, a trimer is definitely shown to result from the oligomerization of an azaphosphole by addition to its endocyclic P=N bond.

*To whom correspondence should be addressed.

RESULTS AND DISCUSSION

In contrast to the behavior of 2-methyl-5-phenyl-1,2,4,3-triazaphosphole **1**, its hydrogen chloride adduct **2** [1,5] does react with sulfur, resulting in the thiochloride **4**. It is better obtained from the reaction of the dimeric dichloride **3** [6,7] by reaction with hydrogen sulfide. As characteristic for the oxidation of tervalent phosphorus, its NMR signal is shifted considerably to higher field in going from **2** to **4** (Table 1).

The triazaphosphole **1** easily reacts with sulfur if, at the same time, hydrogen sulfide is added. In this reaction, no more than half a mole of H_2S is taken up per mole of **1**, even if an excess is available. The resulting anhydrosulfide **5** [8] contains two identical chiral phosphorus atoms and, accordingly, is diastereomeric. It is obtained as a 55:45 mixture of the two diastereomers **5a** and **5b**. For each of them, the ^{31}P NMR spectrum and the NH and methyl ^1H NMR signal represent the A part (Figure 1) and the X and Y parts, respectively, of an $AA'XX'Y_3Y_3'$ spin system (Table 1). The $^{13}C\{^1H\}$ NMR signals of Me and C-5 of each of the two isomers represent the X parts of AA'X spin systems. The outer two lines of the expected five-line pattern are of low intensity', however, due to the large $J_{AA'}$ ($^2J_{PP'}$) coupling relative to J_{AX} ($^2J_{PC}$) (Table 1), and the signals appear almost as triplets.

In warm pyridine solution, **1** is found to react with sulfur alone. We suggest that the pyridine (as the *N*-methylimidazole mentioned previously) adds loosely to the azaphosphole phosphorus and assists its nucleophilicity. This could, in spite of the probably low equilibrium concentration of the adduct, accelerate the reaction. At the same time, the pyridine would stabilize the resulting sulfide **6** as it is

1042-7163/94/$5.00 + .25

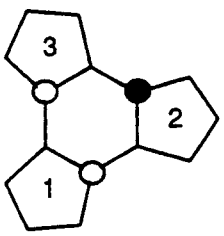
TABLE 1 NMR Data of Compounds **1** [2, 5], **2** [5], **4** and **5** in $CDCl_3$ (**1**, **2**, **5**) or CD_3CN (**4**)

	1	2	4	5a	5b
$\delta^{31}P$	253.3	154.0	64.5	64.9	65.5
$^2J_{PP}$				21.5	18.0 Hz
δ^1H Me	3.97	3.56	3.25	3.33	3.22
$^3J_{PH}$	6.2	15.2	12.5	10.5	10.7 Hz
δ^1H NH		9.00	8.82	7.33[a]	7.32[a]
$^2J_{PH}$			18.3	23.0[a]	23.0[a] Hz
$\delta^{13}C$ Me	38.4		32.5	32.3	33.2
$^2J_{PC}$[b]	9.2		10.3	13.4	13.4 Hz
$\delta^{13}C$ C-*i*			128.5	127.1	127.3
$^3J_{PC}$			3.8		Hz
$\delta^{13}C$ C-*o*			126.2	124.5	124.8
C-*m*			130.0	128.5	128.9
C-*p*			131.7	130.0	129.8
C-5	166.3		148.3	146.2	146.4
$^2J_{PC}$[b]	13.9		15.4	14.8	15.0 Hz

[a]The signals are hidden by the signals of the phenyl protons: shift values are taken from the $^{31}P/^1H$-correlated spectrum, coupling constants from the calculation of the splitting of the phosphorus signals (Figure 1).
[b]In the case of the AA'X spectra of compounds **5**: $N = J_{AX} + J_{A'X}(^2J_{PC} + {}^4J_{PC}$ or $^3J_{PC} + {}^5J_{PC})$. As $^{4,5}J_{PC}$ will be small, N will not deviate much from J_{AX}, however.

known from the pyridine adducts of dithioxophosphoranes [9]. Alternatively, pyridine might accelerate the reaction by activating the sulfur.

