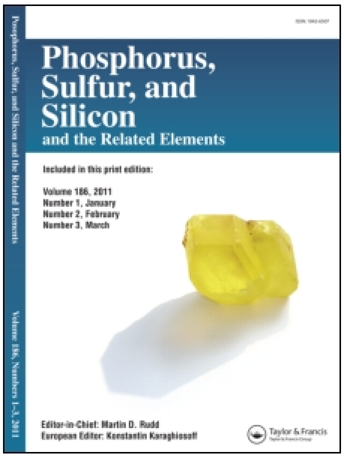


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Reactions Between Aminophosphinyl-Substituted Sulfur Diimides and Amino-Imino-Thiophosphoranes. Cycloaddition or Exchange

Bernd Wrackmeyer[a]; Christian Köhler[a]; Wolfgang Milius[a]; Max Herberhold[a]
[a] Laboratorium für Anorganische Chemie, Universität Bayreuth, Bayreuth, Germany

To cite this Article Wrackmeyer, Bernd , Köhler, Christian , Milius, Wolfgang and Herberhold, Max(1994) 'Reactions Between Aminophosphinyl-Substituted Sulfur Diimides and Amino-Imino-Thiophosphoranes. Cycloaddition or Exchange', Phosphorus, Sulfur, and Silicon and the Related Elements, 89: 1, 151 — 162

To link to this Article: DOI: 10.1080/10426509408020444

URL: http://dx.doi.org/10.1080/10426509408020444

Phosphorus, Sulfur, and Silicon, 1994, Vol. 89, pp. 151-162
Reprints available directly from the publisher
Photocopying permitted by license only

REACTIONS BETWEEN AMINOPHOSPHINYL-SUBSTITUTED SULFUR DIIMIDES AND AMINO-IMINO-THIOPHOSPHORANES. CYCLOADDITION OR EXCHANGE

BERND WRACKMEYER,* CHRISTIAN KÖHLER, WOLFGANG MILIUS and MAX HERBERHOLD*

Laboratorium für Anorganische Chemie, Universität Bayreuth, D-95440 Bayreuth, Germany

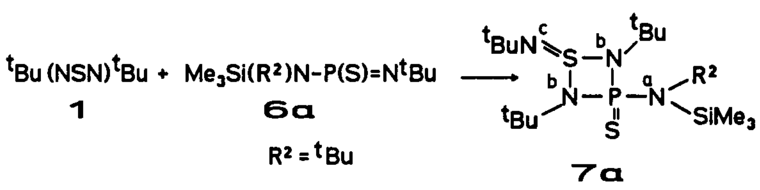
(Received February 3, 1994; in final form March 21, 1994)

Reactions between N,N'-di-tert-butyl sulfur diimide, $^tBu(NSN)^tBu$ (**1**), and the amino-imino-thiophosphoranes $Me_3Si(R)NP(S){=}N^tBu$ [R = ^tBu (**6a**), $SiMe_3$ (**6b**)] afforded the 1,2,4,3-thiadiazaphosphetidines **7a,b** via [2+2]cycloaddition. The corresponding products **8a,b** were obtained when one ^tBu group in **1** was replaced by a 2-(1,3-di-tert-butyl-1,3,2-diazaphosphoridinyl) group (**2**). In contrast, the reactions between **6a** and the three different 2-(1,3-di-tert-butyl-1,3,2-diazaphospholidinyl)-substituted sulfur diimides $[CH_2(N^tBu)]_2P(NSN)R^1$ [R^1 = ^tBu (**3**), Me_3Si (**4**), $[CH_2(N^tBu)]_2P$ (**5**)] gave the same phosphorus compound **9** which was identified as a zwitterionic bicyclic amino-imino-thiophosphorane. Exchange between imino groups at phosphorus and sulfur is the first step in this reaction, followed by 1,3-shifts of Me_3Si and phosphinyl groups and the final intramolecular N—P coordinative stabilization. The products were characterized by multinuclear NMR (^1H-, ^{13}C-, ^{15}N-, ^{29}Si- and ^{31}P NMR). The molecular structures of the cycloadduct **8a** and the zwitterionic compound **9** were determined by single crystal X-ray analyses. In solution, NMR spectra show that **8a** is present as a single isomer in solution, whereas NMR spectra of **9** at 218 K indicate the presence of two isomers (86:14).

Key words: Sulfur diimides; amino-imino-thiophosphoranes; [2+2]cycloaddition; multinuclear NMR; X-ray analyses.

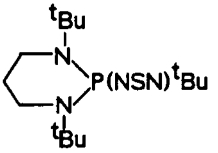
INTRODUCTION

The NSN cumulene system in sulfur diimides (**1**–**5**) is a versatile building block in synthesis.[1] It may function as a Lewis base,[2] it is reactive in cycloadditions,[3] and it undergoes exchange reactions[4] as well as various redox processes.[5] The synthetic potential of sulfur diimides can be further enhanced if functional groups are introduced at one or both nitrogen atoms. In this context we have recently succeeded in preparing aminophosphinyl-substituted sulfur diimides[6] of which the derivatives **2** and **3** are included in this work. In the course of studying reactions of sulfur diimides with unsaturated substrates, we report here on the reactions with amino-imino-thiophosphoranes **6**. It had been found previously[7] that **1** reacts with **6a** to give a $1(\sigma^3\lambda^4)$,2,4,$3(\sigma^4\lambda^5)$-thiadiazaphosphetidine system **7a** via [2+2]cycloaddition [Equation (1)]. We have repeated this reaction in order to collect a more complete set of NMR data.

