I. V. Borisova,^a N. N. Zemlyanskii,^{a*} A. K. Shestakova,^a V. N. Khrustalev,^c Yu. A. Ustynyuk,^{b*} and E. A. Chernyshev^a

^aState Research Center of the Russian Federation

"State Research Institute of the Chemistry and Technology of Organoelement Compounds,"

38 sh. Entuziastov, 111123 Moscow, Russian Federation.

Fax: +7 (095) 273 1323. E-mail: zemlyan@mail.cnt.ru

^bDepartment of Chemistry, M. V. Lomonosov Moscow State University,

Leninskie Gory, 119899 Moscow, Russian Federation.

Fax: +7 (095) 932 8846

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,

28 ul. Vavilova, 117813, Moscow, Russian Federation.

Fax: +7 (095) 135 5085

The $[Ph_3P^+-CMe_2-SiMe_2-SEt]Br^-$ salt was prepared by the reaction of betaine $Ph_3P^+-CMe_2SiMeR-S^-$ (ia: R = Me) with EtBr. Acetylation of betaine 1a or $Et_3P^+-CHMeSiMe_2-S^-$ (2a) afforded 2.2.6-trimethyl-1.3-dioxa-2-silacyclohex-5-ene-4-thione $Me_2SiOC(=S)CH=C(Me)O$ or the $[Et_3P^+-CHMeSiMe_2Cl]Cl^-$ salt depending on the reagent ratio. The reactions of betaines 1a,b (1b: R = Ph) or 2 with compounds $(R_3Sn)_2X$ (X = O or NMe) can be used for the generation of silanones [RMeSi=O] and silaneimines [RMeSi=NMe] in solutions. The reactivity of betaines $Ph_3P^+-CHR^+SiMeR^2-S^-$ ($R^+ = H$ or Ph) is determined by the equilibrium between the zwitterionic and ylide $Ph_3P=CR^+SiMeR^2SH$ tautomers that exist in solutions.

Key words: silicon-containing organophosphorus betaines, phosphorus ylides, isomerism, alkylation, acetylation, silanones, silaneimines, X-ray diffraction analysis.

Previously, we have reported the synthesis² and structures¹ of betaines containing the $^+P-C-Si-S^-$ fragment. Unlike the carbon analogs, which are intermediates in the Wittig reaction for the series of thiocarbonyl compounds, Si-containing betaines are rather stable to decomposition, which opens up new possibilities for their use in different syntheses. The presence of several reaction centers is responsible for the high reactivity of these compounds. In the present work, we studied the reactions of betaines Ph₃P⁺-CHe₂SiMeR-S⁻ (1: R = Me (a) or Ph (b)), Et₃P⁺-CHMeSiMe₂-S⁻ (2), and Ph₃P⁺-CHR¹SiMeR²-S⁻ (3a-c: R¹ = R² = Me (a); R¹ = H and R² = Me (b); or R¹ = H and R² = Ph (c)) in detail.

Results and Discussion

Alkylation and acetylation of betaines $Ph_3P^+CMe_2SiMe_2S^-$ (1a) and $Et_3P^+CHMeSiMe_2S^-$ (2). Heating of a suspension of betaine 1a in THF with ethyl bromide afforded salt 4 in 70% yield (reaction (1)).

* For Part 1, see Ref. 1.

$$Ph_{3}P^{+}-CMe_{2}-SiMe_{2}-S^{-} \xrightarrow{EEBr}$$

$$1a$$

$$(1)$$

$$Ph_{3}P^{+}-CMe_{2}-SiMe_{2}-SEt]Br^{-}$$

$$4$$

According to the data of X-ray diffraction analysis,¹ salt 4 adopts a thermodynamically favorable *trans* conformation, unlike the initial betaine 1a, which has a sterically hindered *gauche* conformation due to the $^+P...S^-$ attractive Coulomb interaction between the cationic and anionic centers.

The reactions of betaines 1a or 2 with acetyl chloride proceed unusually and the results depend on the molar ratio of the reagents. When the reaction was performed in THF with the use of reagents taken in an equimolar ratio, cyclic compound 5 was obtained in 96-98% yield (Scheme 1).

Apparently, the S-acetyl derivative 6 that initially formed underwent subsequent rearrangement with migration of the organosilicon fragment to the oxygen atom. This process is thermodynamically favorable. The second betaine molecule acted as a base and deprotonated thioacetate 7. (This type of deprotonation of thiocarbonyl

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 5, pp. 935-942. May, 2000.

1066-5285/00/4905-0933 \$25.00 © 2000 Kluwer Academic/Plenum Publishers



1a: $R^{1} = Ph$, $R^{2} = Me$ **2:** $R^{1} = Et$, $R^{2} = H$

compounds is well known.³) Acetylation of thioenolate ion 8 afforded β -thiocarbonyl derivative 9. Subsequent enolization and the formation of the extraordinarily strong Si-O bond completed cyclization, yielding compound 5. As expected.⁴ phosphonium salt 10 decomposed with the cleavage of the Si-C bond.

