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1,2λ^5-Azaphosphinines and a New 1λ^5,3λ^5-. Diphosphinine

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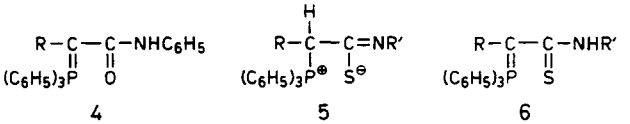
ABSTRACT

The 1,2-azaphosphinine, **9**, *and the 1,3-diphosphinine,* **10**, *can be isolated from a mixture resulting from the reaction of 1,1,3,3-tetrakis(dimethylamino)-1λ^5,3λ^5-diphosphete,* **1**, *and ethyl isothiocyanate. The reaction of* **1** *with phenyl isothiocyanate yields the 1,2-azaphosphinine,* **16**. *Mechanisms for the formation of the compounds* **9**, **10**, *and* **16** *are suggested. The properties, the NMR, mass, and IR spectra, and the molecular and crystal structures of* **9** *and* **10** *are described and discussed.*

INTRODUCTION

In earlier work, we investigated the reaction between 1,1,3,3-tetrakis(dimethylamino)-1λ^5,3λ^5-diphosphete, **1**, and phenyl isocyanate [1]. The first reaction step is believed to be a nucleophilic attack of an ylidic carbon atom of **1** on the carbon atom of the isocyanate group, leading to the intermediate **2** via Equation (1). Compound **2** stabilizes by rearrangement to give the λ^5-azadiphosphinine **3**.

The analogous reaction between C-H-functional phosphorus ylides and isocyanates to give phosphoranylidene acid amides **4** was observed by Trippett and Walker [2]. Bestmann and Pfohl isolated type-**5** betaines by reacting alkylidene-triphenylphosphines with isothiocyanates in which R exerts a +I effect or with ylides 6 having groups R with a −I effect or for R=H [3]. Another reaction of this type between hexaphenylmethylenediphosphorane and phenyl isothiocyanate, leading, according to Birum and Matthews [4], via the isolatable intermediate betaine structure **7** to triphenylphosphoranylideneketenimine **8** and triphenylphosphine sulfide (see Equation (2)), should also be mentioned here.



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Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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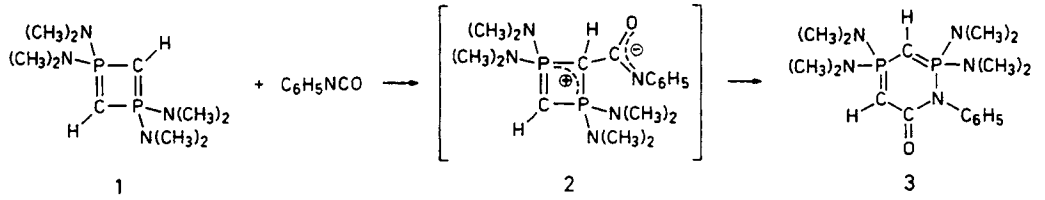
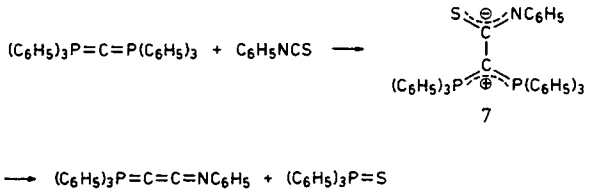


1 2 3 (1)

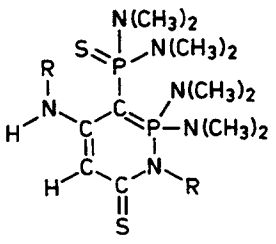


8 (2)

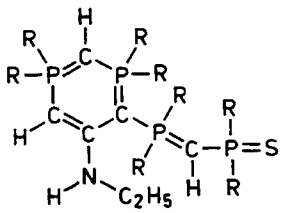
For this reason, and in light of our results of investigations concerning the reaction of **1** with carbon disulfide [5] or carbon oxysulfide [6], we studied the behavior of **1** toward ethyl isothiocyanate and phenyl isothiocyanate.

The Reaction of **1** *with Ethyl Isothiocyanate*

Based on ^{31}P-NMR spectra, equimolar amounts of 1,1,3,3-tetrakis(dimethylamino)-1λ^5,3λ^5-diphosphete, **1**, and ethyl isothiocyanate were observed to react to form a complex mixture of phosphorus-containing compounds, independent of the temperature and the solvent used as the reaction medium. Also, changing the molar ratio of the reactants did not lead to a definitive conversion. Nevertheless, the compounds **9** and **10** could be isolated from the clear, dark yellow to orange-brown reaction solutions. Subsequently, the preparation of **9** and **10** could be somewhat optimized (see Experimental section).