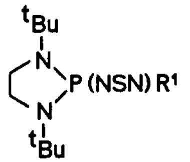


(1)

Furthermore we have investigated the reactivity of the bis(amino)phosphinyl substituted sulfur diimides **2–5** towards **6**. This should provide information about the preferred site of the [2+2]cycloaddition. On the other hand, it was conceivable that the presence of a phosphinyl group as in **2–5** could alter the entire course of the reaction with **6**.



2



3, 4, 5

$R^1 = {}^tBu, SiMe_3, P[N(^tBu)CH_2]_2$

$Me_3Si(R^2)N\text{-}P(S)=N^tBu$

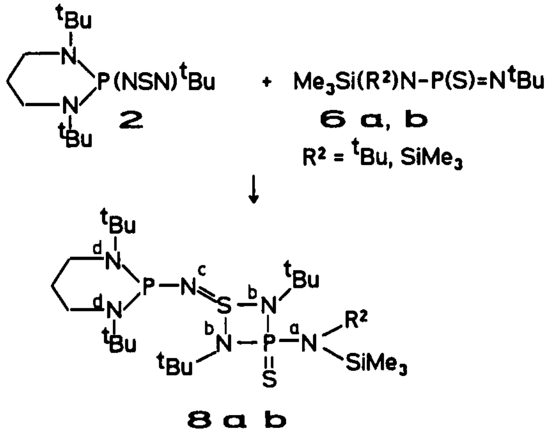
6 a, b

$R^2 = {}^tBu, SiMe_3$

RESULTS AND DISCUSSION

Cycloadditions

The sulfur diimide **1** reacts smoothly with **6a**, as reported,[7] and also with **6b** to give the heterocycles **7a** (R^2 = ^{t}Bu) and **7b** (R^2 = $SiMe_3$), respectively. In the case of the sulfur diimide **2**, the [2+2]cycloaddition products **8a,b** are obtained [Equation (2)]. Apparently, **2** offers selectively the S═N^{t}Bu site for the [2+2]cycloaddition. In each case of **7** and **8**, only one of two possible isomers is formed.



(2)

The structure of the products **7** and **8** in solution follows from a consistent set of ^{13}C-, ^{15}N-, ^{29}Si- and ^{31}P NMR data (Table I). The ^{15}N NMR spectra are particularly informative in this respect, as shown in Figure 1.

X-ray Structure Analysis of **8a**

Recrystallization of **8a** from hexane gave crystals suitable for an X-ray crystal structure analysis. Experimental data are given in Table II, and Table III lists atomic coordinates and anisotropic displacement coefficients. The molecular structure of **8a** is shown in Figure 2, and selected bond lengths and bond angles are given in Table IV. The rhomboidal four-membered ring is non-planar (folding

TABLE I

^{13}C-, ^{15}N-, ^{29}Si- and ^{31}P NMR data[a] of the [2+2]cycloaddition compounds **7** and **8**

	7a	7b	8a	8b
δ^{13}C [b] N^{a}tBu	61.0, 33.9 [6.8], [4.9]	-	61.1, 33.9 [7.1], [4.9]	-
N^{b}tBu	56.7, 30.5 [< 0.5], [3.9]	56.7, 30.3 [1.1], [4.4]	56.7, 30.5 [< 0.5], [4.4; 0.8]	58.7, 30.3 [< 0.5], [4.6; 1.0]
N^{c}tBu	-	-	57.5, 32.7 [< 0.5], [< 0.5]	57.7, 32.7 [1.6], [< 0.5]
N^{d}tBu	-	-	55.4, 30.4 [23.4], [15.3]	55.4, 30.4 [24.5], [14.9]
N^{d}CH$_2$	-	-	38.9 [4.4]	39.0 [4.4]
N^{d}CCH$_2$	-	-	28.6 [< 0.5]	28.5 [< 0.5]
N^{a}SiMe$_3$	10.3 [< 0.5]	6.9 [2.7]	10.3 [1.6]	6.8 [2.7]
N^{a}SiMe$_3$	-	6.5 [2.2]	-	6.3 [2.2]
δ^{15}N [b] N^a	- 269.8 [25.0]	n.o.	- 267.0 [25.1]	-282.5 [25.1]
N^b	- 227.9 [5.5]	- 223.5 [5.1]	- 227.3 [6.6, 2.2]	- 222.8 [6.5, 1.8]
N^c	-188.5 [1.3]	-186.7 [1.1]	[c]	[c]
N^d	-	-	- 306.8 [69.0]	- 306.5 [69.0]
δ^{29}Si	7.0 [12.7]	9.8 , 6.5 [5.9] [4.5]	7.0 [12.9]	9.7, 6.5 [5.9] [3.7]
δ^{31}P	30.1	33.4	86.7[d], 34.1 [4.9], [4.9]	87.0[d], 37.0 [4.9], [4.9]

[a] In C_6D_6; n.o. = not observed; coupling constants $^nJ(^{31}P,X)$ (X = ^{13}C, ^{15}N, ^{31}P) [Hz] are given in square brackets.

[b] Indices a, b, c, d as in Equations (1) and (2).

[c] Not observable by INEPT technique.

[d] P(III).

