Chemistry of the 1,3,5-Triaza-2-phosphorin-4,6-diones, Part XII*. Synthesis and Characterization of 2-Phenyl-2-(*p*-tolylthio)-1,3,5-trimethyl-1,3,5-triaza-4,6-dione-2-phosphorinonium Salts

Vasily A. Pinchuk, Ion Neda, Christian Müller, Holger Thönnessen, Peter G. Jones, Reinhard Schmutzler**

Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, 38023 Braunschweig

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1,3,5-Trimethyl-Substituted 1,3,5-Triaza-4,6-dione-2-phosphorinonium Derivatives, Intramolecular Rearrangement, NMR Spectra, X-Ray

The reaction of 1,5-bis(trimethylsilyl)-1,3,5-trimethylbiuret (**1**) with *p*-tolylsulfenyl chloride (**2**) furnished 1-(*p*-tolylthio)-5-trimethylsilyl-1,3,5-trimethylbiuret (**3**). In the reaction of **3** with phenyldichlorophosphine, 2-phenyl-2-(*p*-tolylthio)-1,3,5-trimethyl-1,3,5-triaza-4,6-dione-2-phosphorinonium chloride (**4**) was formed. The same product was obtained from the reaction of 2-phenyl-1,3,5-trimethyl-1,3,5-triaza-2λ^3- phosphorin-4,6-dione (**6**) with *p*-tolylsulfenyl chloride (**2**). Compound **4** was isolated and characterized in the form of the hexachloroantimonate (**4a**). The spirophosphorane 2-phenyl-1,3,5-trimethyl-1,3,5-triaza-7,10-dioxa-8,9-perchlorobenzo-2λ^5-phosphaspiro-[4.5]decan-4,6-dione (**7**) was prepared by the reaction of **4** with tetrachloroorthobenzoquinone. The new products were characterized by ^{1}H- and ^{13}C NMR spectroscopy, elemental analysis, ^{31}P NMR spectroscopy in the case of **4a**, **6** and **7**, and mass spectrometry (**4a**). Single-crystal X-ray structural analyses of compounds **4a** and **7** were conducted. The phosphorus atom of **4a** has the expected tetrahedral geometry, with a rather short P-S bond of 204.9(2) pm. In **7** the geometry at phosphorus is almost ideal trigonal bipyramidal. Weak hydrogen bonds are formed from a C(:O) group to deuterochloroform of solvation.

Introduction

The first compound involving the 1,3,5-trimethyl-1,3,5-triaza-2λ^4-phosphorin-4,6-dione ring system was obtained in 1966 by H. P. Latscha as a by-product of the reaction of phosphorus pentachloride with N,N'-dimethylurea [1]. In the last three years a large number of 1,3,5-triorgano-1,3,5-triaza-2-phosphorin-4,6-diones, involving phosphorus with coordination numbers from 3 to 5, have been described (see refs. [2–6] and the literature cited therein). These investigations focused on the reactions of 1,3,5-triaza-2λ^3-phosphorin-4,6-diones with oxidizing agents, *e.g.* hexafluoroacetone and tetrachloroorthobenzoquinone, leading to spirophosphoranes, 1,3,5-triaza-7,10-dioxa-8,8,9,9-tetrakis(trifluoromethyl)-2λ^5-phosphaspiro[4.5]decan-4,6-diones and 1,3,5-triaza-7,10-dioxa-8,9-perchlorobenzo-2λ^5-phosphaspiro[4.5]-decan-4,6-diones, respectively [3–5].

Recently we reported an unusual intramolecular rearrangement that took place during the phosphorylation of N-arylthio-N,N'-diorgano-N'-(trimethylsilyl)ureas with dichlorophosphines [7, 8]. The resulting compounds were shown to be four-membered cyclic phosphoranes, the 2-arylthio-2-chloro-1,2,3-triorgano-1,3,2λ^5-diazaphosphetidin-4-ones. We wished to find out if the same kind of rearrangement would be possible in the field of biuret-phosphorus heterocycles, leading, in this case, to the corresponding six-membered cyclic compounds.

Results and Discussion

1,5-Bis(trimethylsilyl)-1,3,5-trimethylbiuret (**1**) was allowed to react with *p*-tolylsulfenyl chloride **2** in a 1:1 molar ratio (Scheme 1). The reaction was carried out in dichloromethane and occurred instantaneously at 0°C, resulting in 1-(*p*-tolylthio)-5-trimethyl-silyl-1,3,5-trimethylbiuret (**3**). This

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* For parts 1–10 see ref. [6] and the literature cited therein, part 11: Z. Naturf. **51b,** in press.