In its composition, the product corresponds to the monosulfide **6**. Its $^{31}P\{^1H\}$ NMR spectrum shows an ABC spin system (Figure 2). Its ^1H and ^{13}C NMR spectra indicate three different *N*-methyl groups, the latter also exhibiting three different C-5 atoms, each coupled to two phosphorus atoms by two-bond coupling constants (Table 2). The spectra thus document the presence of an unsymmetric trimer **7**, which formally has been formed from the addition of three molecules of **6** via the P=N bond, with the sulfur atoms in the *trans* position:



Other types of trimers of **6** formed by the addition to the P=S bond, which would consequently contain the phosphorus atom as the spirocenter of a triazaphosphole and a six-membered ring, can be excluded in view of the observed coupling of C-5 to two phosphorus atoms. Trimerisations of this type via the exocyclic double bond have been observed for the products from 1,2,3-triazaphospholes and diazomethane or phenyl azide [1].

The trimer **7** consists of a six-membered cyclotriphosphazane ring to which three dihydrotriazaphosphole rings are anellated. Nonanellated cyclophosphazanes are mostly four-membered, but six- and eight-membered ones are also known [10]. By the oligomerization of endocylic P=N bonds of azaphospholes, only tetramers have been clearly identified so far [1]. Structurally investigated were tetramers of triazaphospholes [11,12] and a $[Cr(CO)_5]_2$ complex thereof [13], as well as the $[Fe(CO)_5]_4$ complex [14] and the tetraoxide [15] of a 1,3,2-oxazaphosphole tetramer. Compound **7** seems to be the first derivative of an azaphosphole trimer of this type.

The ring size of the azaphosphole oligomers is governed by the need for coplanar pairs of exocyclic bonds at adjacent phosphorus and nitrogen atoms of the phosphazane ring to be present in order to permit annellation of the azaphosphole ring. Larger phosphazane rings obviously can provide them easily. Therefore, no dimers of azaphospholes are known as long as the phosphorus coordination is ψ-tetrahedral or tetrahedral. For tbp-coordinated phosphorus, on the other hand, only azaphosphole dimers such as **3** are known [16].

While sulfides of cyclo*di*phosphazanes are common [10], there is just one report in the literature about cyclo*tri*phosphazane trisulfides [17]. All representatives show a *trans* structure just as did **7**. While a chair conformation is assumed for them, this cannot be right for **7**. A chair configuration in which all of the equatorial phosphorus bonds have to be used for annellating the triazaphosphole rings (see previous discussion) would inevitably result in a *cis* structure. The more flexible boat conformation, on the other hand, readily provides three pairs of coplanar bonds for annellation and leads by this automatically to the *trans* structure. The S–P–N–P dihedral angles estimated from a model of this conformation increase in the order $P^1\text{-}P^3 < P^2\text{-}P^3 < P^1\text{-}P^2$. If we assume a similar dependence of $^2J_{PP}$ in **7**, as observed for $^2J_{PH}$ in phosphine sulfides [18], (the absolute values of) $^2J_{PP}$ should decrease in the previous order. The assignment of $^2J_{PP}$ and $\delta^{31}P$ given in Table 2 is based on this assumption.

The sulfuration of **1** is reversible: tributylphosphine converts **7** slowly (benzene solution 50°C, 18 hours, 40%) to monomeric **1** again. This is reminiscent of the earlier observed reversible tetramerization of a triazaphosphole by complex formation and decomplexation [13]. From the sulfuration of **1** a minor second product **8** is always observed (Figure 2) in addition to **7**. Its NMR spectra are very similar to those of **7** except for the high field chemical shift of the P^1 signal (Table 2). We therefore assign to **8** the same structure with the sulfur atom at P^1 exchanged for oxygen.