The structure of 2,2,6-trimethyl-1,3-dioxa-2-silacyclohex-5-ene-4-thione (5) was established by X-ray diffraction analysis and multinuclear NMR spectroscopy. The overall view of molecule 5 is shown in Fig. 1. The principal bond lengths and bond angles are given in Table 1. The ring in molecule 5 is planar. The tetrahedral geometry of the Si atom in the ring is strongly distorted. The O-Si-O (103.7(1)°) and C-Si-C (115.1(1)°) bond angles differ substantially from the



Fig. 1. Structure of compound 5.

ideal tetrahedral value of 109.5°. The Si—O bond lengths (1.668(2) Å and 1.675(2) Å) are substantially larger than the average value (1.645 Å).⁵ Apparently, these distortions lead to the strain of the ring and are responsible for the high reactivity of compound 5, in particular, with respect to oxygen and moisture.

Heating of betaine 2 with a large excess of acetyl chloride in ether afforded salt 11 in virtually quantitative yield (reaction (2)).



Reactions of betaines 1 and 2 with compounds of the $(R_3Sn)_2X$ type (X = O or NMe). We found that betaines 1 and 2 are convenient starting compounds for the

Table 1. Selected bond lengths (d) and bond angles (ω) in the structure of 5

Bond	d/À	Angle	ω/deg
$\overline{S(1)-C(5)}$	1.645(2)	O(2)-Si(1)-O(6)	103.7(1)
Si(1) - O(2)	1.668(2)	O(2) - Si(1) - C(6)	108.7(1)
Si(1)O(6)	1.675(2)	O(6) - Si(1) - C(6)	110.1(1)
Si(1) - C(6)	1.820(2)	C(6) - Si(1) - C(6A)	115.1(1)
O(6) - C(5)	1.347(3)	C(3) - O(2) - Si(1)	123.2(1)
O(2) - C(3)	1.350(2)	C(5) - O(6) - Si(1)	126.7(2)
C(3) - C(7)	1.486(3)	C(4) - C(3) - O(2)	123.2(2)
C(3) - C(4)	1.350(3)	C(4) - C(3) - C(7)	124.1(2)
C(4) - C(5)	1.435(3)	O(2) - C(3) - C(7)	112.7(2)
		C(3) - C(4) - C(5)	125.6(2)
		O(6) - C(5) - C(4)	117.6(2)
		O(6) - C(5) - S(1)	119.3(2)
		C(4) - C(5) - S(1)	123.1(2)

generation of unstable silanones and silaneimines in solutions. These compounds have been extensively studied in recent years.⁶⁻⁸

The intermediate formation of organosilanones was proved by the identification of their cyclooligomerization products 12 as well as by the reaction with methoxytrimethylsilane (Scheme 2). The reaction of $(Et_3Sn)_2O$ with betaine 1a or 1b afforded a mixture of the cyclic tetramer (D_4) and the pentamer (D_5) of dimethylsilanone (12a) or a mixture of oligomers of methylphenylsilanone (12b). The reactions in the presence of a 10-fold excess of Me₃SiOMe gave methoxypentamethyldisiloxane (13a)(the yield was 83%) or methoxy(tetramethyl)phenyldisiloxane (13b) (the yield was 95%). Note that the reaction of betaine 1a with Me₃SiOMe did not proceed in the absence of hexaalkyldistannoxane under the same conditions.

Scheme 2



 $R^{1} = Me$ (a), Ph (b); $R^{2} = Et$, X = O; $R^{2} = Me$, X = NMe

In the reaction of betaine 1a with $(Me_3Sn)_2NMe$, the latter acts as a "trapping agent" with respect to organosilaneimine that formed. When a twofold excess of organostannane was used, compound 14 was obtained in 90% vield.

The reactions of betaine 2 with compounds of the general formula $(R_3Sn)_2X$ (X = O or NMe) were complicated by the formation of metallated phosphorus ylides $Et_3P=C(Me)SnR_3$ (15) as a result of the reaction of the phosphorus ylide $Et_3P=CHMe$ that formed with $(R_3Sn)_2X$. The resonance signals in the ¹H. ¹³C. ³¹P, and ¹¹⁹Sn NMR spectra of the reaction mixture of betaine 2 and $(Me_3Sn)_2NMe$ are substantially broadened, which may be indicative of complex exchange processes (Scheme 3).

More detailed information on the synthesis of α metallated phosphorus ylides by the reactions of $R^{1}_{3}P=CHR^{2}$ with compounds of the $(R_{3}E)_{2}X$ type (E = Si, Ge, or Sn; X = O, S, or NR) will be published elsewhere.