R = C_2H_5 **9**
R = C_6H_5 **16**



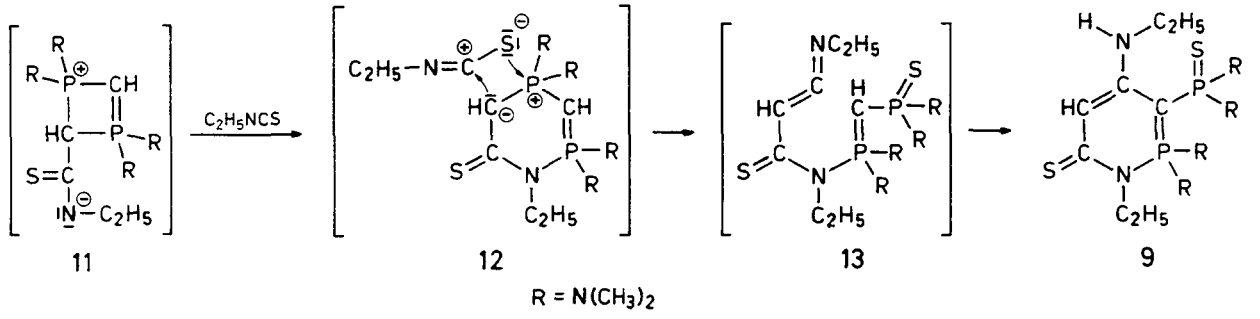
10 R = $N(CH_3)_2$

Compound **9**, (2,2-bis(dimethylamino)-1-ethyl-4-ethylamino-6-thioxo-1,6-dihydro-2λ^5-[1,2]azaphosphinine-3-yl)-phosphonothioic bis(dimethylamide), forms bright yellow crystals that melt at 181°C in a sealed capillary without decomposition, and the compound is readily soluble in $CHCl_3$, CH_2Cl_2, or acetone but less soluble in toluene and tetrahydrofuran. The material is not soluble in diethyl ether and *n*-pentane. Compound **10**, {bis(dimethylamino)-(1, 1, 3, 3-tetrakis(dimethylamino)-5-ethylamino-1λ^5, 3λ^5-[1, 3]diphosphinine-4-yl) - λ^5 - phosphanylidenemethyl}-phosphonothioic bis(dimethylamide), forms colorless crystals that melt at 96°C in a sealed capillary without decomposition. It is quite soluble in toluene, tetrahydrofuran, and $CHCl_3$; fairly soluble in diethyl ether; and poorly soluble in *n*-pentane.

The first step in the reaction of **1** with ethyl isothiocyanate is believed to be a nucleophilic attack on the isothiocyanate by the ylidic ring carbon atom of **1**, as observed in most of the reactions of **1**. In the case of the isothiocyanate, the reaction initiates at the positive carbon atom of this group and leads to the ambivalent intermediate **11** (Schemes 1 and 2). In contrast to the reaction of **1** with phenyl isocyanate, where the −I effect of the phenyl group favors the formation of the nitrogen nucleophile **2** [1], in the case of the ethyl isothiocyanate, the sulfur nucleophile **11** can play a role as well. Reactions of the mesomeric structure at either nucleophilic site may explain the great number of reaction products.

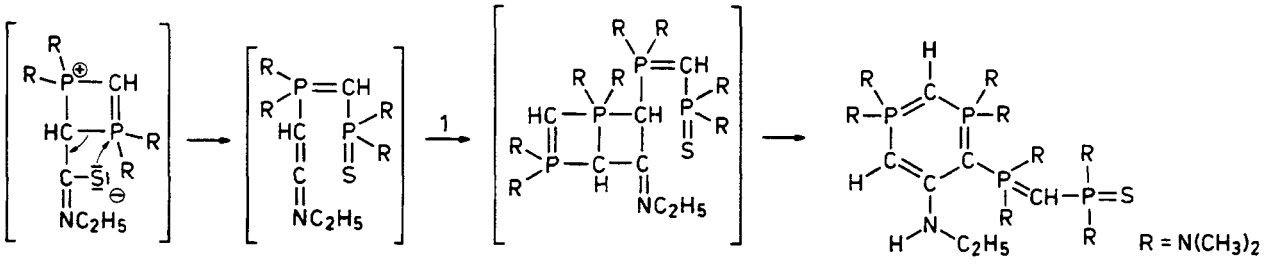
The formation of **9** is thought to proceed by a route schematically shown in Scheme 1: The adduct **11**, analogous to that formed in the reaction between **1** and phenyl isocyanate, initially forms the six-membered heterocycle **12**, which then reacts with a second molecule of ethyl isothiocyanate. It is not clear whether the Wittig reaction indicated in Scheme 1 and resulting in a [2 + 2] cycloaddition proceeds via the acyclic ketenimine **13** to the end product **9** or whether cyclic intermediates are directly and exclusively formed. Spectroscopic evidence for **12** and **13** was not found.

The route proposed for the formation of **10** and schematically depicted in Scheme 2 is highly speculative. The sulfur nucleophile **11** is assumed to react in an intramolecular manner to give the ketenimine **14** which then adds another molecule of diphosphete **1** in a [2 + 2] cycloaddition process to form the bicyclic intermediate **15**. The latter is transformed to the end product **10** by spontaneous valence isomerization. We have frequently observed such cycloaddition processes and subsequent spontaneous valence isomerization reactions [7,8,13].