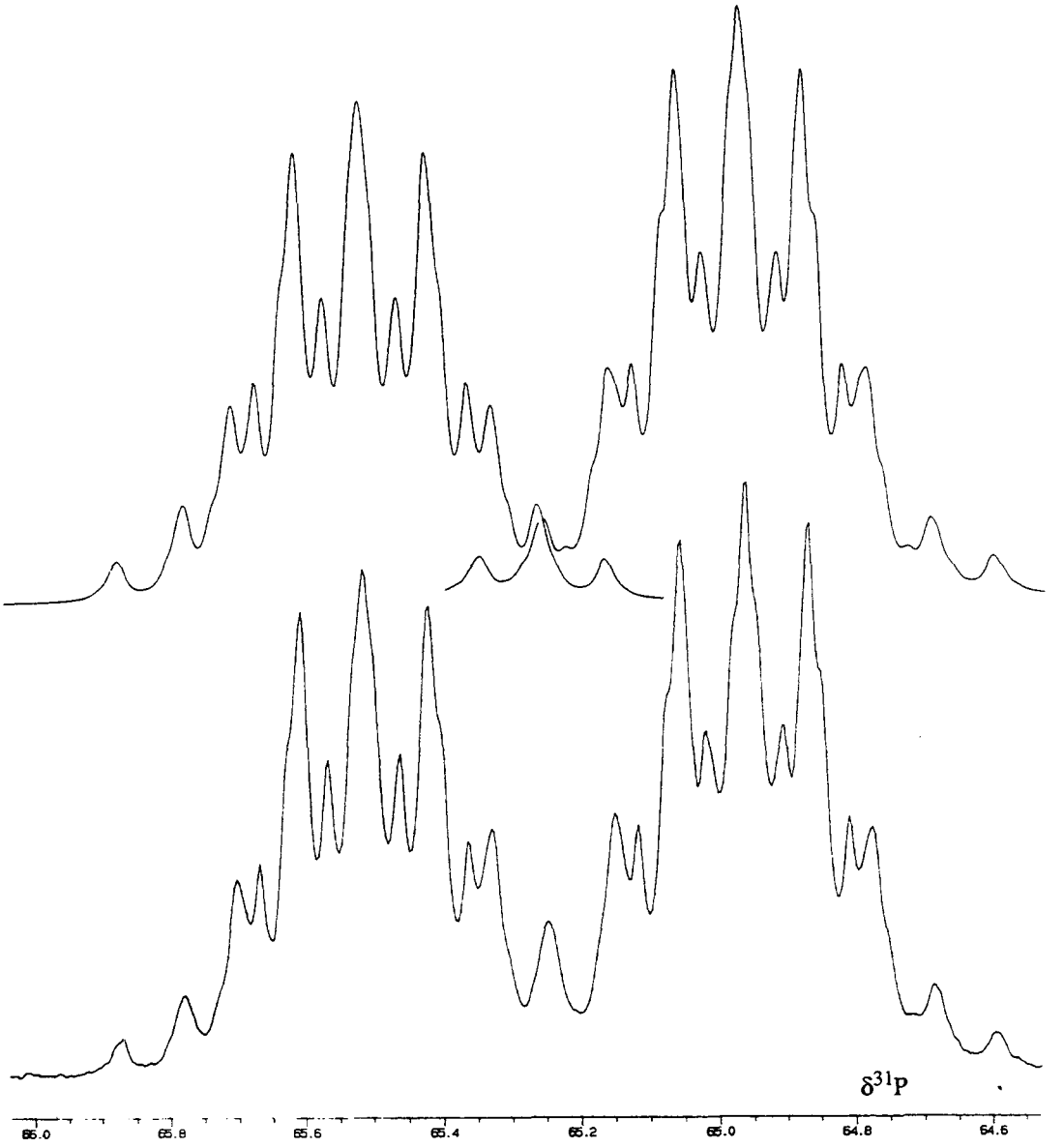
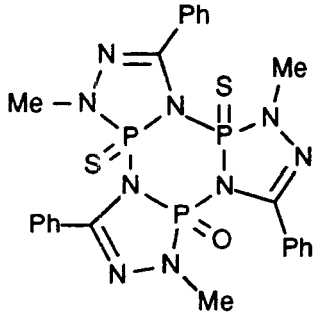