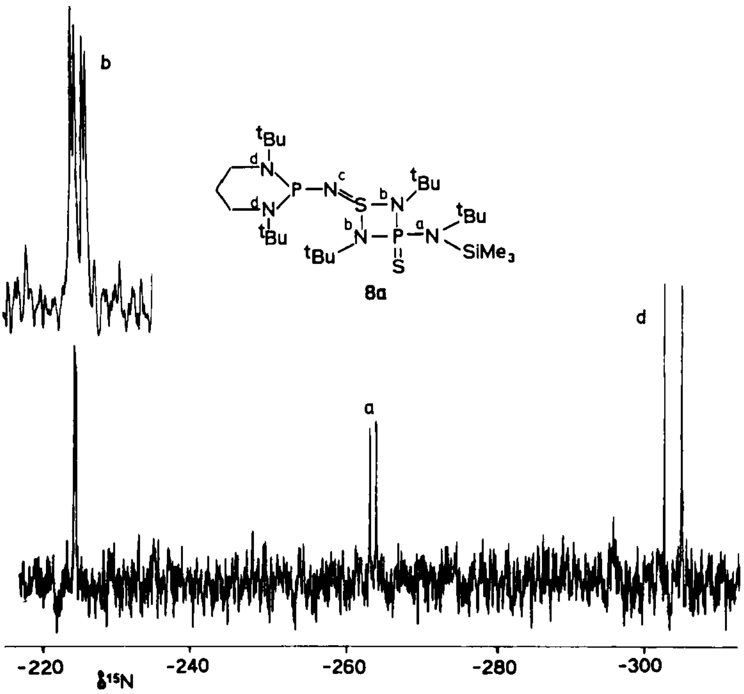


FIGURE 1 30.4 MHz ^{15}N NMR spectrum of compound **8a**, recorded by using the refocused INEPT pulse sequence [based on $^3J(^{15}N^1H)$] with ^{1}H-decoupling.

TABLE II

Experimental data for the X-ray analyses of **8a** and **9**[12]

	8a	9
Crystal size [mm³]	0.2x0.2x0.25	0.3x0.2x0.2
Space group; Z	$P\bar{1}$; 2	$P2_1/n$; 4
a, b, [Å]	10.785, 12.355	13.822, 9.229
c [Å]	14.636	19.829
β [°]	98.24(3)	104.84(3)
Volume [Å³]	1723.0(6)	2445.1(9)
Density (calcd.) [Mg/m³]	1.178	1.148
Absorption coeff. [mm⁻¹]	0.307	0.321
Diffractometer	Siemens, P4	
Radiation	Mo, K_α - graphite monochromator	
Temperature [K]	173	173
2 Θ range [°]	3.0 to 45.0	3.0 to 50.0
Scan type	ω	ω
Independent reflections	3840	4242
Observed reflections	3840	4242
Solution	direct methods	
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0000F^2$	
Parameters refined	335	227
R indices (all data) [%]	R=6.97; wR=5.61	R=7.93; wR=3.55
Largest diff. peak [e/Å³]	0.44	0.63
Largest diff. hole [e/Å³]	-0.46	-0.57

TABLE III

Compound **8a**: Atomic coordinates (× 10^4) and equivalent isotropic displacement factors [$Å^2$ × 10^3][a]

	x	y	z	U(eq)
S(1)	715(1)	4416(1)	6982(1)	20(1)
S(2)	2446(1)	7376(1)	6620(1)	28(1)
P(1)	2739(1)	6330(1)	7326(1)	19(1)
P(2)	-704(1)	2476(1)	7578(1)	22(1)
Si	5361(1)	8344(1)	8037(1)	25(1)
N(1)	2188(4)	4836(3)	6624(3)	22(2)
N(2)	1605(4)	5859(3)	7917(3)	20(2)
N(3)	693(4)	3381(3)	7346(3)	26(2)
N(4)	4293(4)	6885(3)	8011(3)	21(2)
N(5)	-447(4)	1118(3)	7207(3)	25(2)
N(6)	-2000(4)	2248(3)	6668(3)	27(2)
C(1)	-2003(5)	1628(4)	5632(3)	31(2)
C(2)	-1830(6)	415(5)	5484(3)	35(2)
C(3)	-542(5)	550(4)	6145(3)	28(2)
C(4)	2309(5)	4208(4)	5614(3)	29(2)
C(5)	2203(6)	2919(4)	5506(4)	47(2)
C(6)	1250(6)	4225(6)	4812(4)	51(3)
C(7)	3699(5)	4881(4)	5547(4)	36(2)
C(8)	947(5)	6507(4)	8611(3)	25(2)
C(9)	1898(6)	7789(4)	9186(4)	34(2)
C(10)	-311(6)	6555(5)	8037(4)	44(2)
C(11)	610(6)	5838(5)	9308(4)	43(2)
C(12)	4867(5)	6244(4)	8642(4)	29(2)
C(13)	5135(6)	6995(5)	9738(4)	43(2)
C(14)	6134(7)	6096(5)	8352(5)	51(3)
C(15)	3960(7)	4967(5)	8462(5)	52(3)
C(16)	7013(6)	9019(5)	8988(4)	46(2)
C(17)	5869(6)	8162(5)	6838(4)	40(2)
C(18)	4700(6)	9612(4)	8450(4)	37(2)
C(19)	593(6)	936(4)	7883(4)	31(2)
C(20)	675(7)	1662(6)	8947(4)	48(3)
C(22)	145(7)	-405(5)	7739(5)	55(3)
C(23)	-3273(5)	2415(4)	6838(4)	29(2)
C(24)	-3146(6)	3014(5)	7946(4)	39(2)
C(25)	-4401(6)	1207(5)	6459(5)	51(3)
C(26)	-3606(7)	3234(5)	6315(4)	49(3)
C(21)	1962(6)	1339(5)	7677(5)	44(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