** Reprint requests to R. Schmutzler.

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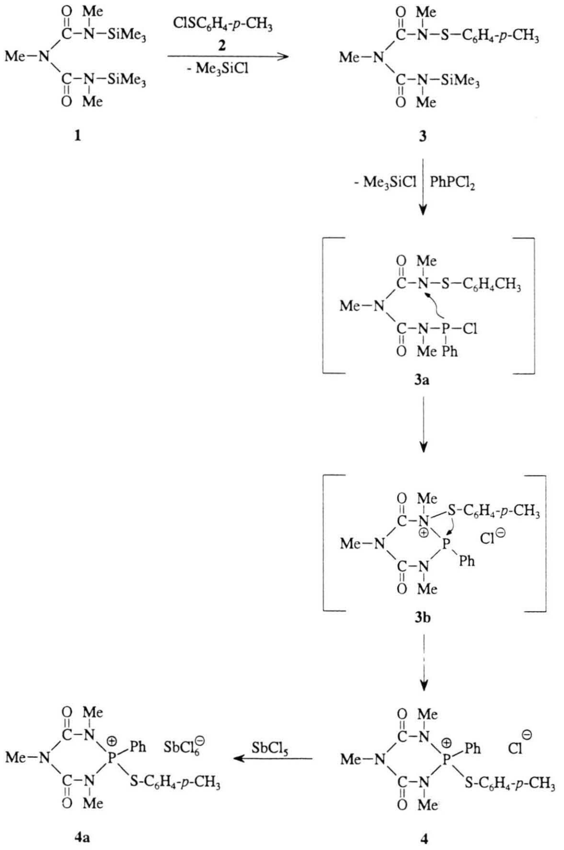
product was characterized by ^1H and ^{13}C NMR spectroscopy and by elemental analysis (see Experimental section), and was used in the subsequent phosphorylation reaction without further purification.

2-Phenyl-2-(*p*-tolylthio)-1,3,5-trimethyl-1,3,5-triaza-4,6-dione-2-phosphorinonium chloride (**4**) was obtained through phosphorylation of the derivative **3** with phenyldichlorophosphine. Its formation was observed in the ^{31}P NMR spectrum ($\delta(^{31}P) = 69.46$), but it proved to be unstable and was finally isolated in the form of the hexachloroantimonate **4a** (Scheme 1). In the ^1H NMR spectrum a doublet for the $P(NCH_3)_2$ groups and a singlet due to the $((O:)C)_2NCH_3$ protons were observed (see Experimental section). As for the urea-based compounds [7, 8], both $\delta(^{13}C)$ values of the C(:O) groups of **4a** lie to higher field than those of the acyclic educt **3** (see Experimental Part). In the FAB-MS mass spectrum (NBA matrix) a $[cation]^+$ peak of 100% intensity was observed. The fragmentation is presented in the Experimental section.



Scheme 1. Synthesis and mechanism of formation of compound **4**.

The proposed mechanism of formation of the cyclic derivative **4** is similar to that of thiochlorophosphoranes [7, 8]. The chloroaminophosphine **3a** is first formed and then undergoes rearrangement. The first stage involves an electrophilic attack of phosphorus at nitrogen, resulting in an increase of electrophilicity of sulphur, which subsequently attacks phosphorus (Scheme 1). It should be emphasized that in this case the phosphonium salt is formed, whereas in the case of N,N'-disubstituted urea derivatives the formation of phosphoranes (the 1,3,2λ^5-diazaphosphetidin-4-ones) was observed. This illustrates the special stabilizing influence of diazaphosphetidine rings on pentacoordinated phosphorus.

For the thiophosphonium salt **4a** a single-crystal X-ray structure analysis was conducted (Fig. 1, Tables I, II and III). The asymmetric unit consists of a phosphonium cation and a hexachloroantimonate anion. The phosphorus atom has a somewhat distorted tetrahedral coordination geometry, with the largest deviations from ideal angles for N(1)-N-P(3) 102.7(2)° and N(1)-P-C(6) 113.9(2)°; the phosphorus atom lies 23 pm out of the plane formed by N(1), N(2), N(3), C(2) and C(4) (mean deviation of 1 pm), which subtends with the phenyl group C(6)-C(11) and the *p*-tolyl group C(21)-C(27) interplanar angles of 66° and 28°, respectively. Both P-N bond lengths [P-N(1) 164.3(3) pm, P-N(3) 164.5(3) pm] are of the same order as for the biuret-based heterocycles described previously

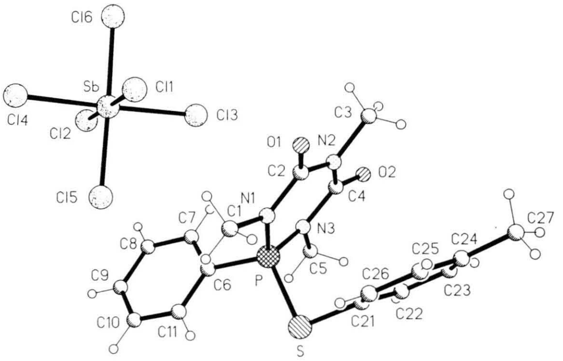


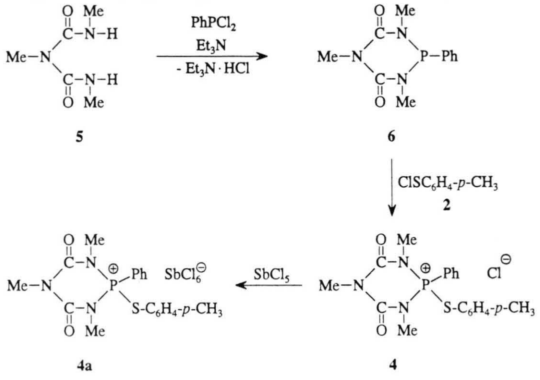
Fig. 1. The formula unit of compound **4a** in the crystal (excluding solvent).