Isomerization of betaines $Ph_3P^+CHR^1SiMeR^2S^-$ (3). Betaines 3a-c are isomerized in solutions yielding silylated phosphorus ylides 16a-c (reaction (3)). This

Scheme 3

$$Et_{3}P^{+}-CHMe-SiMe_{2}-S^{-} \xrightarrow{(Me_{3}Sn)_{2}NMe}$$
2
$$(Me_{2}Si=NMe] + Et_{3}P=CHMe + (Me_{3}Sn)_{2}S,$$

2
$$Ft_2P = CHMe \frac{(Me_3Sn)_2NMe}{2}$$

$$2 \text{ Et}_{3}\text{P}=C(\text{Me})\text{SnMe}_{3} + \text{MeNH}_{2} = 15$$

$$Et_{3}\text{P}=CHMe + \text{Me}_{3}\text{SnNHMe} = 15$$

$$[Et_{4}\text{P}]^{+}[\text{MeNSnMe}_{3}]^{-},$$

$$[Et_{4}P]^{+}[MeN^{-}SnMe_{3}]^{-} + Me_{2}Si(NMeSnMe_{3})_{2} \longrightarrow 14$$

$$Me_{2}Si < N^{+}MeSnMe_{3} + [Et_{4}P]^{+}[MeNSnMe_{3}]^{-}$$

$$NMeSnMe_{2} + [Et_{4}P]^{+}[MeNSnMe_{3}]^{-}$$

process is clearly detected by the emergence of the ¹H, ¹³C, and ³¹P NMR signals characteristic of phosphorus ylides.^{9,10} including α -silylated phosphorus ylides.^{11,12}

$$Ph_{3}P^{+}-CHR^{1}-SiMeR^{2}-S^{-} =$$

$$3a-c$$

$$Ph_{3}P=CR^{1}-SiMeR^{2}-SH$$

$$(3)$$

$$16a-c$$

$$R^1 = R^2 = Me(a); R^1 = H, R^2 = Me(b); R^1 = H, R^2 = Ph(c)$$

Previously, it was suggested that isomerization of this type occurred in the reactions of phosphorus ylides with small silacycles. 13-16

An increase in the temperature or a decrease in the solvent polarity is favorable for the formation of phosphorus ylides 16. Betaine 3a is virtually insoluble in benzene. However, the ¹³C and ³¹P NMR spectra, which were measured after heating of a suspension of 3a in benzene-d₆ in a sealed evacuated tube at 150 °C, have signals characteristic of phosphorus ylide 16a whose content reached 8.5% with respect to the amount of the initial betaine 3a. When zwitterion 3a was synthesized in benzene, up to 62% of ylide 16a along with betaine 3a were registered in the resulting mixture, whereas the content of compound 16a in a pyridine solution was no more than 1.4% and 3.6% at -20 and 90 °C, respectively.

In solutions, equilibrium processes of intermolecular proton transfer between the thiolate center and the sulfohydryl group (reaction (4)) were observed along with isomerization of betaine **3b** to ylide **16b**. The ²⁹Si NMR spectrum of a solution of betaine **3b** in THF-d₈

has four resonance doublets. Two of these doublets undoubtedly belong to betaine 3b (the major isomer) and to isomeric phosphorus ylide 16b. The two remaining doublets are quite similar to those of compounds 3band 16b and, apparently, can be assigned to the cationic and anionic components of salt 17b.

 $= [Ph_3P^--CH_2-SiMe_2-SH][Ph_3P=CH-SiMe_2-S^-] (4)$

17b

An equilibrium of this type has been observed previously in the studies of the reactions of triphenylalkylidenephosphoranes with carbon disulfide.¹⁷

Equilibrium (3) was chemically confirmed in the studies of the reactions of betaines 3 with EtBr and alcohols. As expected, the reaction of EtBr with $Ph_3P^+CHMeSiMe_3S^-$ (3a), unlike the reaction of betaine 1a (see reaction (1)), afforded a complex mixture of products. In this case, alkylation of the thiolate center was followed by the cleavage of the C—Si bond in ylide 16a under the action of the bromide ion which acted as a nucleophile. The resulting phosphorus ylide $Ph_3P=CHMe$ underwent successive conversions, which have been described previously for analogous systems in detail.¹¹ In the case of betaine 3a, $Ph_3P=C(Me)SiMe_2X$, $[Ph_3P^+C(H)MeSiMe_2X]Y^-$, and Me_2SiXY (X and Y = Br or SEt) as well as $[Ph_3P^+Et]Br^-$ and $Ph_3P=CHMe$ were obtained as the final reaction products.

The isomerization of betaines **3a.b** was also confirmed by their reactions with methanol- d_1 , which proceeded rather rapidly at room temperature to form Me₂Si(OMe)₂ and a mixture of α -deuterated phosphonium salts **18a,b** (Scheme 4). In this case, the reactions most likely proceed primarily through intermediate formation of α -silylated phosphorus ylides **16**. Their further transformations in MeOD follow the general regularities.