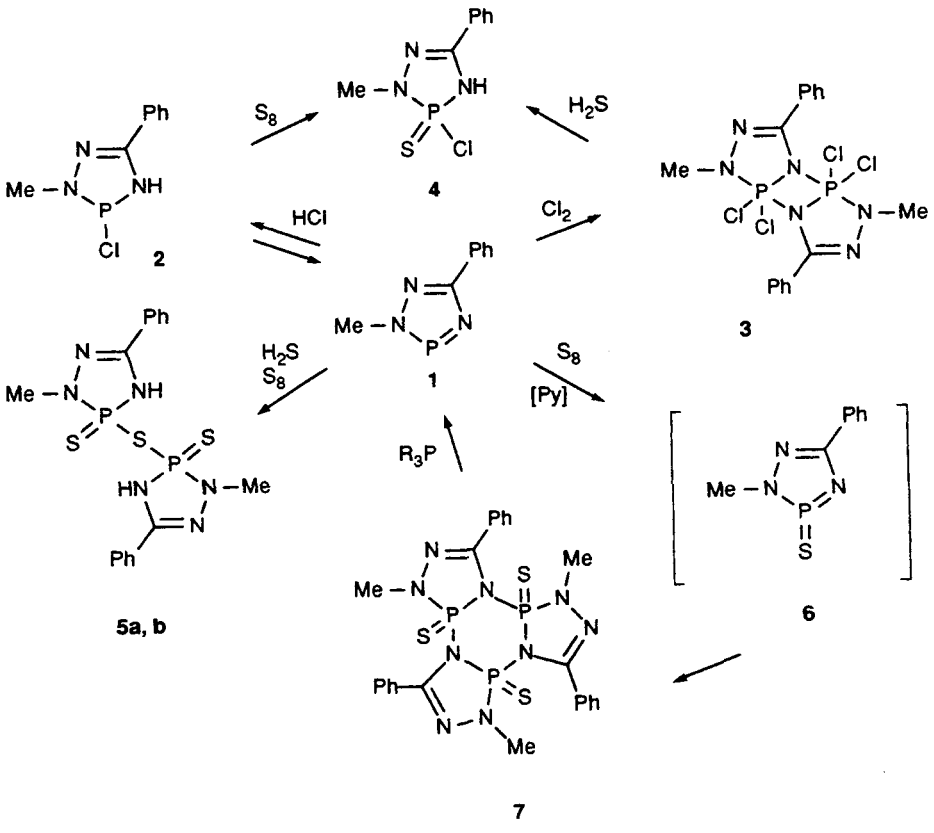
FIGURE 1 Recorded (lower) and calculated (upper) proton coupled ^{31}P NMR signals of **5a** (right) and **5b** (left). A parts of $AA'XX'Y_3Y'_3$ spin systems.



8

EXPERIMENTAL

All manipulations were carried out in dry glass equipment under an argon atmosphere using the Schlenk technique. The solvents were dried according to common methods. Triethylamine was distilled from sodium/benzophenone. PCl_3 was freshly distilled before use. Melting points were determined on a Lintström apparatus and are uncorrected. ^{31}P NMR: JEOL GSX-270 at 109.7 MHz. ^1H and ^{13}C NMR: JEOL EX-400 at 400 MHz and 100.5 MHz, respectively. Chemical shifts refer to 85% H_3PO_4 (^{31}P) as external and TMS (^1H, ^{13}C) as internal standards. The ^{31}P NMR spectra in Figure 1 were calculated using the DAISY program package



SCHEME 1

age [19] on a Cyber 2000 computer at the Leibniz-Rechenzentrum, Munich.

3-Chloro-2-methyl-5-phenyl-dihydro-1,2,4,3-triazaphosphole (**2**) [*5*]

When 1.86 g (10.0 mmol) of N^1-methyl-benzamidrazone hydrochloride [20] and 1.37 g (10.0 mmol) of PCl_3 in 100 mL of benzene were heated to reflux, hydrogen chloride was evolved. After 24 hours, the yellow mixture was filtered and the filtrate evaporated under vacuum. **2** was left as a viscous yellow oil. Yield 90%.

3-Methyl-5-phenyl-1,2,4,3-triazaphosphole (**1**) [*2*]

To 2.14 g (10.0 mmol) of **2** in 100 mL of benzene, 1.01 g (10.0 mmol) of triethylamine in 30 mL of benzene was added. After 1 hour, the precipitated triethylammonium chloride was separated, the filtrate evaporated, and the residue distilled at 100–110°C/0.1 mbar; mp 43–45°C. Yield 1.70 g (96%).