11 12 13 9

SCHEME 1



11 14 15 10

SCHEME 2

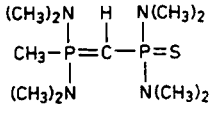
The Reaction of **1** *with Phenyl Isothiocyanate*

The reaction of **1** with phenyl isothiocyanate, just as the one with ethyl isothiocyanate, yields a multitude of phosphorus-containing products. The main product, though, is the 1,2-azaphosphinine **16**, i.e., the phenyl derivative analogous to **9**. Compound **16** forms yellow crystals and melts at 204°C without decomposition. The compound is readily soluble in $CHCl_3$ and CH_2Cl_2 but not in diethyl ether and *n*-pentane.

Reacting **1** with a twofold molar amount of phenyl isothiocyanate in toluene at −50°C quickly yields a yellow suspension that dissolves on warming to room temperature. In contrast to the reaction of **1** with ethyl isothiocyanate, the proposed zwitterionic nitrogen nucleophile analogous to **11** (see Scheme 1) is suspected to be metastable at lower temperatures, favored by the −I effect of the phenyl group. The structure of **16** could be confirmed by NMR and mass-spectrometric investigations.

The NMR Spectra of **9**, **10**, *and* **16**

The $^{31}P\{^1H\}$ NMR spectra of **9** and **16** exhibit two doublets each, which at low field strengths are assigned to the $SP[N(CH_3)]_2$ groups and the others to the endocyclic phosphorus atoms P_X (see Table 1, where the atoms are identified). This can be concluded from the ^{31}P chemical shifts of the thiophosphoryldiamide groups of compounds **17** (δ82.5; [9]) and $SP[N(CH_3)_2]_2R$, where R = C_6H_5 (δ81.7) or $N(CH_3)_2$ (δ82.0) [10]. $\delta^{31}P_x$ of **9** and **16** are within the ^{31}P shift range of the 2λ⁵,4λ⁵-diphosphapyridines (1,2λ⁵,4λ⁵-azadiphosphinines) [11,12].



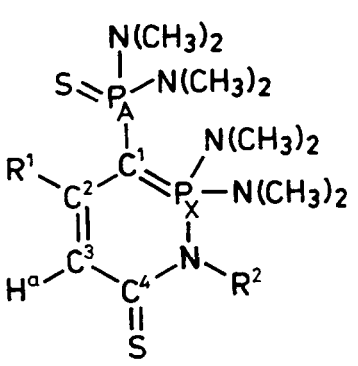
17

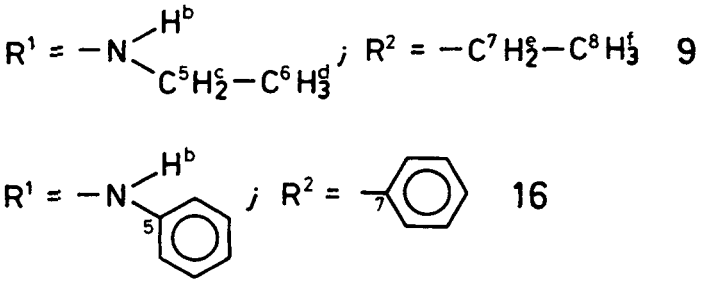
In the $^{13}C\{^1H\}$ NMR spectra of **9** and **16**, only the C^1 carbon atoms exhibit four lines each, the splitting values of which suggest two $^1J(PC)$ coupling constants. The individual $^1J(PC)$ values can be definitively determined from the $^{31}P\{^1H\}$ NMR spectra with the help of the ^{13}C satellite multiplets.

^{13}C-DEPT measurements identified the three endocyclic carbon atoms C^i, i = 1, 2, 4, and the C^3H^a methine groups of the two heterocycles. As expected, $\delta^{13}C^4$ lies within the $^{13}C{=}S$ shift range of thioamides, the C^4 carbon atom of **9** having the same value for the ^2J and ^4J couplings to the endo- and exocyclic phosphorus atom, respectively. The H^b triplet in the ^1H-NMR spectrum of **9** is noticeably broadened. ^1H homodecoupling experiments revealed $^3J(H^bH^c)$ and confirmed a splitting, found in the ^1H coupled ^{31}P NMR spectrum of **9**, as a $^4J(P_AH^a)$ coupling.

The $^{31}P\{^1H\}$ NMR spectrum of the C^4,C^5-disubstituted 1λ⁵,3λ⁵-diphosphabenzene **10** shows a AMRX spin system. The ^{31}P chemical shifts were

TABLE 1 NMR Spectral Data of the 1,2λ^5-Azaphosphinines **9** and **16** in $CDCl_3$ at 300 K