Scheme 4



which have been established previously for the reactions of alcohols with $R_{3}^{1}P=CHR^{2}$ ($R^{1} = Alk$ or Ph; $R^{2} = H$, Alk, or Me₃Si).^{18.19a}

Betaines that do not contain the α -proton at the carbon atom or contain alkyl groups at the phosphorus atom, for example, $Ph_3P^+CMe_2SiMe_2S^-$ (1a) or $Et_3P^+CHMeSiMe_2S^-$ (2), were converted into $Me_2Si(OMe)_2$ and mono- α -deuterated phosphonium salts 19a,b (reaction (5)) in virtually quantitative yields only upon prolonged storage (30-70 days) of their solutions with CH₃OD in sealed evacuated tubes. Taking into account that alcoholysis of betaine 2 did not give the di-a-deuterated salt [Et3P+CD2Me]SH- in noticeable amounts, it is reasonable to conclude that the contribution of an equilibrium of type (3) is insignificant. Apparently, this is due to the lower α -CH-acidity of phosphonium salts of the alkyl series compared to that of arylphosphonium salts and, correspondingly, due to the higher basicity (nucleophilicity) of the conjugate bases, viz., phosphorus ylides.19b

$$R^{1}_{3}P^{+}-CMeR^{2}-SiMe_{2}-S^{-} \xrightarrow{MeOD}$$

$$1a, 2$$

$$(R^{1}_{3}P^{+}-CDMeR^{2}]SH^{-} + Me_{2}Si(OMe)_{2} \qquad (5)$$

19a.b

1a, 19a: R¹ = Ph. R² = Me **2, 19b:** R¹ = Et, R² = H



Fig. 2. Structure of salt 18a.



Fig. 3. Structure of salt 19a. Two pyridine molecules of solvation are shown.

Data on the structures of phosphonium hydrosulfides are lacking due, apparently, to the mistaken opinion that these compounds are unstable by analogy with unstable hydroxides.²⁰ The SH⁻ anions in the crystals of hydrosulfides **18a** and **19a** are not stabilized by hydrogen bonds (Figs. 2 and 3, respectively), unlike those in tetraorganylammonium hydrosulfides whose structures were studied in sufficient detail.²¹⁻²⁵

To summarize, we demonstrated prospects of the use of new silicon-containing organophosphorus betaines with the $^+P-C-Si-S^-$ structural fragment in the synthesis of different organosilicon compounds, including compounds that were previously difficultly accessible or unavailable. Betaines containing the α -proton at the "former ylide" carbon atom are potential synthons for preparing α -silylated phosphorus ylides containing the sulfohydryl group at the silicon atom.

Experimental

The ¹H, ¹³C, ²⁹Si, ³¹P, and ¹¹⁹Sn NMR spectra were recorded on a Bruker AM-360 instrument in C_6D_6 , THF- d_8 , C_5D_5N , or MeOD. The chemical shifts (in ppm) in the ¹H and ¹³C NMR spectra were measured relative to signals of the solvent and were converted to the δ scale using standard formu-

las; the chemical shifts in the ²⁹Si, ³¹P, and ¹¹⁹Sn NMR spectra were measured relative to Me₄Si, a 85% H₃PO₄ solution in D₂O, and a solution of Me₄Sn in C₆D₆, respectively, as the external standard. The accuracy of measurements of the ¹H. ¹³C, ³¹P, ²⁹Si, and ¹¹⁹Sn chemical shifts was ± 0.01 , ± 0.05 , ± 0.1 , ± 0.2 , and ± 0.2 ppm, respectively. The accuracy of measurements of the spin-spin coupling constants (J_{HH}, J_{HP}, J_{CP}, J_{SiP}, J_{CSi}, J_{HSn}, J_{CSn}, J_{PSn}, and J_{SiSn}) was ± 0.1 Hz. The assignment of the signals in the ¹³C NMR spectra was made with the use of the 1NEPT and DEPT procedures and offresonance experiments. In some cases, the monoresonance ¹³C NMR spectra were recorded.

All operations were carried out under an atmosphere of dry oxygen-free argon using the standard Schlenk technique or in a dry box under an inert atmosphere. Some syntheses were carried out *in vacuo* (10^{-3} Torr) in seamless-soldered apparatus with the use of techniques of broken walls and tubes (the vacuum method). The solvents THF, Et₂O, and C₆H₆ were distilled from Na or LiAlH₄, stored over sodium benzophenone ketyl, and distilled into reaction vessels immediately before use. Pyridine was distilled and stored over CaH₂. The alcohols were distilled from Sodium or LiAlH₄. All solvent used in NMR spectroscopy were purified as described for the corresponding nondeuterated solvents.

Elemental analysis was performed on an automated CHNmicroanalyzer (Klinlaborpribor, Klin, Russian Federation). The GLC analysis was carried out on an LKhM-80 chromatograph equipped with a thermal conductivity detector (a 2 m \times 3-mm column, 5% SE-30 on silanized Chromosorb G (80/100 mesh) as the stationary phase, helium as the carrier gas, the column temperature was 50-290 °C).

Procedures for the synthesis of betaines 1a.b, 2, and 3a-c have been reported previously.²

3-Methoxy-1,1,1,3-tetramethyl-3-phenyldisiloxane was prepared by the reaction of equimolar amounts of Me₃SiOLi ²⁶ and (methyl)methoxy(phenyl)chlorosilane²⁷ in ether. The yield was 67%, b.p. 71–72 °C (0.1 Torr), n_D^{20} 1.4592. Found (%): C, 55.82; H, 8.51; Si, 23.94. C₁₁H₂₀O₂Si₂. Calculated (%): C, 54.95; H, 8.38; Si, 23.36.