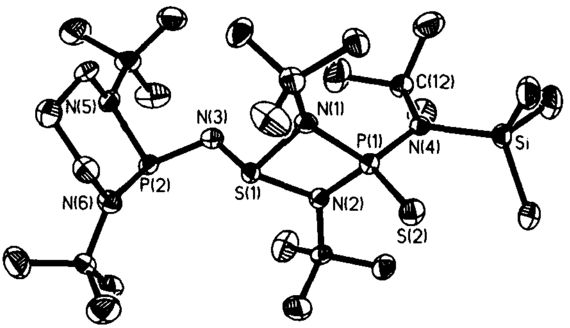


FIGURE 2 Molecular structure of compound **8a** (see Table IV for selected bond distances and bond angles).

TABLE IV

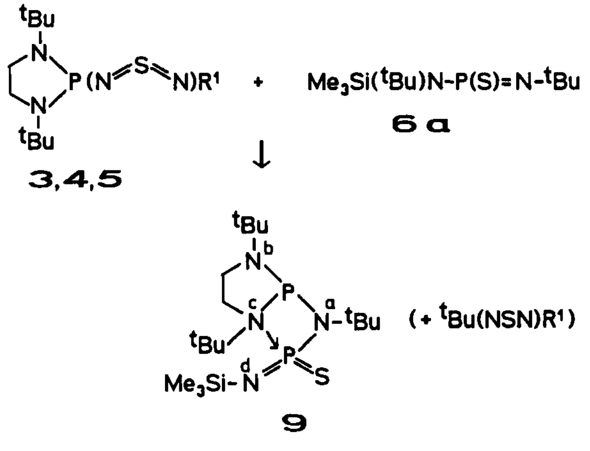
Some selected structural data of **8a** (standard deviations are given in parentheses)

Bond lengths	[pm]	Bond angles	[°]
N(1)-P(1)	169.2(3)	N(1)P(1)N(2)	82.7(2)
N(1)-S(1)	173.1(4)	N(1)S(1)N(2)	78.7(2)
N(2)-P(1)	166.8(4)	P(1)N(1)S(1)	97.3(2)
N(2)-S(1)	177.1(3)	P(1)N(2)S(1)	96.7(2)
N(3)-S(1)	152.3(5)	N(1)P(1)N(4)	115.0(2)
P(1)-S(2)	194.7(2)	N(2)P(1)N(4)	113.5(2)
N(4)-P(1)	165.1(4)	N(1)P(1)S(2)	115.0(2)
N(3)-P(2)	174.4(4)	N(2)P(1)S(2)	118.0(2)
N(5)-P(2)	171.6(4)	N(4)P(1)S(2)	110.5(2)
N(6)-P(2)	167.9(4)	P(2)N(3)S(1)	124.8(3)
N(4)-Si	182.6(4)	N(1)S(1)N(3)	107.7(2)
N(4)-C(12)	155.7(8)	N(2)S(1)N(3)	112.6(2)

angle along the N(1)N(2) axis: 155.1°). The SN single bonds in the four-membered ring ($d_{S(1)N(1)}$ = 173.1 and $d_{S(1)N(2)}$ = 177.1 pm) are significantly longer than the exocyclic SN double bond ($d_{S(1)N(3)}$ = 152.3 pm). The four-membered and the six-membered ring are arranged in trans-position. Therefore, the aminophosphinyl substituent in the sulfur diimide **2** must have been in E-position when the [2 + 2]cycloaddition took place. The three-coordinate nitrogen atoms N(1) and N(2) in the four-membered ring as well as N(5) are pyramidal whereas both N(4) and N(6) are trigonal planar.

Exchange Reactions

In spite of the apparent similarity between the sulfur diimides **2** and **3–5**, the reactions of **3–5** with the amino-imino-thiophosphorane **6a** take a completely different course, and [2 + 2]cycloaddition was not observed at all. The surprising result is shown in Equation (3).

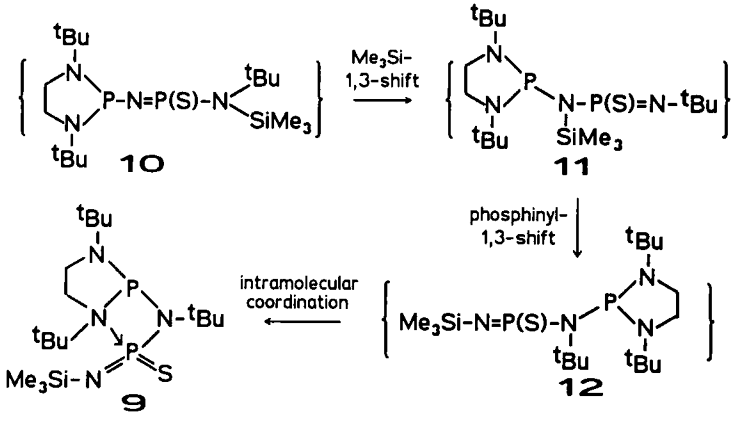


(3)