	δ/ppm[a]		9	16		J/Hz		9	16
^{31}P:	P_A		78.5	78.5	^{1}J:	C^1P_A		139.0	134.8
	P_X		51.0	48.7		C^1P_X		171.7	165.4
^{13}C:	C^1		51.0	53.7	^{2}J:	P_AP_X		67.5	65.1
	C^2		156.8	154.7		$C^2P_{A,X}$[f]		11.4	13.2
	C^3		96.9	100.8				2.9	3.2
	C^4		180.1	185.8[b]		C^4P_X		1.3	<0.3
	C^5		37.6	141.8[c,d]		C^7P_X		3.4	2.2
	C^6		14.4	—					
	C^7		41.4	140.4[d]					
	C^8		15.3	—	^{3}J:	$C^3P_{A,X}$[f]		8.8	8.6
								8.2	5.8
						C^8P_X		1.1	—
^{1}H:	H^a		5.89	6.21		H^bH^c		4.6	—
	H^b		8.09	10.13[e]		H^cH^d		7.2	—
	H^c		3.15			H^eH^f		6.9	—
	H^d		1.10			P_XH^e		7.1	—
	H^e		3.99						
	H^f		1.28						
					^{4}J:	C^4P_A		1.3	<0.3
						$C^5P_{A,X}$[f]		1.9	2.6
								<0.2	<0.3
						P_AH^a		5.8	5.2

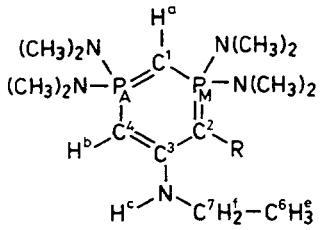
[a]Range of δ^{13}C and δ^1H of dimethylamino groups of **9**: 36.9–37.4 ppm and 2.43–2.61 ppm, respectively, and of **16**: 37.0–37.4 ppm and 2.50–2.68 ppm, respectively.
[b]Triplet.
[c]Broadened doublet (by a factor of about 2).
[d]δ^{13}C range of remaining phenyl carbon atoms: 123.7–130.4 ppm.
[e]δ^1H (phenyl) between 7.0 and 7.4 ppm.
[f]Not assigned.

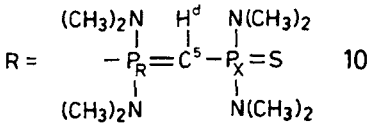
assigned to the phosphorus atoms by means of the splitting pattern and the number of ^{13}C satellite multiplets of the four ^{31}P line groups (see Table 2, which also identifies the atoms for the NMR parameters). $\delta^{31}P_A$ and $\delta^{31}P_M$ lie within the narrow shift interval of these λ^5-diphosphinines [8,13]. $\delta^{31}P_R$ and especially $\delta^{31}P_X$ of the thiophosphoryl group of the C^4 substituent with a PCPS framework differ only slightly from the respective δ^{31}P values of compound **17** (4.6 or 1.4 ppm upfield shift relative to **17** [9]). In contrast to the C^4,C^5-bisdiphenylphosphinoyl substituted diphosphabenzene, a $^4J(P_AP_R)$ long-range coupling could be detected [14].

The seven ^{1}J(PC) coupling constants, recognized by their characteristic values in the $^{13}C\{^1H\}$ NMR spectrum, and the highfield position of the ^{13}C lines of the ylidic carbon atom C^1, and the downfield position of the ^{13}C multiplet of C^3 expected for λ^5-diphosphinines confirm the structure of **10** [8,13]. ^{13}C-DEPT spectroscopy showed two endocyclic quaternary carbon atoms. One of these exhibits two ^{1}J(PC) coupling constants, and, therefore, the substituent group $-R_2PCHP(S)R$, R = $N(CH_3)_2$, is positioned on the heterocycle at this carbon atom (C^2). This assignment cannot be made definitely on the basis of the individual, tabulated J(PP) values.

The H^a and C^5 atoms are deshielded compared

TABLE 2 NMR-Parameter of the 1λ⁵, 3λ⁵-Diphosphabenzene Derivative **10** in C_6D_6 at 300 K





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		δ/ppm[a]			J/Hz
^{31}P:	P_A	54.9	^1J:	C^1P_A	134.1
	P_M	64.7		C^1P_M	134.1
	P_R	59.1		$C^2P_{M,R}$[f]	149.2
	P_X	81.1			145.2
				C^4P_A	148.8
				C^5P_R	166.8
^{13}C:	C^1	3.9		C^5P_X	152.4
	C^2	44.7			
	C^3	165.1			
	C^4	46.5	^2J:	P_AP_M	63.9
	C^5	25.2		P_MP_R	37.7
	C^6	15.0		P_RP_X	46.1
	C^7	38.7[b]		$C^3P_{A,M,R}$[f]	21.4
					18.2
					1.5
^1H:	H^a	0.63		$P_{A,M}H^a$	13.4
	H^b	—[c]			7.9
	H^c	6.50[d]			
	H^d	1.55[e]			
	H^e	1.03	^3J:	C^1P_R	5.6
	H^f	2.92		$C^2P_{A,X}$[f]	9.9
					1.4
				$C^4P_{M,R}$[f]	10.0
					3.5
				C^5P_M	<0.3
				H^eH^f	7.2
				H^cH^f	2.2
			^4J:	P_AP_R	2.6
				$C^7P_{A,M,R}$	<0.5
				H^aH^b	3.7

[a] Range of $\delta^{13}C$ and δ^1H of dimethylamino groups: 37.2–39.2 ppm and 2.4–2.9 ppm, respectively (four doublets, in each case).
[b] Broadened singlet (by a factor of about 2).
[c] Multiplet, partially hidden under four $N(CH_3)_2$ lines at about 2.85 ppm.
[d] Doublet (total linewidth about 15 Hz; see text).
[e] Doublet (splitting 4.7 Hz; total linewidth 20 Hz).
[f] Not assigned.

with the analogous data of **17**, in contrast to P_R and P_X (shown earlier) [9]. The resonance lines of the hydrogen atoms H^c and H^d in the ^1H-NMR spectrum at 300 K are noticeably broadened (see Table 2). This suggests a restricted rotation of the monoethylamino group around the C^3N axis, which, in turn, may be due to the bulky second substituent at the heterocycle or a partial double-bond character of the C^3N bond (coalescence temperature: 333 K). The NMR-spectroscopically determined structure of **10** was confirmed by a crystal structure analysis.