$C_8H_8N_3P$	calcd. C 54.24	H 4.55	N 23.72
(177.1)	found 54.35	4.88	23.59

3-Chloro-2-methyl-5-phenyl-dihydro-1,2,4,3-triazaphosphole-3-sulfide (**4**)

(a) 360 mg (1.69 mmol) of **2** and 54 mg (1.66 mmol) of sulfur formed a clear melt at 155°C, and this was dissolved in 6 mL of acetonitrile. **4** was identified as almost the only product by its ^{31}P NMR spectrum but could not be induced to crystallize from this solution.

(b) Dry H_2S was slowly passed through a suspension of 1.54 g (3.10 mmol) of **3** in 40 mL of dichloromethane, which turned clear after 30 minutes. After 90 minutes, the solvent was removed under reduced pressure and the residue recrystallized from 10 mL of acetonitrile, mp 109–110°C. Yield 1.12 g (73%).

$C_8H_9N_3PSCl$	calcd. C 39.11	H 3.69	N 17.10	S 13.05
(245.7)	found 39.16	4.08	16.87	13.70

2-Methyl-5-phenyl-dihydro-1,2,4,3-triazaphosphole-3-sesquisulfide (**5**)

Dry H_2S was slowly passed through a suspension of 660 mg (3.72 mmol) of **1** and 119 mg (3.72 mmol) of sulfur in 50 mL of acetonitrile. After 18 hours, the mixture was filtered and the filtrate heated and reduced to 8 mL. On cooling, colorless crystals of **5** separated, mp 113–114°C. Yield 470 mg (55%).