Starting from either **3**, **4**, or **5**, the same product **9** was always formed in high yield. The second product is a sulfur diimide, e.g., ^{t}Bu(NSN)^{t}Bu (**1**) in the case of **3** and **5**, or ^{t}Bu(NSN)SiMe$_3$ in the case of **4**. This formation of a sulfur diimide as the second product explains the reaction mechanism (Scheme I). Apparently, the reaction starts with an exchange process. The =N^{t}Bu group of the thiophosphorane **6a** changes place with the [CH$_2$N(^{t}Bu)]$_2$P—N= group of the sulfur diimides **3**–**5** to afford the sulfur diimide ^{t}Bu(NSN)R^1 and the unstable thiophosphorane **10**. A 1,3-shift of the Me$_3$Si group in **10** leads to **11**, and another 1,3-shift, this time of the phosphinyl group, to **12**. The 1,3-shifts of the Me$_3$Si— and the [CH$_2$N(^{t}Bu)]$_2$P group may occur simultaneously or one after the other. 1,3-Shifts of trimethylsilyl groups in N—P—N systems have been reported,[8] whereas, to the best of our knowledge, 1,3-shifts of phosphinyl groups have not been observed previously. It is evident that all conditions are fulfilled in **12** for an intramolecular stabilization of this thiophosphorane via the coordinative N—P bond to give **9**.

Compared to the exchange reaction, the [2+2]cycloaddition between either ^{t}Bu(NSN)^{t}Bu (**1**) or ^{t}Bu(NSN)SiMe$_3$ and **6a** takes place much more slowly. If only one equivalent of **6a** is available for reaction with the sulfur diimide **5**, only half of **5** is consumed, as shown by ^{31}P NMR. Therefore, **3** and **9** must be formed in the first step, and then **3** reacts with a second equivalent of **6a** to give **9** and ^{t}Bu(NSN)^{t}Bu (**1**). When this reaction between the sulfur diimide **5** and an excess of **6a** in ether was monitored by using ^{31}P NMR, the ^{31}P NMR signals of the excess of **6a** (δ + 137.9) and of the product **9** (δ 112.8, 62.7) were accompanied by two doublets ($^2J(^{31}P^{31}P)$ = 22 Hz) at δ + 63.7 and +34.0 which can be tentatively assigned to one of the proposed intermediates **10** or **11**. The ^{31}P NMR signals of the starting sulfur diimide **5** and of the sulfur diimide **3**, formed in the first step of the exchange reaction, were not detected under these conditions. This indicates that the two exchange processes (between **5** and **6a** as well as between **3** and **6a**) are fast as compared to the NMR timescale.

The reasons for the different behavior of **3**–**5** as compared to **2** are not clear, although one can speculate that the phosphorus atom in the 1,3,2-diazaphospholidinyl ring is more reactive than in the 1,3,2-diazaphosphoridinyl system. This



SCHEME I Proposed mechanism of the formation of **9**.

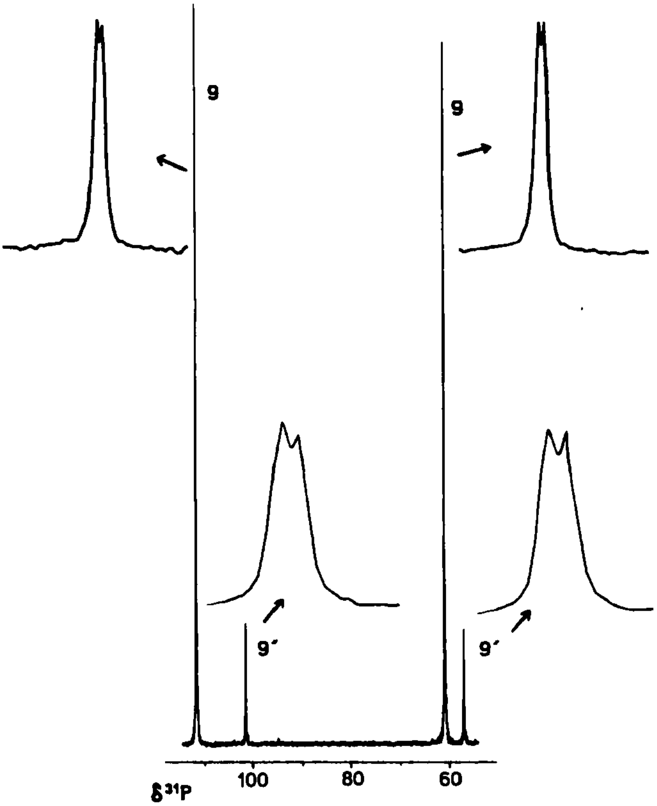
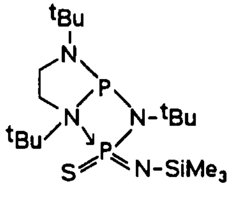


FIGURE 3 121.5 MHz $^{31}P\{^1H\}$ NMR spectrum of product **9** in [D_8]toluene/Et_2O (1:10) at 220 K, showing the presence of the second isomer **9'** (≈14%): $\delta^{31}P$ [$J(^{31}P,^{31}P)$] = 112.0 [4.9] P(III), 61.0 [4.9] P(V) (**9**); 101.5 [7.3] P(III), 56.9 [7.3] P(V) (**9'**); (298 K) 112.8 [br] P(III), 62.7 [br] P(V).

could lead to weak bonding interactions with nucleophilic sites of the amino-imino-thiophosphorane (e.g. to a P—S—P bridge) and, by such a preorientation, the reaction might take a different course. In principle, transimidation of sulfur diimides is a well known type of reaction.[4]

At room temperature in solution, the structure of **9** was shown to be fluxional because of the labile coordinative N—P bond (^{1}H-, ^{13}C-, ^{15}N- and ^{31}P NMR). Thus, the ^{31}P NMR spectrum of **9** at −53°C (see Figure 3) showed two sets of signals with different intensities (86:14). Hence, two isomers **9** and **9'** are present at low temperature in solution. Assuming that the more abundant isomer crystallizes preferentially (vide infra), it has the structure **9**. ^{13}C and ^{15}N NMR data are listed in Table V.