Table I. Summary of X-ray data for compounds **4a** and **7**.

Compound	**4a**·0.5 CH_2Cl_2·0.5 CH_3CN	**7**·2 $CDCl_3$
Formula	$C_{19.5}H_{23.5}Cl_7N_{3.5}O_2PSSb$	$C_{19}H_{14}Cl_{10}D_2N_3O_4P$
M_r	771.85	737.87
Crystal habit	colourless prism	colourless tablet
Crystal size (mm)	0.50×0.50×0.25	0.96×0.60×0.28
Temperature (°C)	−130	−100
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Cell constant		
a (pm)	1058.7(2)	791.7(4)
b (pm)	1199.9(2)	1240.1(5)
c (pm)	1217.4(2)	1512.5(7)
α (°)	96.85(3)	80.17(3)
β (°)	91.77(3)	76.69(3)
γ (°)	102.88(3)	80.13(3)
U (nm^3)	1.4942(5)	1.4103(11)
Z	2	2
D_x ($Mg\ m^{-3}$)	1.716	1.738
μ (mm^{-1})	1.697	1.079
$F(000)$	764	740
Absorption correction	psi-scans	
min and max. trans.	0.692 and 0.980	
$2\theta_{max}$(°)	50	50
No. of reflns.:		
measured	6307	5224
independent	5275	4823
R_{int}	0.010	0.027
$wR(F^2$, all refl.)	0.120	0.220
$R(F, > 4\sigma(F))$	0.042	0.073
No. of parameters	327	337
S	1.056	1.115
max. Δ/σ	<0.001	<0.001
max. $\Delta\varrho$ (e nm^{-3})	1422	855

[3, 4] and for *tert*-butyl-dimethylamino-phenyl-*p*-tolylthiophosphonium tetraphenylborate [8]. The P-S bond [204.9(2) pm] is shorter than in the thiophosphonium salt in ref. [8] (207.37(9) pm).

Compound **4** could also be obtained via another route, namely the reaction of 2-phenyl-1,3,5-trimethyl-1,3,5-triaza-2λ^3-phosphorin-4,6-dione **6** with *p*-tolylsulfenyl chloride **2** (Scheme 2). Reactions of sulfenyl chlorides with compounds of trivalent phosphorus leading to phosphonium salts have been thoroughly studied [9, 10]. Compound **6** was obtained by the usual method [2] viz. the reaction of 1,3,5-trimethylbiuret **5** with phenyldichlorophosphine in the presence of triethylamine (Scheme 2). All the spectroscopic data of **6** are comparable to those of the related 2-organo-substituted triazaphosphorinediones [2], and are presented in the Experimental Section.



Scheme 2. Alternative synthesis of compound **4**.

The reaction of 2-phenyl-2-(*p*-tolylthio)-1,3,5-trimethyl-1,3,5-triaza-4,6-dione-2-phosphorinonium chloride (**4**) with tetrachloroorthobenzoquinone in refluxing toluene resulted in the formation of the spirocyclic phosphorane, 2-phenyl-1,3,5-trimethyl-1,3,5-triaza-7,10-dioxa-8,9-perchloro-benzo-2λ^5-phosphaspiro[4.5]decan-4,6-dione (**7**) (eq. (1)). Its $\delta(^{31}P)$ value of -29.5 ppm is characteristic of compounds of this class (see, *e.g.*, [3–5]). Com-