The Molecular and Crystal Structures of **9** *and* **10**

Figures 1 and 2 each give a perspective view of the structures **9** and **10**, respectively, together with the appropriate numerical schemes. Compound **9** crystallizes in the orthorhombic space group Pbca with

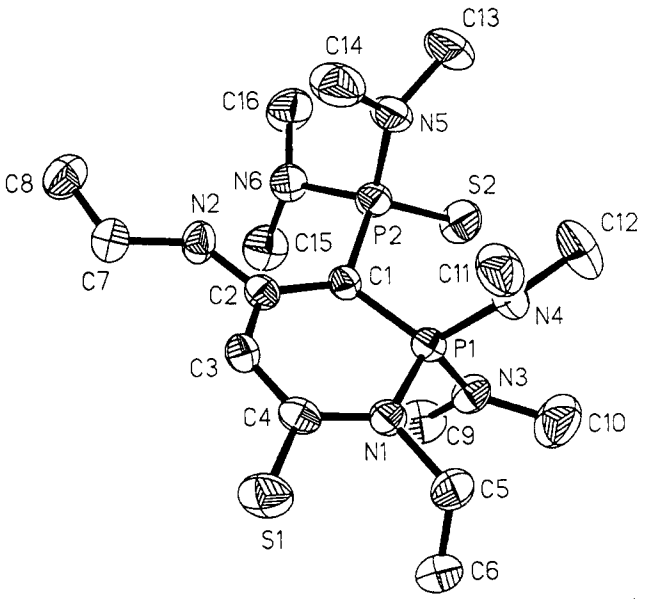

FIGURE 1 Molecular structure of **9**. The thermal ellipsoids are drawn on the 50% probability level.

TABLE 3 Selected Bond Lengths [pm] and Angles [°] for Molecule **9** (Standard Deviations in Parentheses)

S1–C4	170.6 (2)	S2–P2	195.4 (1)
P1–N1	166.3 (2)	P1–N3	162.4 (2)
P1–N4	163.6 (2)	P1–C1	172.5 (2)
P2–N5	165.6 (2)	P2–N6	169.7 (2)
P2–C1	179.5 (2)	N1–C4	141.0 (3)
N1–C5	148.3 (3)	N2–C2	135.1 (3)
N2–C7	144.3 (3)	C1–C2	143.7 (3)
C2–C3	140.3 (3)	C3–C4	137.8 (3)
N1–P1–N3	108.8 (1)	N1–P1–N4	104.2 (1)
N1–P1–C1	106.4 (1)	N3–P1–N4	105.2 (1)
N3–P1–C1	113.7 (1)	N4–P1–C1	118.0 (1)
S2–P2–N5	111.1 (1)	S2–P2–N6	111.2 (1)
S2–P2–C1	116.1 (1)	N5–P2–N6	106.2 (1)
N5–P2–C1	107.5 (1)	N6–P2–C1	104.0 (1)
P1–N1–C4	125.6 (1)	P1–N1–C5	114.5 (2)
C4–N1–C5	119.7 (2)	C2–N2–C7	127.3 (2)
P1–C1–P2	115.6 (1)	P1–C1–C2	118.5 (1)
P2–C1–C2	124.5 (1)	N2–C2–C1	119.8 (1)
N2–C2–C3	117.3 (2)	C1–C2–C3	122.9 (2)
C2–C3–C4	127.4 (2)	S1–C4–N1	119.9 (1)
S1–C4–C3	121.7 (2)	N1–C4–C3	118.4 (2)

eight molecules per unit cell and compound **10** in the triclinic space group $P\bar{1}$ with two molecules per unit cell. Details of both crystal structure determinations are summarized in Table 5 and in the Experimental section.