9'

X-ray Structure Analysis of **9**

Recrystallization of **9** from toluene afforded single crystals suitable for an X-ray structure determination. The experimental data are given in Table II; Table VI contains the atomic coordinates and isotropic displacement coefficients. Selected bond lengths and bond angles are listed in Table VII. The molecular structure of **9** is shown in Figure 4. The longest PN bond ($d_{P(2)N(2)}$ = 194.8 pm) is found for the labile coordinative N—P bond. The surrounding of the nitrogen atoms N(1)

TABLE V

^{13}C- and ^{15}N NMR data[a] of **9**

	N^a ^tBu	N^b ^tBu	N^c ^tBu	N^d $SiMe_3$[b]	CH_2
$\delta^{13}C$	54.9, 30.6 [9.8],[<1, <1]	54.3, 29.6 [16.4], [9.8]	64.3, 30.0 [10.9], [18.5]	3.3 [4.9]	49.5, 47.9 [<1], [7.1]
$\delta^{15}N$	- 251.2[c] [58.6, 5.5]	- 278.1 [84.4]	- 251.0[c] [58.6, 4.9]	- 248.3 [20.8, 1.8]	- -

[a] In CD_2Cl_2 at −50°C; indices as in Equation (3); coupling constants $^nJ(^{31}P,X)$ (X = ^{13}C, ^{15}N) [Hz] are given in square brackets.

[b] $\delta^{29}Si$ = −9.0 [18.3] (298 K).

[c] Assignment uncertain.

TABLE VI

Compound **9**: Atomic coordinates (×10^4) and equivalent isotropic displacement factors [$Å^2$ × 10^3][a]

	x	y	z	U(eq)
S	6837(1)	-2823(1)	3261(1)	38(1)
P(1)	5592(1)	1140(1)	3620(1)	29(1)
P(2)	6657(1)	-1366(1)	3938(1)	26(1)
Si	7930(1)	-2773(1)	5220(1)	38(1)
N(1)	5504(2)	-677(3)	3783(1)	23(1)
N(2)	6881(2)	577(3)	3625(1)	26(1)
N(3)	7169(2)	-1544(3)	4714(1)	27(1)
N(4)	5248(2)	1337(3)	2762(1)	35(1)
C(1)	6912(2)	530(4)	2863(2)	33(1)
C(2)	5845(3)	417(4)	2421(2)	36(1)
C(3)	7740(3)	1520(4)	4067(2)	33(1)
C(4)	7601(3)	1686(3)	4807(2)	40(1)
C(5)	7700(3)	3046(3)	3752(2)	54(2)
C(6)	8726(2)	795(4)	4079(2)	50(2)
C(7)	7165(3)	-4332(4)	5387(2)	69(2)
C(8)	8535(3)	-1900(4)	6072(2)	60(2)
C(9)	8961(3)	-3440(4)	4849(2)	53(2)
C(10)	4561(3)	-1456(4)	3779(2)	32(1)
C(11)	3826(2)	-398(4)	3973(2)	48(2)
C(12)	4771(3)	-2689(4)	4307(2)	48(2)
C(13)	4099(3)	-2050(4)	3042(2)	52(2)
C(14)	4648(3)	2554(4)	2372(2)	45(2)
C(15)	4109(3)	3348(4)	2832(2)	66(2)
C(16)	5321(3)	3595(4)	2111(2)	69(2)
C(17)	3865(3)	1901(5)	1759(2)	77(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE VII

Structural data of the zwitterionic bicylic compound **9** (standard deviations are given in parentheses)

Bond lengths [pm]		Bond angles [°]	
N(1)-P(1)	171.8(3)	N(1)P(1)N(2)	80.8(1)
N(1)-P(2)	166.9(3)	N(1)P(2)N(2)	79.3(1)
N(2)-P(1)	185.5(3)	P(1)N(1)P(2)	107.2(1)
N(2)-P(2)	194.8(3)	P(1)N(2)P(2)	91.6(1)
N(3)-P(2)	152.9(2)	N(2)P(1)N(4)	93.3(1)
N(4)-P(1)	165.6(3)	P(1)N(2)C(1)	105.9(2)
N(1)-C(10)	148.6(4)	N(2)C(1)C(2)	107.8(3)
N(2)-C(1)	152.2(4)	P(1)N(4)C(2)	111.3(2)
N(2)-C(3)	155.0(4)	N(4)C(2)C(1)	105.8(2)
N(4)-C(2)	146.4(5)	N(1)P(1)N(4)	106.5(1)
N(4)-C(14)	149.0(4)	P(2)N(2)C(1)	109.7(2)
N(3)-Si	169.1(3)	P(2)N(3)Si	136.7(2)
P(2)-S	196.1(1)		

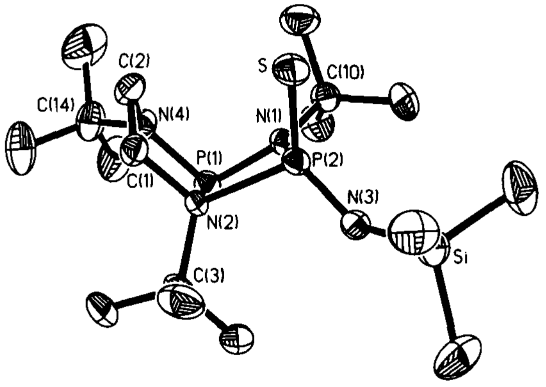


FIGURE 4 Molecular structure of the zwitterionic compound **9** (see Table VII for selected bond distances and bond angles).