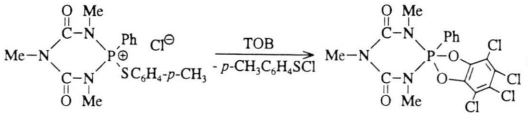
Table II. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2 x 10^{-1}) for compound **4a**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
P	1275.7(8)	2281.0(7)	−2947.3(7)	26.1(2)
S	1242.4(10)	1127.6(9)	−4337.7(8)	37.5(2)
O(1)	4343(3)	2707(3)	−1101(3)	54.7(8)
O(2)	3322(3)	5221(3)	−3284(3)	59.3(9)
N(1)	2366(3)	2177(3)	−1999(2)	29.6(6)
N(2)	3800(3)	3955(3)	−2203(3)	46.4(9)
N(3)	1761(3)	3622(3)	−3200(3)	31.1(6)
C(1)	2152(4)	1097(4)	−1480(3)	40.9(9)
C(2)	3561(4)	2940(4)	−1723(3)	38.9(9)
C(3)	5104(5)	4733(6)	−1899(7)	93(2)
C(4)	2998(4)	4328(3)	−2917(4)	39.9(9)
C(5)	954(4)	4028(4)	−4026(3)	41.2(9)
C(6)	−324(3)	2034(3)	−2505(3)	28.4(7)
C(7)	−748(4)	2962(3)	−1953(3)	32.5(8)
C(8)	−2015(4)	2780(3)	−1622(3)	37.4(8)
C(9)	−2838(4)	1696(4)	−1832(4)	42.3(9)
C(10)	−2400(4)	771(4)	−2361(4)	43.4(10)
C(11)	−1152(4)	930(3)	−2702(4)	35.9(8)
C(21)	2941(4)	1571(3)	−4550(3)	33.1(8)
C(22)	3380(4)	2472(4)	−5146(4)	44.9(10)
C(23)	4707(5)	2821(4)	−5267(4)	53.0(11)
C(24)	5582(4)	2263(4)	−4821(4)	46.2(10)
C(25)	5089(4)	1338(4)	−4253(4)	44.1(9)
C(26)	3776(4)	981(4)	−4112(3)	39.1(9)
C(27)	7026(5)	2631(5)	−4939(5)	68.1(15)
Sb	700.0(2)	2970.9(2)	1705.4(2)	28.5(1)
Cl(1)	2481.3(12)	2108.3(11)	1857.5(11)	54.9(3)
Cl(2)	−1044.0(11)	3879.1(9)	1539.5(11)	50.4(3)
Cl(3)	1726.8(11)	3977.2(9)	290.9(8)	45.1(3)
Cl(4)	−286.9(12)	1990.1(10)	3148.5(9)	50.3(3)
Cl(5)	−389.5(11)	1421.4(8)	398.6(8)	43.6(3)
Cl(6)	1762.9(10)	4527.3(8)	3052.5(8)	38.1(2)
C(99)	5833(12)	1701(11)	960(9)	68(3)
Cl(98)	5715(4)	1561(4)	2403(3)	97.3(12)
Cl(99)	5244(5)	306(3)	275(3)	115(2)
N(99)	5545(9)	728(9)	2419(8)	59(2)
C(97)	5646(10)	1312(9)	1692(9)	50(2)
C(96)	5780(11)	2408(9)	1112(9)	59(3)

Table III. Selected bond lengths [pm] and angles [°] for compound **4a**.

P−N(1)	164.3(3)	P−N(3)	164.5(3)
P−C(6)	176.5(4)	P−S	204.9(2)
S−C(21)	179.4(4)	O(1)−C(2)	120.6(5)
O(2)−C(4)	119.4(5)	N(1)−C(2)	139.2(5)
N(1)−C(1)	148.4(5)	N(2)−C(4)	137.6(6)
N(2)−C(2)	138.8(6)	N(2)−C(3)	149.2(6)
N(3)−C(4)	140.0(5)	N(3)−C(5)	149.3(5)
N(1)−P−N(3)	102.7(2)	N(1)−P−C(6)	113.9(2)
N(3)−P−C(6)	110.4(2)	N(1)−P−S	111.63(12)
N(3)−P−S	111.82(12)	C(6)−P−S	106.46(13)
C(21)−S−P	95.55(13)	C(2)−N(1)−C(1)	115.3(3)
C(2)−N(1)−P	126.3(3)	C(1)−N(1)−P	117.6(3)
C(4)−N(2)−C(2)	128.6(3)	C(4)−N(2)−C(3)	116.4(4)
C(2)−N(2)−C(3)	115.0(4)	C(4)−N(3)−C(5)	115.6(3)
C(4)−N(3)−P	125.5(3)	C(5)−N(3)−P	117.2(3)
O(1)−C(2)−N(2)	122.6(4)	O(1)−C(2)−N(1)	120.3(4)
N(2)−C(2)−N(1)	117.1(3)	O(2)−C(4)−N(2)	122.3(4)
O(2)−C(4)−N(3)	120.2(4)	N(2)−C(4)−N(3)	117.5(3)
C(7)−C(6)−C(11)	120.7(3)	C(7)−C(6)−P	118.5(3)
C(11)−C(6)−P	120.8(3)		

pound **7** is the first of its type for which a single crystal X-ray analysis has been conducted (Fig. 2, Tables I, IV, V).