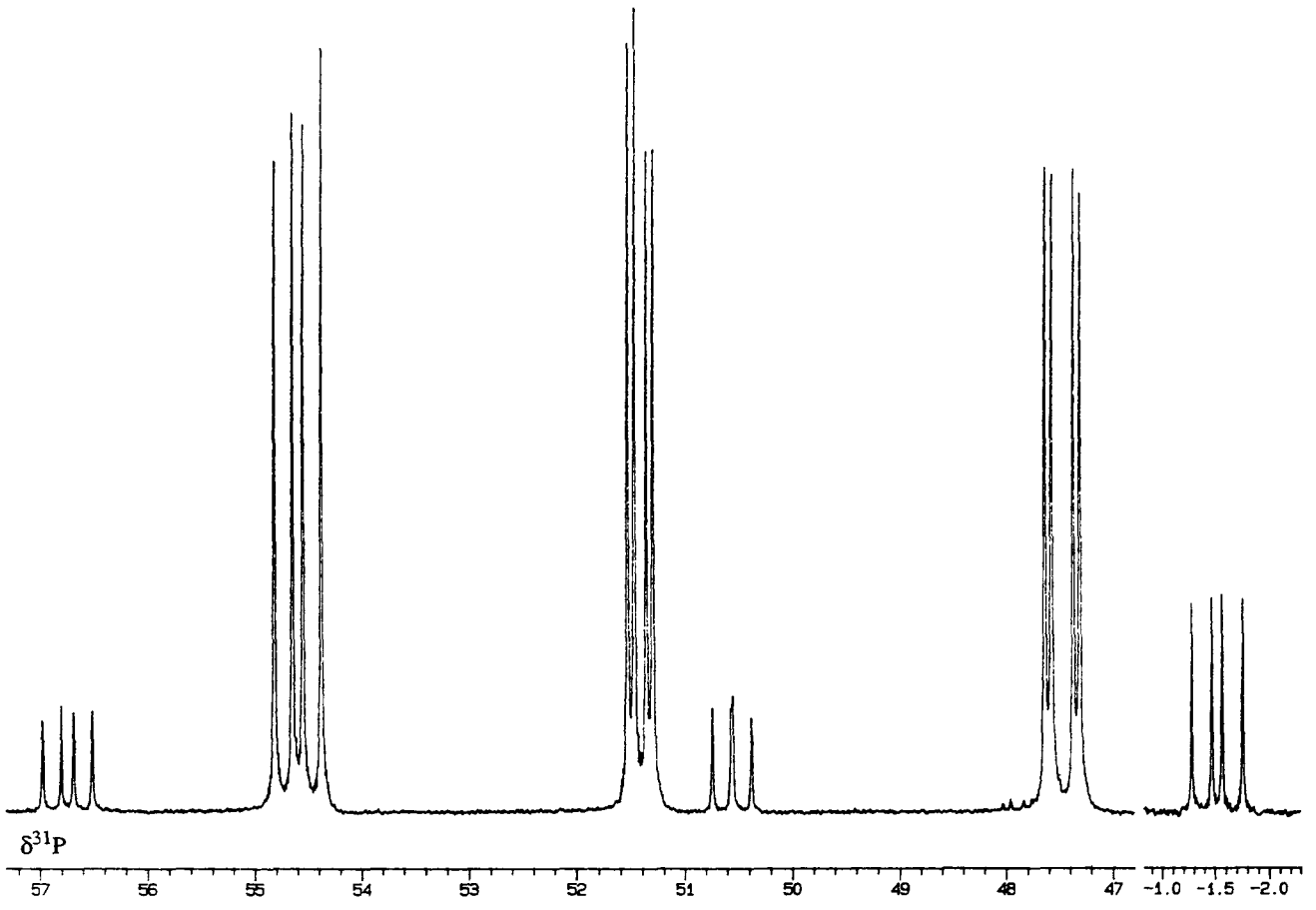


FIGURE 2 $^{31}P\{^{1}H\}$ NMR spectrum of **7** and **8** (minor component).

TABLE 2 NMR Data of Compounds **7** and **8** in $CDCl_3$ (The Numbering of the Three Nonequivalent Triazaphosphole Rings Refers to the Schematic Formula in the Text)

	7			**8**		
Ring	*1*	*2*	*3*	*1*	*2*	*3*
$\delta^{31}P$	47.5	51.4	54.6	−1.5	50.5	56.7
$^{2}J_{PP}$	6.8[a]	18.5[b]	29.5[c]	20.5[a]	19.3[b]	31.8[c] Hz
$\delta^{1}H$ Me[d]	3.24	3.06	2.60	3.35	3.13	2.58
$^{3}J_{PH}$	9.8	11.1	10.1	7.9	10.6	10.7 Hz
$\delta^{13}C$ Me[d]	35.3	33.5	32.4	34.8	33.6	32.9
$^{2}J_{PC}$	9.5	13.3	12.3	13.7	8.1	10.9 Hz
$\delta^{13}C$ C-5[d]	145.2	148.5	149.2	[e]	[e]	[e]
$^{2}J_{PC}$	18.0	18.9	20.4 Hz			
	5.7	3.3	3.3 Hz			

[a]Coupling P^1-P^2, [b]coupling P^2-P^3, and [c]coupling P^1-P^3.
[d]The assignment of the ^{1}H NMR signals was checked by a $^{31}P/^{1}H$-correlated spectrum. The ^{13}C NMR signals are tentatively assigned.
[e]Too low intensity.

The analytical data of **5** were not completely satisfactory.

$C_{16}H_{18}N_6P_2S_3 \cdot 0.25\ CH_3CN$	calcd.	C 42.83	H 4.08	N 18.92	S 20.79
(462.8)	found	43.47	4.17	18.42	20.18

2-Methyl-5-phenyl-1,2,4,3-triazaphosphole-3-sulfide trimer (**7**)

2.17 g (12.3 mmol) of **1** and 1.41 g (44.0 mmol) of sulfur in 20 mL of pyridine were kept at 50°C for 9 days. The pyridine was distilled under vacuum, the residue dissolved in 20 mL of acetonitrile, and the filtered solution cooled to −195°C and then kept at −20°C for 1 day. The resulting crystalline precipitate was separated, washed with cold acetonitrile, and dried; mp 182–186°C. Yield 1.27 g (50%).

$C_{24}H_{24}N_9P_3S_3$	calcd.	C 45.93	H 3.85	N 20.09
(627.6)	found	46.11	3.98	19.85

ACKNOWLEDGMENT

We are grateful to the Fonds der Chemischen Industrie for financial support.

REFERENCES

[1] A. Schmidpeter, K. Karaghiosoff: in M. Regitz, O. J. Scherer; (eds.): *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Thieme Verlag, Stuttgart, 1990, p. 258.