(sum of bond angles 360.0 (5)°) and N(4) (sum of bond angles 357.7 (7)°) is trigonal planar or close to trigonal planar.

There are no structural data of amino-imino-thiophosphoranes available in the literature. A comparison of the bond lengths $d_{P(2)N(3)}$ = 152.9 pm in **9** with those in amino-bis(imino)phosphoranes[13] (151.8 and 151.3 pm) where the surrounding of the phosphorus is trigonal planar, indicates little change. The bond angle P(2)N(3)Si in **9** (136.7°) is smaller by ≈10° as compared with the corresponding angle in the bis(imino)-phosphoranes. This can be attributed either to the influence of replacing an imino group by the sulfur atom or to the additional coordinative N(2)—P(2) bond.

EXPERIMENTAL

The synthetic work was carried out in an atmosphere of Ar, by observing all precautions to exclude oxygen and traces of moisture. The solvents pentane, toluene and diethyl ether were distilled from

Na/K alloy prior to use. The sulfur diimides **1**,[9] **2–5**[6] and the amino-imino-thiophospharanes **6a**,**b**[10] were prepared following procedures reported in the literature.

NMR spectra were recorded from samples (ca. 10–20% in C_6D_6, $[D_8]$toluene or CD_2Cl_2) in 5 mm tubes by using JEOL FX 90 Q (^{31}P NMR) and Bruker AC 300 spectrometers (^1H-, ^{13}C-, ^{15}N NMR), both equipped with multinuclear and variable temperature units. Chemical shifts are given with respect to Me_4Si [$\delta^1H(C_6D_5H) = 7.15$, $(CDHCl_2) = 5.33$, $(C_6D_5CD_2H) = 2.03$; $\delta^{13}C(C_6D_6) = 128.0$, $(CD_2Cl_2) = 53.8$, $(C_6D_5CD_3) = 20.4$; $\delta^{29}Si$, $\Xi(^{29}Si) = 19.867184$ MHz], external neat $MeNO_2$ ($\delta^{15}N$, $\Xi(^{15}N) = 10.136767$ MHz) and external H_3PO_4 (aq. 85%) ($\delta^{31}P$, $\Xi(^{31}P) = 40.480747$ MHz). ^{15}N and ^{29}Si NMR spectra were measured by using the refocused INEPT[11] pulse sequence [based on coupling constants $^3J(^{15}N, ^1H) \approx 1.5–2.3$ Hz and $^2J(^{29}Si^1H) \approx 7$ Hz] with ^1H decoupling. Mass spectra (El, 70 eV) were recorded on a VARIAN MAT CH-7 instrument.

3-(tert-Butyl)trimethylsilylamino- and 3-Bis(trimethylsilyl)amino-2,4-di-tert-butyl-1-(tert-butyl)imino-3-thio-1,2,4,3-thiadiazaphosphetidines (**7a**, **7b**) *and 3-(tert-Butyl)trimethylsilylamino- and 3-Bis(trimethylsilyl)-amino-2,4-di-tert-butyl-1-[2-(1,3-di-tert-butyl-1,3,2-diazaphosphoridinyl)]imino-3-thio-1,2,4,3-thiadiazaphosphetidines* (**8a**,**8b**). At room temperature, a solution of 50 mmol of the sulfur diimide **1** or **2** in 50 ml of diethyl ether is added to a solution of 50 mmol of the amino-imino-thiophosphorane **6a** or **6b** in 50 ml of ether. After stirring the mixture for 24 h at room temperature the ether is removed in vacuo, the residue dissolved in 30 ml of pentane and stored at −78°C. The products **7a**,**b** and **8a**,**b** crystallize from this solution. They are obtained as colorless crystals in 60–70% yield after repeated recrystallization from a small amount of pentane at −30°C.

7a: mp. 75°C; ^1H NMR (300 MHz in $[D_6]$benzene) $\delta^1H = 1.62$ s, 9H, N^{t}Bu; 1.44 s, 18H, N^{t}Bu; 1.19 s, 9H, N^{t}Bu; 0.71 s, 9H, $SiMe_3$; El-MS [$C_{19}H_{45}N_4PS_2Si$, 452.770] m/z (%): 452 (7, M).
7b: mp. 71°C; ^1H NMR (300 MHz in $[D_6]$benzene): $\delta^1H = 1.55$ s, 18H, N^{t}Bu; 1.31 s, 9H, N^{t}Bu; 0.62 s, 9H, $SiMe_3$; 0.61 s, 9H, $SiMe_3$.
8a: mp. 108–109°C; ^1H NMR (300 MHz in $[D_6]$benzene): δ^1H [$J(^{31}P, ^1H)$] = 3.30 m, 4H, NCH_2; 2.70 m, 2H, CH_2; 1.68 s, 9H, N^{t}Bu; 1.54 s, 18H, N^{t}Bu; 1.21 [2.1] d, 18H, N^{t}Bu; 0.64 s, 9H, $SiMe_3$.
8b: 105°C; ^1H NMR (300 MHz in $[D_6]$benzene): $\delta^1H = 3.40$ m, 4H, NCH_2; 2.80 m, 2H, CH_2; 1.51 s, 18H, N^{t}Bu; 1.21 s, 18H, N^{t}Bu; 0.55 s, 9H, $SiMe_3$, 0.53 s, 9H, $SiMe_3$.