(1)

4 **7**

The sum of the squares of the angle deviation at phosphorus from idealised values determines the degree of distortion from trigonal bipyramidal or square planar geometry [11]. This sum in the case of **7** amounts to 293.45 (TBP) or 1819.31 (SQP), and thus the geometry at phosphorus is only slightly distorted from trigonal bipyramidal. The equatorial angles vary from 110.5(2)° [N(1)-P-C(1)] to 125.4(2)° [O(1)-P-C(1)]. The angles between axial and equatorial substituents vary from 85.8(2)° [O(1)-P-N(3)] to 94.9(2)° [N(3)-P-C(1)]. The axial bonds are markedly longer than the equatorial bonds for chemically equivalent atoms; P-O 178.3(4), 166.2(4), P-N 175.8(5), 168.1(5)°. The heterocycle displays a flattened boat conformation, with P 60 and N2 20 pm out of the plane of the other atoms (mean deviation 1 pm). The interplanar angle to the perchlorobenzo system is 85°. The atom O4 is the recipient for two weak C-H···O hydrogen bonds from the solvent; O4 … D98 215 pm, O4 … D99 (1-*x*, 1-*y*, 1-*z*) 229 pm.

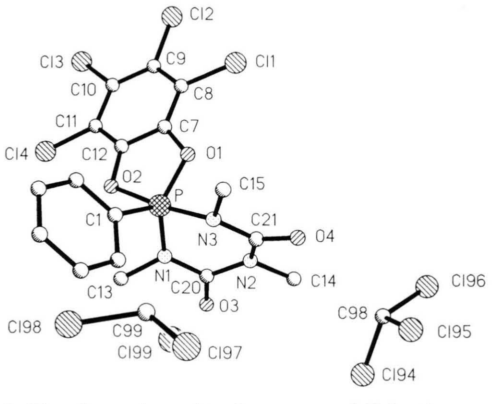


Fig. 2. The formula unit of compound **7** in the crystal. (H atoms omitted for clarity).

Table IV. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2 x 10^{-1}) for compound **7**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
P	5045(2)	3497.6(11)	8291.5(9)	24.4(3)
Cl(1)	3324(2)	97.0(12)	8071.7(12)	41.8(4)
Cl(2)	1896(2)	−1124.8(13)	10051.3(14)	49.2(5)
Cl(3)	1809(2)	−34(2)	11778.0(13)	54.2(5)
Cl(4)	3069(2)	2305.4(14)	11531.3(10)	41.8(4)
Cl(99)	4771(4)	8147(3)	5308(2)	94.9(9)
Cl(98)	1793(3)	9726(2)	5850(2)	78.2(7)
Cl(97)	3237(4)	9571(2)	3922(2)	72.7(7)
Cl(96)	11297(3)	2342.5(13)	3943.4(13)	51.4(5)
Cl(95)	10095(2)	4563.7(15)	3174.8(12)	50.4(5)
Cl(94)	12185(2)	4214.6(13)	4553.5(12)	43.5(4)
O(1)	4415(5)	2328(3)	8174(3)	26.5(8)
O(2)	4214(5)	3193(3)	9493(3)	29.6(9)
O(3)	9943(5)	3062(4)	8310(3)	37.1(10)
O(4)	7747(5)	3046(3)	5857(3)	34.6(10)
N(1)	7014(6)	3583(4)	8496(3)	26.1(10)
N(2)	8649(6)	2801(4)	7188(3)	26.9(10)
N(3)	5805(6)	3647(4)	7096(3)	25.3(10)
C(1)	3690(7)	4826(4)	8294(4)	27.9(12)
C(2)	1959(7)	4949(5)	8781(4)	30.0(12)
C(3)	975(8)	5980(5)	8784(4)	34.8(13)
C(4)	1702(8)	6896(5)	8312(5)	39.7(15)
C(5)	3413(8)	6784(5)	7821(5)	40.0(15)
C(6)	4393(8)	5763(5)	7802(4)	36.1(14)
C(7)	3747(7)	1694(4)	8970(4)	28.4(12)
C(8)	3206(7)	674(5)	9042(4)	32.6(13)
C(9)	2611(7)	144(5)	9921(4)	33.4(14)
C(10)	2536(7)	625(5)	10692(4)	36.1(14)
C(11)	3085(7)	1684(5)	10598(4)	30.0(13)
C(12)	3667(7)	2190(4)	9735(4)	26.7(12)
C(13)	7094(8)	4084(5)	9300(4)	35.3(14)
C(14)	10357(8)	2243(5)	6734(5)	40.2(15)
C(15)	4486(8)	3880(6)	6526(4)	39.1(15)
C(20)	8634(8)	3140(4)	8030(4)	30.2(13)
C(21)	7400(7)	3166(4)	6660(4)	26.9(12)
C(98)	10560(8)	3705(5)	4158(4)	35.4(14)
C(99)	2813(9)	8847(5)	5033(5)	43(2)

Table V. Selected bond lengths [pm] and angles [°] for compound **7**.