The heterocyclic six-membered rings of compounds **9** and **10** can be considered to be planar with a maximal deviation of the best plane of 6.7 and 7.0 pm, respectively, as has been found in similar phosphinines [20–22] and diphosphinines [7,23,24]. This fact indicates the existence of an extended delocalized π system, which is further confirmed by the length of the C–C bonds (averaging

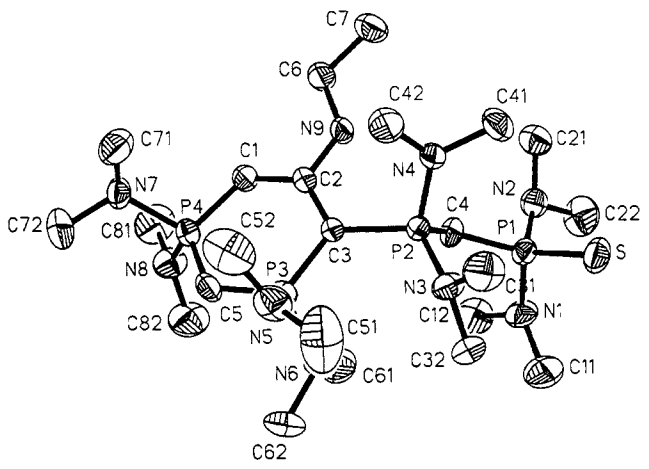

FIGURE 2 Molecular structure of **10**. The thermal ellipsoids are drawn on the 50% probability level.

TABLE 4 Selected Bond Lengths [pm] and Angles [°] for Molecule **10** (Standard Deviations in Parentheses)

S–P1	196.6 (1)	P1–N1	167.4 (2)
P1–N2	169.4 (2)	P1–C4	172.9 (3)
P2–N3	165.9 (2)	P2–N4	168.3 (2)
P2–C3	178.6 (2)	P2–C4	168.8 (3)
P3–N5	167.8 (3)	P3–N6	168.2 (3)
P3–C3	174.1 (2)	P3–C5	169.9 (3)
P4–N7	168.6 (2)	P4–N8	166.2 (2)
P4–C1	170.2 (2)	P4–C5	167.5 (3)
N9–C2	137.4 (3)	N9–C6	143.8 (4)
C1–C2	139.5 (4)	C2–C3	145.6 (3)
S–P1–N1	110.3 (1)	S–P1–N2	113.7 (1)
S–P1–C4	116.6 (1)	N1–P1–N2	99.0 (1)
N1–P1–C4	111.6 (1)	N2–P1–C4	104.6 (1)
N3–P2–N4	104.0 (1)	N3–P2–C3	114.6 (1)
N3–P2–C4	111.9 (1)	N4–P2–C3	103.9 (1)
N4–P2–C4	113.7 (1)	C3–P2–C4	108.5 (1)
N5–P3–N6	100.1 (1)	N5–P3–C3	116.2 (1)
N5–P3–C5	106.1 (1)	N6–P3–C3	110.2 (1)
N6–P3–C5	111.9 (1)	C3–P3–C5	111.8 (1)
N7–P4–N8	98.2 (1)	N7–P4–C1	106.7 (1)
N7–P4–C5	116.4 (1)	N8–P4–C1	115.0 (1)
N8–P4–C5	112.1 (1)	C1–P4–C5	108.4 (1)
C2–N9–C6	125.4 (2)	P4–C1–C2	127.2 (2)
N9–C2–C1	116.0 (2)	N9–C2–C3	116.9 (2)
C1–C2–C3	127.1 (2)	P2–C3–P3	121.2 (1)
P2–C3–C2	118.9 (2)	P3–C3–C2	119.8 (2)
P1–C4–P2	133.2 (2)	P3–C5–P4	124.7 (1)

TABLE 5 Crystal Parameters and Details of Structure Determination of **9** and **10**

Diffractometer used	Four circle diffractometer CAD4
Radiation	Cu-$K\alpha$ (graphite monochromator)
Measuring range	$2° < \Theta < 60°$ (**9**); $2° < \Theta < 65°$ (**10**)
Procedure	ω-Scans
Corrections	Lorentz and polarization factor; empirical absorption correction μ = 38.4 cm^{-1} (**9**), 34.7 cm^{-1} (**10**); extinction correction [15]
Structure solution	Direct methods [15]
Refinement method	Least-squares
Restrictions	CH_3 and CH_2 groups tetrahedral with C-H 96 pm and H-C-H 109.5°; C–H planar with C–H 96 pm.
Programs used	SHELXTL [15], PLATON [16], SCHAKAL [17]
Scattering factors	[18,19]

Compound	**9**	**10**
Crystal system, space group	Orthorhomic, Pbca	Tr clinic, $P\bar{1}$
Lattice constants	a = 14.872 (1) pm b = 15.845 (1) pm c = 19.813 (1) pm $\alpha = \beta = \gamma = 90°$	a = 10.354 (2) pm b = 10.908 (1) pm c = 15.701 (2) pm α = 92.62 (1)° β = 99.84 (1)° γ = 103.30 (1)°
Volume	4669 × 10^{16} pm^3	1694 × 10^{16} pm^3
Formula units	8	2
Density (calculated)	1.25 g/cm^3	1.21 g/cm^3
Temperature	292 K	292 K
Selected reflections for determination of unit cell constants	24	24
Number of		
(a) measured reflections	8589	6092
(b) independent reflections	3957	5740
(c) unobserved reflections	605 [$\|F_o\| < 4\sigma(\|F_o\|)$]	710 [$\|F_o\| < 4\sigma(\|F_o\|)$]
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.036	0.039
$wR = \left(\frac{\Sigma(w(\|F_o\| - \|F_c\|))^2}{\Sigma(w\|F_o\|)^2}\right)^{1/2}$	0.034	0.041