2,5,7-Tri-tert-butyl-6-trimethylsilylimino-6-thio-bicyclo[3.2.0]-1($\sigma^3\lambda^3$),6($\sigma^4\lambda^5$),2,5,7-diphosphatriazaheptane (**9**). A solution of **3**,**4** (10 mmol, each) or **5** (5 mmol) in 25 ml of diethyl ether is added at room temperature to a solution of the amino-imino-thiophosphorane **6a** (2.78 g, 10 mmol) in 25 ml of diethyl ether. After stirring the reaction mixture for 48 h at room temperature, the ether is removed in vacuo. A white solid which forms immediately when pentane is added to the residue is filtered off. Recrystallization of the white raw material from toluene affords pure **9** (1.40 g, 33%) as colorless crystals (mp. 120–121°C).

^1H NMR (300 MHz in $[D_8]$toluene): $\delta^1H = 4.20$ m, 2H, NCH_2; 2.91 m, 2H, NCH_2; 2.11 s, 9H, N^{t}Bu; 1.49 s, 9H, N^{t}Bu; 0.85 s, 9H, N^{t}Bu; 0.64 s, 9H, $SiMe_3$. El-MS [$C_{17}H_{40}N_4P_2SSi$, 422.625] m/z (%): 422 (4, M).

ACKNOWLEDGEMENT

Support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

REFERENCES

1. R. Bussas, G. Kresze, H. Münsterer and A. Schwöbel, *Sulfur Reports*, **2**, 215 (1983).
2. H. W. Roesky, H.-G. Schmidt, M. Noltemeyer and G. M. Sheldrick, *Chem. Ber.*, **116**, 1411 (1983).
3. (a) H. Gotthardt, T. Löhr and D. J. Brauer, *Chem. Ber.*, **120**, 751 (1987); (b) C. Bessenbacher and W. Kaim, *J. Chem. Soc., Chem. Commun.*, 469 (1989).
4. R. Neidlein, P. Leinberger, A. Gieren and B. Dederer, *Chem. Ber.*, **110**, 3149 (1977).
5. (a) M. Herberhold, S. M. Frank, B. Wrackmeyer, H. Borrmann and A. Simon, *Chem. Ber.*, **123**, 75 (1990); (b) B. Wrackmeyer, S. M. Frank, M. Herberhold, A. Simon and H. Borrmann, *J. Chem. Soc. Dalton Trans.*, 2607 (1991); (c) C. Habben and A. Meller, *Chem. Ber.*, **119**, 9 (1986); (d) C. Habben, A. Meller and S. Pusch, *Z. Naturforsch., Teil B*, **43**, 859 (1988).

6. (a) M. Herberhold, C. Köhler and B. Wrackmeyer, *Phosphorus, Sulfur and Silicon*, **68**, 219 (1992); (b) M. Herberhold, C. Köhler and B. Wrackmeyer, *Phosphorus, Sulfur and Silicon*, **71**, 75 (1992).
7. N. T. Kulbach and O. J. Scherer, *Tetrahedron Letters*, 2297 (1975).
8. (a) O. J. Scherer, *Angew. Chemie*, **81**, 871 (1969); *Angew. Chem. Int. Ed. Engl.*, **8**, 861 (1969); (b) E. Niecke and H. G. Schäfer, *Chem. Ber.*, **115**, 185 (1982); (c) E. Niecke and W. Flick, *Angew. Chemie*, **86**, 128 (1974); *Angew. Chem. Int. Ed. Engl.*, **13**, 134 (1974); (d) O. J. Scherer and N. Kuhn, *J. Organomet. Chem.*, **82**, 3 (1974); (e) M. Regitz and O. J. Scherer, (eds.), "Multiple Bonds and Low Coordination in Phosphorus Chemistry," G. Thieme Verlag, Stuttgart, 1991.
9. D. H. Clemens, A. J. Bell and J. L. O'Brien, *Tetrahedron Letters*, **20**, 1487 (1965).
10. (a) O. J. Scherer and N. Kuhn, *Angew. Chemie*, **86**, 899 (1974); *Angew. Chem. Int. Ed. Engl.*, **13**, 811 (1974); (b) O. J. Scherer and N. Kuhn, *J. Organomet. Chem.*, **82**, C3 (1974); (c) O. J. Scherer and N. Kuhn, *J. Organomet. Chem.*, **78**, C17 (1974).
11. (a) G. A. Morris and R. Freeman, *J. Am. Chem. Soc.*, **101**, 760 (1979); (b) D. P. Burum and R. R. Ernst, *J. Magn. Reson.*, **39**, 163 (1980); (c) G. A. Morris, *J. Magn. Reson.*, **41**, 185 (1980).
12. Further details of the crystal structure determinations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Informationen mbH, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the depository numbers CSD 400790 (**9**) and CSD 400791 (**8a**), the authors and the journal citation.
13. (a) S. Pohl, E. Niecke and B. Krebs, *Angew. Chem.*, **87**, 284 (1975); *Angew. Chem. Int. Ed. Engl.*, **14**, 261 (1975); (b) S. Pohl and B. Krebs, *Chem. Ber.*, **110**, 3183 (1977); (c) S. Pohl, Habilitationsschrift, Universität Bielefeld 1977.