P–O(1)	166.2(4)	P–N(1)	168.1(5)
P–N(3)	175.8(5)	P–O(2)	178.3(4)
P–C(1)	180.5(6)	Cl(1)–C(8)	171.7(6)
Cl(2)–C(9)	172.7(6)	Cl(3)–C(10)	172.3(6)
Cl(4)–C(11)	171.6(6)	O(1)–C(7)	136.9(7)
O(2)–C(12)	135.0(6)	O(3)–C(20)	119.1(7)
O(4)–C(21)	121.2(7)	N(1)–C(20)	138.5(7)
N(1)–C(13)	147.5(7)	N(2)–C(21)	138.1(8)
N(2)–C(20)	140.4(8)	N(2)–C(14)	148.1(7)
N(3)–C(21)	137.0(7)	N(3)–C(15)	146.4(8)
C(1)–C(2)	139.5(7)	C(1)–C(6)	139.7(8)
C(7)–C(8)	138.2(8)	C(7)–C(12)	138.5(8)
C(8)–C(9)	139.3(9)	C(9)–C(10)	138.3(9)
C(10)–C(11)	142.7(8)	C(11)–C(12)	136.1(8)
O(1)–P–N(1)	124.0(2)	O(1)–P–N(3)	85.8(2)
N(1)–P–N(3)	93.3(2)	O(1)–P–O(2)	87.5(2)
N(1)–P–O(2)	90.0(2)	N(3)–P–O(2)	173.3(2)
O(1)–P–C(1)	125.4(2)	N(1)–P–C(1)	110.5(2)
(3)–P–C(1)	94.9(2)	O(2)–P–C(1)	89.4(2)
C(7)–O(1)–P	116.0(3)	C(12)–O(2)–P	113.0(3)
C(20)–N(1)–C(13)	113.9(5)	C(20)–N(1)–P	126.8(4)
C(13)–N(1)–P	119.1(4)	C(21)–N(2)–C(20)	125.7(5)
C(21)–N(2)–C(14)	117.1(5)	C(20)–N(2)–C(14)	115.2(5)
C(21)–N(3)–C(15)	113.2(5)	C(21)–N(3)–P	124.5(4)
C(15)–N(3)–P	117.3(4)	C(2)–C(1)–C(6)	118.7(5)
C(2)–C(1)–P	122.0(4)	C(6)–C(1)–P	119.3(4)
O(1)–C(7)–C(8)	126.2(5)	O(1)–C(7)–C(12)	111.9(5)
C(8)–C(7)–C(12)	121.8(5)	O(2)–C(12)–C(11)	127.4(5)
O(2)–C(12)–C(7)	111.2(5)	C(11)–C(12)–C(7)	121.5(5)
O(3)–C(20)–N(1)	122.7(5)	O(3)–C(20)–N(2)	121.5(5)
N(1)–C(20)–N(2)	115.7(5)	O(4)–C(21)–N(3)	123.7(6)
O(4)–C(21)–N(2)	119.7(5)	N(3)–C(21)–N(2)	116.6(5)

Experimental

All experiments were carried out with exclusion of air and moisture; solvents were purified and dried according to the usual methods [12].

NMR: Bruker AC 200 (^{1}H at 200.1 MHz, ^{13}C at 50.3 MHz, ^{31}P at 81.3 MHz); reference substances were $SiMe_4$ (TMS) int. (^{1}H, ^{13}C), 85% H_3PO_4 ext. (^{31}P); high-field shifts were given negative, low-field shifts positive signs.

Materials: 1,5-bis(trimethylsilyl)-1,3,5-trimethylbiuret [13] and *p*-tolylsulfenyl chloride [14] were synthesized according to the procedures described in the literature.

"In vacuo" (i.v.) refers to a pressure of 0.1 Torr, unless otherwise stated.

1,3,5-Trimethylbiuret was a donation from BAYER AG.

1-(p-Tolylthio)-5-trimethylsilyl-1,3,5-trimethylbiuret (**3**)

A solution of *p*-tolylsulfenyl chloride (**2**) (1.08 g, 6.8 mmol) in 5 ml of dichloromethane was added dropwise with stirring at -20°C over 15 min to a solution of 1,5-bis(trimethylsilyl)-1,3,5-trimethylbiuret (**1**) (1.97 g, 6.8 mmol) in 5 ml of dichloromethane. The solvent was removed i.v. and the oily residue was used in subsequent experiments without further purification.

^{1}H NMR ($CDCl_3$): δ = 0.30 (s, $Si(CH_3)_3$), 2.42 (s, $p\text{-}H_3CC_6H_4$), 2.78, 3.04, 3.09 (s, NCH_3), 7.78–8.13 (m, C_6H_4). – ^{13}C NMR ($CDCl_3$): -0.12 (s, $Si(CH_3)_3$), 21.37 (s, $p\text{-}H_3CC_6H_4$), 29.2, 31.9, 32.4 (s, NCH_3), 120.14–135.15 (m, C_6H_4); 163.5, 165.2 (s, $C(:O)$).

$C_{15}H_{25}N_3O_2SSi$ (339.5)
Calcd C 53.06 H 7.42 N 12.38%,
Found C 52.67 H 7.12 N 13.05%.