Alkylation of 2,3-dimethyl-3-triphenylphosphonio-2-silabutane-2-thiolate, Ph₃P⁺CMe₂SiMe₂S⁻ (1a). Heating of a suspension of betaine 1a (0.1 g, 0.25 mmol) in THF (3 mL) with EtBr (0.67 g, 6.15 mmol) for 1 h afforded {1-methyl-1-[dimethyl(ethylthio)silyl]ethyl}triphenylphosphonium bromide (4) as colorless crystals in a yield of 0.089 g (70%), m.p. 150–151 °C (with decomp., from pyridine). Found (%): C, 59.93; H, 6.34; Br. 16.17; S, 6.64. C₂₅H₃₂BrPSSi. Calculated (%): C. 59.60; H, 6.45; Br. 15.86; S, 6.36. ¹H NMR (C₅D₅N), δ : 0.31 (s, 6 H, Me₂Ci); 1.15 (t, 3 H, MeCH₂S, ³J_{HH} = 7.4 Hz); 1.79 (d, 6 H, Me₂C, ³J_{HP} = 19.3 Hz); 2.50 (q, 2 H, MeCH₂S, ³J_{HH} = 7.4 Hz); 7.62-8.21 (m. 15 H, Ar). ¹³C NMR (C₅D₅N), δ : 0.07 (s. Me₂Si); 18.32 (s. MeCH₂S); 22.60 (s. MeCH₂S); 23.14 (d. Me₂C. ²J_{CP} = 2.6 Hz); 25.10 (d. Me₂CP, ¹J_{CP} = 31.1 Hz); 119.53 (d. C_a, ⁴J_{CP} = 31.3 Hz); 130.53 (d. C_m, ³J_{CP} = 11.6 Hz); 135.19 (d. C_a, ⁴J_{CP} = 3.2 Hz); 135.76 (d. C_a, ²J_{CP} = 8.9 Hz). ³¹P NMR (C₅D₅N), δ : 36.81. ²⁹Si NMR (C₅D₅N), δ : 24.03 (d. ²J_{SIP} = 3.5 Hz).

Acetylation of betaine 1a and 3-triethyl-2-methylphosphonio-2-silabutane-2-thiolate, Et₃P+CHMeSiMe₂S- (2). A. A solution of acetyl chloride (Reakhim) (0.23 g. 2.98 mmol or 0.3 g. 3.98 mmol) in THF (5 or 10 mL, respectively) was added dropwise with stirring to a suspension of betaine 1a (1.18 g. 2.99 mmol) in THF (40 mL) or betaine 2 (0.94 g, 3.92 mmol) in THF (50 mL). The precipitate of the betaine was gradually dissolved. After ~5 min, the reaction solution turned yellow and then orange and an amorphous precipitate formed. The reaction mixture was kept at +5 °C for 5 days after which a light-claret solution and a white precipitate formed. The precipitate was filtered off and dried in vacuo; (Ph₂P⁺Prⁱ)Cl⁻ and (Et₄P⁺)Cl⁻ (m.p. 320 °C; cf. Ref. 28) were obtained in yields of 1.02 g (100 %) and 0.73 g (100%), respectively. Volatile compounds were removed from the solution in vacuo. Pentane (50 mL) was added to the residue, the solution was filtered, and the pentane was distilled off at 20 °C (1 Torr) until copious crystallization started. The reaction mixture was kept at -12 °C for 12 h and then the precipitate was filtered off and dried at 20 °C (1 Torr). 2,2,6-Trimethyl-1,3-dioxa-2-silacyclohex-5-ene-4-thione (5) was obtained in a yield of 0.25 g (96%, for 1a) or 0.34 g (98%, for 2). The resulting compound was readily sublimed at 50-70 °C (1 Torr) to give yellow crystals, which were studied by X-ray diffraction analysis (see Fig. 1). We failed to obtain reliable data of elemental analysis because this compound is extremely unstable in the presence of traces of atmospheric oxygen and moisture. ¹H NMR (C_6D_6), δ : 0.07 (s, 6 H, Me₂Si, ² $J_{SiH} = 7.5$ Hz); 1.45 (d, 3 H, MeC, ⁴ $J_{HH} = 0.7$ Hz); 6.13 $J_{SiH} = 7.5 \text{ Hz}$; 1.45 (d, 5 H, (MeC, $J_{HH} = 0.7 \text{ Hz}$), 6.15 (q, 1 H, CH=C, ${}^{4}J_{HH} = 0.7 \text{ Hz}$), ¹³C NMR (C₆D₆), δ : -2.01 (Me₂Si, ¹J_{CH} = 121.5 Hz, ¹J_{CSi} = 73.6 Hz); 21.73 (MeC, ¹J_{CH} = 128.7 Hz, ${}^{4}J_{CH} = 3.0 \text{ Hz}$); 112.54 (=CH, ¹J_{CH} = 170.3 Hz, ³J_{CH} = 3.9 Hz); 159.59 (=CMe, ²J_{C=CH} = ²J_{CMe} = 6.5 Hz); 203.20 (C=S, ²J_{CH} = 4.8 Hz). ²⁹Si NMR (C₆D₆), δ : 10.40. According to the data of GLC analysis and ¹H and ¹³C NMR spectroscopy, $(Me_2SiS)_3$ was present in the mother liquors that remained after crystallization of compound 5.