139 pm; bond lengths and angles, see Tables 3 and 4). Only compound **10** and a number of asymmetrically substituted analogs [7,23] exhibit significantly shorter and (between the electron withdrawing substituents) longer C–C bonds. To these substituents, in the case of compounds **9** and **10**, belong NH-Et groups, originating from the ethyl isothiocyanate. They are linked to the phosphinine rings by C–N bonds with a distinct double bond character (135.1 and 137.1 pm). The shorter distance of the N atoms from the plane of the rings (13 and 2.7 pm) serves as an additional indication for their electronic involvement with the π systems of the rings. Compounds **9** and **10** possess similar thiophosphine groups that also show an agreement with their geometric parameters. The sole exception is the P–C bond that due to its partial ylidic character in compound **10**, is rather short (172.9 pm). A similar length is observed for the endocyclic P1–C1 bond in compound **9** (172.5 pm), while the quasi-ylidic group P3–C5–P4, which is completely incorporated into the heterocyclic system, exhibits an even shorter P–C bond length (169.9 and 167.5 pm). These values are in good agreement with those in comparably substituted compounds [7,23].

EXPERIMENTAL

All operations were performed under an argon blanket. The handling equipment was evacuated to 10^{-3} Torr and flooded with dry high-purity argon. The solvents were dried by the usual procedures and saturated with argon.

The NMR spectra were taken with AM200 (^{1}H: 200.132 MHz) and AC250 (^{1}H: 250.133 MHz) NMR spectrometers of Bruker Analytische Meβtechnik GmbH, Rheinstetten. The δ^{31}P chemical shifts were referenced to 85% aqueous orthophosphoric acid as external standard, while δ^{13}C and δ^1H were referred to tetramethylsilane (TMS) (using in each

TABLE 6 Abstracts of the EI Mass Spectrum of **10** at 70 eV and 430 K (Me= CH_3; Et=C_2H_5; R=$P(NMe_2)_2$ $CHP(S)(NMe_2)_2$)

m/e	Relative Intensity (%)	Fragment
615	42.5	M^+
571	15.2	$[M - NMe_2]^+$; $[M - HNEt]^{+a}$
528	64.8	$[M - 2NMe_2 + H]^+$; $[M - NMe_2 - HNEt + H]^{+a}$
526	18.5	$[M - HNEt - H]^+$
483	11.7	$[M - 3NMe_2]^+$
438	18.1	$[M - 4NMe_2 - H]^+$
421	10.3	$[M - SP(NMe_2)_2 - NMe_2 + H]^+$
407	15.9	$[M - CHP(S)(NMe_2)_2 - NMe_2]^+$
333	10.6	$[M - R + H]^+$
332	14.4	$[M - R]^+$
288	10.0	$[M - R - NMe_2]^{+a}$
244	13.9	$[M - R - 2NMe_2]^+$
166	12.7	$[CHP(S)(NMe_2)_2 + 2H]^+$
119	100	$[P(NMe_2)_2]^+$
90	15.5	$[CH_3PNMe_2]^{+b}$
76	41.3	$[PNMe_2 + H]^+$
44	39.8	$[NMe_2]^+$

[a] NMe_2 and HNEt are indistinguishable.
[b] See mass spectrum of **17** [9].

case the respective signals of the deuterated solvents with the usual sign convention).

The mass spectra of **9**, **10**, and **16** (shown later and in Table 6) were recorded with a Varian type MAT711 spectrometer. The molecular peaks of the compounds exhibit high intensity: **9**: 100% (70 eV, sample temperature, 445 K); **10**: 42.5% (70 eV, 430 K); **16**: 53.9% (70 eV, 340 K).

The IR spectra were registered with Perkin Elmer type 283, 684, and 883 spectrometers.

The experimental details of the crystal structure determinations on compounds **9** and **10** can be seen in Table 5 [25].

(2,2-Bis(dimethylamino)-1-ethyl-4-ethylamino-6-thioxo-1,6-dihydro-2λ⁵-[1,2]azaphosphinine-3-yl)-phosphonothioic Bis(dimethylamide) **9**

1.5 g (5.7 mmol) of **1** was dissolved in 10 mL toluene; 1.0 g (11.5 mmol) of ethyl isothiocyanate in 10 mL toluene was slowly added drop by drop under stirring to the −30°C precooled solution. Then the reaction mixture was warmed to room temperature, followed by stirring for 2 hours and removal of the solvent under reduced pressure. The brown, oily residue was first washed with 20 mL of pentane and then extracted three times with 20 mL of diethyl ether each time. Upon adding 5 mL tetrahydrofuran to the mother liquor, the major portion of **9** crystallized within 12 hours. After several more days, some more of the bright yellow, crystalline material precipitated. Yield: 1.15 g (46.0%); mp 181°C; anal calcd for $C_{16}H_{36}N_6P_2S_2$ (438.6): C, 43.82; H, 8.27; N, 19.17. Found: C, 43.81; H, 8.41; N, 19.40.