2-Phenyl-2-(p-tolylthio)-1,3,5-trimethyl-1,3,5-triaza-4,6-dione-2-phosphorinonium hexachloroantimonate (**4a**)

A solution of $PhPCl_2$ (0.82 g, 4.6 mmol) in 3 ml of dichloromethane was added dropwise with stirring at -20°C over 15 min to a solution of **3** (1.56 g, 4.6 mmol) in 3 ml of dichloromethane. The solvent and the volatile by-products of the reaction were removed i.v., and 5 ml of dichloromethane was added to the oily residue. To this solution a solution of $SbCl_5$ (1.4 g, 4.6 mmol) in 5 ml of dichloromethane was added dropwise with stirring at -60°C over 30 min. The solvent was removed i.v. to 1/2, and the product was obtained as colorless crystals after leaving the resulting solution at -20°C for 48 h. Yield 2.87 g (88%), m.p. >200°C.

^{1}H NMR (CD_3CN): δ = 2.41 (d, J(HP) = 2.65 Hz, p-$H_3CC_6H_4$), 2.82 (s, $((O:)C)_2NCH_3$), 3.06 (d, ^{3}J(HP) = 11.26 Hz, $P(NCH_3)_2$), 7.37–8.18 (m, C_6H_4, C_6H_5). – ^{13}C NMR (CD_3CN): δ = 21.32 (s, p-$H_3CC_6H_4$), 31.50 (s, $((O:)C)_2NCH_3$), 32.07 (d, ^{2}J(CP) = 6.55 Hz, $P(NCH_3)_2$), 117.81–139.89 (m, C_6H_4, C_6H_5), 145.76, 149.43 (d, ^{2}J(CP) = 3.70 Hz, 2.28 Hz, (C(:O)). – ^{31}P NMR (CD_3CN): δ = 69.0. – FAB-MS (NBA): *m/z* (%): 374 (100) [Cation]$^+$; 91 (38) $[H_3CC_6H_4]^+$, 77 (40) $[Ph]^+$.

$C_{18}H_{21}Cl_6N_3O_2PSSb$ (708.9)
$[C_{18}H_{21}N_3O_2PS]^+$ (374.4)

Calcd	C 30.50	H 2.99	N 5.93%,
Found	C 29.97	H 2.89	N 5.90%.

2-Phenyl-1,3,5-trimethyl-1,3,5-triaza-2λ³-phosphorin-4,6-dione (**6**)

A mixture of 1,3,5-trimethylbiuret (3.1 g, 21.4 mmol), $PhPCl_2$ (3.8 g, 21.4 mmol), and triethylamine (2.2 g, 21.8 mmol) in 25 ml of toluene was heated with stirring at 80°C for 3 h. The solvent was removed i.v. and 15 ml of diethyl ether and 15 ml of toluene were added to the residue. The precipitate was filtered off and the solvent was removed from the filtrate i.v. To the residue 20 ml of light petroleum ether (b.r. 30–40°C) was added and the product was obtained as a slightly yellow amorphous substance on cooling this solution to -20°C. Yield 3.4 g (63%), m.p. 67–68°C.

^{1}H NMR ($CDCl_3$): δ = 3.03 (s, $((O:)C)_2NCH_3$), 3.18 (d, ^3J(HP) = 12.16 Hz, $P(NCH_3)_2$), 7.14–7.37 (m, C_6H_5). – ^{13}C NMR ($CDCl_3$): 29.79 (s, $((O:)C)_2NCH_3$), 31.02 (d, ^2J(CP) = 6.51 Hz, $P(NCH_3)_2$), 120.43–137.17 (m, C_6H_5), 150.22 (d, ^{2}J(CP) = 8.72 Hz, (C(:O)).- ^{31}P NMR ($CDCl_3$): δ = 70.6.

$C_{11}H_{14}N_3O_2P$ (251.2)

Calcd	C 52.59	H 5.62	N 16.73%,
Found	C 52.10	H 5.63	N 16.64%.

Alternate synthesis of 2-phenyl-2-(p-tolylthio)-1,3,5-trimethyl-1,3,5-triaza-4,6-dione-2-phosphorinonium hexachloroantimonate (**4a**)

A solution of p-tolylsulfenyl chloride (**2**) (0.2 g, 1.26 mmol) in 3 ml of dichloromethane was added dropwise with stirring at 0°C over 15 min to a solution of **6** (0.3 g, 1.26 mmol) in 3 ml of dichloromethane. The solvent was removed i.v. and to the residue 5 ml of dichloromethane was added. To this solution a solution of $SbCl_5$ (0.4 g, 1.26 mmol) in 3 ml of dichloromethane was added dropwise with stirring at -60°C over 15 min. Half of the solvent was removed i.v. and the product was obtained as colorless crystals on leaving the resulting solution at -20°C for 48 h; its physical and spectroscopic data were identical to those of **4a** obtained as above.