B. MeCOCl (4.67 g, 59.5 mmol) was added with stirring to a suspension of betaine 2 (1.77 g, 7.5 mmol) in diethyl ether (50 mL). The local reddish coloring of the precipitate was observed, but the color rapidly disappeared. After heating for 20 min, the precipitate was separated and dried *in vacuo*. [(1-Dimethylchlorosilyl)ethyl]triethylphosphonium chloride (11) was obtained in a yield of 2.0 g (97.1%). Found (%): C, 43.07: H, 9.39: Cl, 25.35. C₁₀H₂₅Cl₂PSi. Calculated (%): C, 43.63; H, 9.15; Cl, 25.76. ¹H NMR (C₅D₅N), & 0.91 (s, 6 H, Me₂Si); 1.32 (dt, 9 H, MeCH₂P⁺, ³J_{PH} = 18.0 Hz, ³J_{HH} = 7.6 Hz); 1.49 (dd. 3 H, MeCH²P⁺, ³J_{PH} = 17.4 Hz, ³J_{HH} = 7.3 Hz); 2.64-2.94 (complex m, 6 H. CH₂P⁺, AB portion of the ABMX₃ spectrum); 4.14 (dq, 1 H, CHP⁺, ²J_{PH} = 20.1 Hz, ³J_{HH} = 7.3 Hz). ¹³C NMR (C₅D₅N), &: 3.29 (br.s, Me₂Si, ¹J_{SiC} = 59.9 Hz); 6.77 (d, MeCH₂-P⁺, ²J_{PC} = 5.3 Hz); 9.23 (d, MeCHP⁺, ²J_{PC} = 4.6 Hz); 13.16 (d, CH₂P⁺, ¹J_{PC} = 47.9 Hz); 13.36 (d, CHP⁺, ¹J_{PC} = 38.6 Hz). ³¹P NMR (C₅D₅N), 8: 44.41. ²⁹Si NMR (C₅D₅N), 8: 30.91 (d, ²J_{PSi} = 3.2 Hz). **Beaticips of betaine 1a with hex-aethyldistannovane (xacuum**

Reaction of betaine 1a with hexaethyldistannoxane (vacuum method). A. A mixture of hexaethyldistannoxane²⁹ (0.41 g. 0.96 mmol) and Me₃SiOMe ³⁰ (1 g, 9.6 mmol) was added to a suspension of betaine 1a (0.38 g, 0.96 mmol) in pyridine-d₅ (1.5 mL). The reaction mixture was kept at -20 °C for 12 h. According to the data of GLC and ¹H, ¹³C, ²⁹Si, and ³¹P NMR spectroscopy, the reaction proceeded quantitatively to form $Ph_3P=CMe_2$, $(Et_3Sn)_2S$, methoxypentamethyldisiloxane (13a) (the yield was 83%), and a mixture of oligomers 12a (17%). $\frac{Ph_3P=CMe_2}{Ph_3P=CMe_2} \stackrel{1}{\to} NMR (C_5D_5N), \ \delta: \ 2.00 \ (d, \ Me_2C, \ J_{PH} = 16.5 \ Hz); \ 7.38-7.80 \ (m, \ Ph_3P). \ ^{13}C \ NMR \ (C_5D_5N), \ \delta: \ 8.72$ 10.5 riz), (.50-7.60 (iii, ru₃r). The (MMR (C₅U₅(v), 6; 8.72) (d. P=C, ${}^{1}J_{PC} = 123.9$ Hz); 20.69 (d. Me₂CP, ${}^{2}J_{PC} = 13.7$ Hz); 128.41 (d. C_m, ${}^{3}J_{PC} = 11.0$ Hz); 130.78 (d. C_p, ${}^{4}J_{PC} = 2.6$ Hz); 133.88 (d, C_o, ${}^{2}J_{PC} = 8.9$ Hz); 133.31 (d. C_i, ${}^{1}J_{PC} = 81.3$ Hz). ³¹P NMR (C₅D₅N), δ : 10.69. (Et₃Sn)₂S. ¹H NMR (C₅D₅N), δ : 1.07-1.28 (m. CH₂Sn); 1.33-1.54 (t. Me₂CH₂Sn). ¹³C NMR (C_5D_5N) , δ : 7.22 (s. CH₂Sn, $J_{117SnC} = 323.9$ Hz, $J_{119SnC} =$ 338.9 Hz); 10.77 (s, MeCH₂Sn, $J_{117/119SnC} = 24.0$ Hz). $\frac{Me_{3}SiOSiMe_{2}OMe_{-}(13a)}{Me_{3}Si); 0.17 (s, Me_{2}Si); 3.54 (s, SiOMe). {}^{13}C NMR (C_{5}D_{5}N), \delta: 0.20 (s, Me_{3}Si); 0.17 (s, Me_{2}Si); 3.54 (s, SiOMe). {}^{13}C NMR (C_{5}D_{5}N), \delta: 0.20 (s, Me_{3}Si); 0.17 (s, Me_{3}Si); 0.17$ δ: 1.32 (Me₂Si); 1.89 (Me₃Si); 49.76 (SiOMe). ²⁹Si NMR (C_5D_5N) , δ : -11.19 (Me₂Si); 7.81 (Me₃Si).