IR Spectrum. Rubbing in nujol between CsBr discs (in cm^{-1}): 3215 vw, 3182 vw, 1574 vs, 1565 sh, 1557 w, 1545 w, 1510 vs, 1505 sh, 1335 m, 1315 sh, 1300 sh, 1283 vs, 1188 m, 1175 sh, 1170 s, 1165 sh, 1126 m, 1077 s, 1070 m, 1048 w, 1018 s, 1007 m, 987 vs, 977 vs, 931 s, 912 m, 889 w, 769 s, 749 s, 633 s, 622 s, 585 vw, 536 s, 491 m, 477 s, 458 vs (where vs = very strong, s = strong, m = middle, w = weak, vw = very weak, b = broad, and sh = shoulder).

Abstracts of the EI Mass Spectrum (70 eV; 445 K). *m/e* 438 (100%; M^+), 393 (13.4; $[M\text{-}HNEt\text{-}H]^+$ or $[M\text{-}NMe_2\text{-}H]^+$), 351 (42.0; M-EtNCS), 350 (23.5; $[M\text{-}2NMe_2]^+$), 306 (16.7; $[M\text{-}3NMe_2]^+$), 151 (8.3; $[SP(NMe_2)_2]^+$), 119 (31.0; $[P(NMe_2)_2]^+$), 76 (30.0; $[PNMe_2 + H]^+$), 44 (24.9; $[NMe_2]^+$).

{Bis(dimethylamino)-(1,1,3,3-tetrakis(dimethylamino)-5-ethylamino-1λ⁵,3λ⁵-[1,3]diphosphinine-4-yl)-λ⁵-phosphanylidenemethyl}-phosphonothioic Bis(dimethylamide), **10**

A solution of 0.33 g (3.8 mmol) ethyl isothiocyanate in 10 mL toluene was added at room temperature slowly to 2.0 g (7.6 mmol) of **1** in 5 mL of toluene under stirring. When the reaction mixture was slightly warmed, its color changed from dark yellow to brown. After the mixture had been stirred for about 2 hours at room temperature, the solvent was removed by distillation under reduced pressure. The residue was extracted three times with 20 mL of diethyl ether each time. Pure **10** precipitated from 5 mL of the concentrated extract after several days at −28°C. The light yellow, nearly colorless crystals melt at 96°C. Yield: 0.65 g (27.9%); anal calcd for $C_{23}H_{57}N_9P_4S$ (615.7): C, 44.87; H, 9.33; N, 20.47. Found: C, 45.18; H, 9.64; N, 20.82.

IR Spectrum. Rubbing in nujol between CsBr discs (in cm^{-1}): 3170 vw, 1580 w, 1306 s, 1295 sh, 1195 sh, 1169 s, 1090 sh, 1067 m, 969 vs, 915 w, 891 m, 845 vw, 807 w, 668 m, 602 m, 558 w.

Refer to Table 6 for EI mass spectrum.

(4-Anilino-2,2-bis(dimethylamino)-1-phenyl-6-thioxo-1,6-dihydro-2λ⁵-[1,2]azaphosphinine-3-yl)-phosphonothioic Bis(dimethylamide) **16**

1.1 g (8.1 mmol) of phenyl isothiocyanate was added under stirring to a −50°C precooled solution of 1.0 g (3.8 mmol) of **1** in 10 mL of toluene. The yellow suspension, formed after a short time, was gradually allowed to warm (within 6 hours) to room temperature. The reaction mixture was then stirred

for several additional hours while it turned yellow. The toluene was distilled off under reduced pressure. The residue was thoroughly washed with diethyl ether, and the remaining solid was purified by recrystallization from 3 mL of toluene/tetrahydrofuran at −16°C, yielding an intensely yellow-colored, crystalline powder with a melting point of 204°C. Yield: 0.7 g (34.5%) Anal calcd for $C_{24}H_{36}N_6P_2S_2$ (534.6): C, 53.91; H, 6.79; N, 15.72. Found: C, 53.82; H, 6.76; N, 15.79.

IR Spectrum. Rubbing in nujol between CsBr discs (in cm^{-1}): 1573 s, 1510 vs, 1334 m, 1300 sh, 1282 s, 1170 s, 1135 sh, 1126 m, 1077 s, 1070 sh, 1047 w, 1018 s, 987 vs, 980 sh, 931 s, 889 w, 769 s, 749 s, 634 m, 622 m, 536 w, 491 vw, 477 w, 459 s, 379 w, 344 w.

Abstracts of the EI Mass Spectrum (70 eV; 340 K). *m/e* 534 (53.9%; M^+), 489 (18.9; $[M\text{-}NMe_2\text{-}H]^+$), 446 (25.9; $[M\text{-}2NMe_2]^+$), 402 (9.8; $[M\text{-}3NMe_2]^+$), 383 (38.3; $[M\text{-}SP(NMe_2)_2]^+$), 339 (13.7; $[M\text{-}SP(NMe_2)_2\text{-}NMe_2]^+$), 151 (7.7; $[SP(NMe_2)_2]^+$), 122 (25.7; $[PNC_6H_5]^+$), 119 (35.9; $[PNMe_2]^+$), 77 (23.2; $[C_6H_5]^+$), 76 (39.4; $[PNMe_2+H]^+$), 44 (100; $[NMe_2]^+$).

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