2-Phenyl-1,3,5-trimethyl-1,3,5-triaza-7,10-dioxa-8,9-perchlorobenzo-2λ⁵-phosphaspiro-[4.5]-decan-4,6-dione (**7**)

A solution of $PhPCl_2$ (1 g, 5.6 mmol) in 5 ml of dichloromethane was added dropwise with stirring at -20°C over 15 min to a solution of **3** (2.2 g, 5.6 mmol) in 5 ml of dichloromethane. The solvent was removed i.v. and to the oily residue 10 ml of toluene was added. To the resulting solution a solution of tetrachloroorthobenzoquinone (1.37 g, 5.6 mmol) in 5 ml of toluene was added dropwise with stirring at 0°C during 15 min. The reaction mixture was heated for 2h at 110°C. The product was precipitated as a colorless crystalline substance on cooling the reaction mixture to room temperature, and was recrystallized from the same solvent. Yield 1.6 g (57%), m.p. 159–160°C.

^{1}H NMR ($CDCl_3$): δ = 2.92 (d, ^3J(HP) = 9.76 Hz, $P(NCH_3)_2$), 3.34 (s, $((O:)C)_2NCH_3$), 7.48–7.59 (m, C_6H_5); ^{31}P NMR ($CDCl_3$): δ = -29.5.

$C_{17}H_{14}Cl_4N_3O_4P$ (497.1)

Calcd	C 41.08	H 2.84	N 8.45%,
Found	C 41.23	H 2.81	N 8.53%.

X-Ray Crystal Structure Determinations

For a summary of the crystal data: see Table I.

Data collection and reduction: Crystals were mounted on glass fibres in inert oil and transferred to the cold gas stream of the diffractometer (Stoë STADI-4 for **4a**, Siemens P4 for **7**, both with LT-2 low temperature attachment). The cell constants for **4a** were refined from ± ω angles of 56 reflections in the 2θ range 20–23° (monochromated MoK_α radiation). The orientation matrix for **7** was refined from setting angles of 63 reflections in the 2θ range 8–25°.

Structure solution and refinement: The structures were solved by direct methods and refined anisotropically on F^2 (program system: SHELXL-93, G.M. Sheldrick, University of Göttingen). H atoms were included using a riding model or rigid methyl groups. The weighting schemes were of the form $w^{-1} = [\sigma^2(F_o2) + (aP)^2 + bP]$, with $P = (F_o2 + 2F_c2)/3$. For **4a** residual electron density was interpreted as half-occupied dichloromethane and acetonitrile disordered over the same region. Further details of the structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, from where this material may be obtained on quoting the reference numbers CSD 404759 (**4a**) and CSD 404758 (**7**).

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[1] H. P. Latscha, Z. Anorg. Allg. Chem. **346**, 166 (1966).
[2] C. Müller, T. G. Meyer, M. Farkens, R. Sonnenburg, R. Schmutzler, Z. Naturforsch. **47b**, 760 (1992).
[3] I. Neda, M. Farkens, A. Fischer, P. G. Jones, R. Schmutzler, Z. Naturforsch. **48b**, 443 (1993).
[4] M. Farkens, I. Neda, A. Fischer, P. G. Jones, R. Schmutzler, Z. Naturforsch. **48b**, 853 (1993).
[5] M. Farkens, T. G. Meyer, I. Neda, R. Sonnenburg, C. Müller, A. Fischer, P. G. Jones, R. Schmutzler, Z. Naturforsch. **49b**, 145 (1994).
[6] I. Neda, M. Farkens, H. Thönnessen, P. G. Jones, R. Schmutzler, Z. Naturforsch. **50b**, 1833 (1995).
[7] V. A. Pinchuk, I. Neda, C. Müller, A. Fischer, P. G. Jones, Yu. G. Shermolovich, R. Schmutzler, Chem. Ber. **127**, 1395 (1994).
[8] V. A. Pinchuk, C. Müller, A. Fischer, H. Thönnessen, P. G. Jones, R. Schmutzler, L. N. Markovskii, Yu. G. Shermolovich, A. M. Pinchuk, Z. Anorg. Allg. Chem. **621**, 2001 (1995).
[9] E. Kühle, Synthesis **1971**, 563.
[10] I. V. Koval', Uspekh. Khim. **64**, 781 (1995); Russ. Chem. Rev. (Engl. Transl.) **64**, 731 (1995).
[11] W. S. Sheldrick, Top. Curr. Chem. **73**, 1 (1978).
[12] Autorenkollektiv, Organikum, Reprint of the 15th Ed., p. 783; VEB Deutscher Verlag der Wissenschaften, Berlin (1973).
[13] J. F. Klebe, J. B. Bush (Jr.), J. E. Lyons, J. Am. Chem. Soc. **86**, 4400 (1964).
[14] H. Lecher, F. Holschneider, K. Köberle, W. Speer, P. Stöcklin, Ber. Dtsch. Chem. Ges. 58, 409 (1925).