B. $(Et_3Sn)_2O(0.43 \text{ g}, 1.02 \text{ mmol})$ was added to a suspension of betaine 1a (0.4 g, 1.02 mmol) in pyridine-d₅ (2 mL). After 5-10 min, the reaction solution turned pink. After 2-3 h, the solution turned dark-claret and betaine 1a was simultaneously dissolved. According to the data of GLC and ¹H, ¹³C, ²⁹Si, and ³¹P NMR spectroscopy, the reaction was virtually completed in 5 days. Ph₃P=CMe₂, (Et₃Sn)₂S, and a mixture of oligomers 12a (the yield was approximately quantitative) were obtained as the major reaction products. ²⁹Si NMR (C₅D₅N), δ : -18.90, -21.28.

Reaction of 3-methyl-2-phenyl-3-triphenylphosphonio-2-silabutane-2-thiolate, $Pb_3P^+CMe_2SiMePhS^-$ (1b), with hexaethyldistannoxane (vacuum method). A. Betaine 1b (0.56 g. 1.23 mmol) was mixed with (Et₃Sn)₂O (0.49 g, 1.16 mmol) and Me₃SiOMe (1 g, 9.6 mmol) in pyridine-d₅ (1.5 mL). After ~12 h, the reaction mixture contained (according to the data of GLC and ¹H, ¹³C, ²⁹Si, and ³¹P NMR spectroscopy) Ph₃P=CMe₂, (Et₃Sn)₂S, and 3-methoxy-1,1.1,3-tetramethyl-3-phenyldisiloxane (13b) (the yield was 95%) along with a small amount of oligomers of methylphenylsilanone (12b). Me₃SiOSiMePhOMe_13b. ¹H NMR (C₅D₃N), &: 0.28 (s, Me₃Si); 0.44 (s, MeSi); 3.57 (s, SiOMe); 7.39--7.84 (m, Ar). ¹³C NMR (C_5D_5N), δ : -2.17 (MeSi); 1.93 (Me₃Si); 50.16 (SiOMe); 128.24 (C_n); 130.26 (C_p); 134.10 (C_o); 136.65 (C_i). ²⁹Si NMR (C_5D_5N), δ : -24.08 (MeSi); +9.11 (Me₃Si).

B. According to the ¹H, ¹³C, ²⁹Si, and ³¹P NMR spectra measured within 7 days after mixing of betaine **1b** (0.56 g, 1.23 mmol) with (Et₃Sn)₂O (0.52 g, 1.23 mmol) in pyridine-d₅, the solution contained the initial compounds (-65%). Ph₃P=CMe₂, (Et₃Sn)₂S, and oligomers of methylphenylsilanone **12b.** The ²⁹Si NMR spectrum of compounds **12b** corresponds to the literature data.³¹