[2] Y. Charbonnel, J. Barrans, *C. R. Acad. Sci. Paris. Ser. C 278*, 1974, 355; Y. Charbonnel, J. Barrans, *Tetrahedron, 32*, 1976, 2039.

[3] J.-M. Alcaraz, F. Mathey, *J. Chem. Soc., Chem. Commun.*, 1984, 508; S. Holand, J.-M. Alcaraz, L. Richard, F. Mathey, *Heteroatom Chem., 1*, 1990, 37.

[4] In the case of a special phosphinine, a reaction with sulfur in benzene at room temperature resulting in a stable monosulfide has also been reported: D. G. Holah, A. N. Hughes, K. L. Knudsen, *J. Chem. Soc., Chem. Commun.*, 1988, 493; A. Hughes, K. L. Knudsen, *Heterocycles, 30*, 1990, 543.

[5] H. Tautz: Thesis, Universität München, München, 1980; A. Schmidpeter, *Phosphorus Sulfur, 28*, 1986, 71.

[6] A. Schmidpeter, J. Luber, H. Tautz, *Angew. Chem., 89*, 1977, 554; *Angew. Chem. Int. Ed. Engl., 16*, 1977, 546.

[7] R. O. Day, R. R. Holmes, H. Tautz, J. H. Weinmaier, A. Schmidpeter, *Inorg. Chem., 20*, 1981, 1222.

[8] An anhydrosulfide corresponding to **5** with S in place of NH and Ph in place of Me, 3,5-diphenyl-dihydro-1,3,4,2-thiadiazaphosphole-2-sesquisulfide, is known from a dissimilar method of synthesis: W. Zeiss, A. Schmidpeter, *Z. Naturforsch. B, 34*, 1979, 1042.

[9] E. Fluck, H. Binder, *Z. Anorg. Allg. Chem., 354*, 1967, 113; M. Meisel: in M. Regitz, O. J. Scherer (eds): *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Thieme Verlag, Stuttgart, 1990, p. 415.

[10] R. Keat: in I. Haiduc, D. B. Sowerby, (eds): *The Chemistry of Inorganic Homo- and Heterocycles*, Academic Press, London, 1987, vol. 2, p. 467.

[11] M. Haddad, F. Dahan, J.-P. Legros, L. Lopez, M.-T. Boisdon, J. Barrans, *J. Chem. Soc., Perkin Trans., 2*, 1992, 671.

[12] C. Malavaud, Th. N'Gando M'Pondo, L. Lopez, J. Barrans, J.-P. Legros, *Can. J. Chem., 62*, 1984, 43.

[13] A. Schmidpeter, H. Tautz, J. von Seyerl, G. Huttner, *Angew. Chem., 93*, 1981, 420; *Angew. Chem. Int. Ed. Engl., 20*, 1981, 408.

[14] A. N. Chernega, M. Yu. Antipin, Yu. T. Struchkov, Yu. V. Balitskii, Yu. G. Gololobov, I. E. Boldeskul, *Zh. Obshch. Khim., 54*, 1984, 271; *J. Gen. Chem. USSR, 54*, 1984, 238.

[15] M. Yu. Antipin, Yu. T. Struchkov, Yu. V. Balitskii, Yu. G. Gololobov, *Zh. Strukt. Khim., 22*, 1981, 98; Yu. G. Gololobov, Yu. V. Balitzki, *Rev. Heteroatom Chem., 6*, 1992, 25.

[16] A. Schmidpeter: in I. Haiduc, D. B. Sowerby (eds): *The Chemistry of Inorganic Homo- and Heterocycles*, Academic Press, London, 1987, vol. 2, p. 617.

[17] W. Zeiss, H. Klehr, *Z. Naturforsch. B, 35*, 1980, 1179.

[18] W. G. Bentrude, W. N. Setzer: in J. G. Verkade, L. D. Quin, (eds): *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, VCH Publishers, Deerfield Beach, FL, 1987, p. 380.

[19] G. Hägele, M. Engelhardt, W. Boenig: QCPE Program No. 518.

[20] M. R. Atkinson, J. B. Polya, *J. Chem. Soc.*, 1954, 3319.