Reactions of betaine 1a and betaine 2 with heptamethyldistannazane (vacuum method). A. (Me₃Sn)₂NMe (0.67 g. 1.88 mmol) was added to a suspension of betaine 1a (0.37 g, 0.94 mmol) in C₅D₅N (1.4 mL). After 5-10 min, the solution turned pink. After 2-3 h, the reaction mixture turned darkclaret and betaine la was simultaneously dissolved. According to the ¹H, ¹³C, ²⁹Si, ³¹P, and ¹¹⁹Sn NMR spectra, the reaction was virtually completed in 5 days. Ph3P=CMe2, (Me3Sn)2S, and $Me_2Si(NMeSnMe_3)_2$ (14) were obtained as the major products (the yields were virtually quantitative). (Me₃Sn)₂S. ¹H NMR (C_5D_5N) , δ : 0.54 (s. Me_3Sn, ${}^2J_{H^{-1}\theta_2 II7Sn} = 56.3/54.7$ Hz). ${}^{13}C$ NMR (C_5D_5N) , δ : -5.31 (Me_3Sn, ${}^1J_{C^{-1}\theta_2 II7Sn} = 384.5/364.8$ Hz). ${}^{19}Sn$ NMR (C_5D_5N) , δ : 65.68 (${}^1J_{19}S_{nC} = 384.5$ Hz). Me_2Si(NMeSnMe_31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe_31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ : 0.17 (s, 6 H, MeSnMe31; (14). ¹H NMR (C_5D_5N) , δ (15). ¹H NMR (C_5D_5N) , δ (16). ¹H NMR $(C_5D_5$ Me_2SiN , ${}^2J_{HSi} = 6.1$ Hz); 0.32 (s. 18 H. Me_3SnN , ${}^2J_{H^{119/117}Sn} =$ 55.9/53.5 Hz); 2.77 (s, 6 H, MeNSn. ${}^{3}J_{H119/17Sn} =$ 45.3/43.6 Hz). ${}^{13}C$ NMR (C₅D₅N), 6: -1.37 (Me₃Sn, ${}^{1}J_{C^{119/117}Sn} = 359.5/343.5 \text{ Hz}$; 1.07 (Me₂SiNSn, ${}^{1}J_{CSi} = 61.5 \text{ Hz}$, ${}^{3}J_{C^{119}Sn} = 3.5 \text{ Hz}$; 33.48 (MeN), ${}^{29}Si \text{ NMR} (C_{5}D_{5}N)$, $\begin{array}{l} & 5.054 \ (^2J_{2951/1195n} = 23.8 \ Hz). \ ^{149}\text{Sn} \ \text{NMR} \ (C_5D_5N), \\ & 5.054 \ (^2J_{2951/1195n} = 23.8 \ Hz). \ ^{149}\text{Sn} \ \text{NMR} \ (C_5D_5N), \\ & 5.054 \ (^2J_{2951/1195n} = 359.8 \ Hz). \ ^{149}\text{Sn} \ \text{NMR} \ (C_5D_5N), \\ & 5.052 \ (s.18 \ \text{H}, \ \text{Me}_3\text{Sn}, \ ^2J_{\text{H19}/1175n} = 51.5/52.4 \ \text{Hz}); \\ & 5.10 \ (s.6 \ \text{H}, \ \text{MeNSn}, \ ^3J_{\text{H19}/1175n} = 53.0/51.3 \ \text{Hz}). \ ^{13}\text{C} \ \text{NMR} \ (C_5D_5N), \\ & 5.552 \ \text{MeR} \ (c.5D_5N), \\$ $δ: -5.80 (Me_3Sn, {}^{1}J_{C110(1)2Sn} = 371.0/355.1 Hz); 38.84 (MeNSn, {}^{2}J_{C110Sn} = 12.1 Hz). {}^{119}Sn NMR (C_5D_5N). δ: 81.96 ({}^{1}J_{119SnC} =$ 371.0 Hz).

B. Analogously, Me₂Si(NMeSnMe₃)₂ (14) (78%), (Me₃Sn)₂S (91%), ylide Et₃P=CMe(SnMe₃) (15) (29%), and the [Et₄P⁺][Me₃SnNMe]⁻ salt (58%) were obtained from a solution of betaine 2 (0.24 g, 1.02 mmol) and (Me₃Sn)₂NMe (0.91 g, 2.54 mmol) in C₃D₅N (1 mL). Ylide 15 was prepared by independent synthesis by mixing stolchiometric amounts of Et₃P=CHMe and (Me₃Sn)₂NMe in C₆D₆ *in vacuo*. **1**-(**Trimethylstannyl)ethylidene(triethyl)phosphorane (15)**. ¹H NMR (C₆D₆), & 0.36 (s, 9 H. Me₃Sn, ²J_{H10Sn} = 49.0 Hz); 0.88 (dt. 9 H. MeCH₂P, ³J_{HP} = 15.4 Hz, ³J_{HH} = 7.7 Hz); 1.28 (dq. 6 H. MeCH₂P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H. MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H. MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H. MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H. MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H. MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H. MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H. MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H. MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H. MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H. MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H. MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H. MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H. MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H. MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H. MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H. MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H. MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H, MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 2.02 (d, 3 H, MeC=P, ³J_{HP} = 10.4 Hz, ³J_{HH} = 7.7 Hz); 1.28 (d, 4 Hz, ³J_H = 1.7 Hz, ³J_H = 1.7 Hz, ³J_H = 1.7 Hz, ³J_H = 1.7 Hz); 1.1458 (d, MeC=P, ²J_{CP} = 5.3.7 Hz, ³J_{CP} = 9.6 Hz). ³¹P NMR (C₆D₆), &: 25.43 (²J_{P119/117Sn} = 213.5

Synthesis and isomerization of 2-methyl-3-triphenylphosphonio-2-silabutane-2-thiolate, $Ph_3P^+CHMeSiMe_2S^-$ (3a). When a solution of $Ph_3P=CHMe$ (6.35 g, 21.90 mmol) was added to a solution of $(Me_2SiS)_n$ (1.95 g, 21.67 mmol per monomer unit) in benzene (60 mL), two layers formed. The layers were separated and the solvent was removed *in vacuo* from both portions. Solid yellow substances were obtained. According to the ¹H, ¹³C, and ³¹P NMR spectra in C₆D₆, the solid substance from the upper layer contained ylide $Ph_3P=C(Me)SiMe_2SH$ (16a) and betaine $Ph_3P^+CHMeSiMe_2S^-$ (3a) in a ratio of 62 : 38, and the substance from the lower layer in C₅D₅N contained compounds **16a** and **3a** in a ratio of 1.4 : 98.6. <u>Ph₃P=C(Me)SiMe₂SH</u> (**16a**). ¹H NMR (C₆D₆), δ : 0.50 (s, 6 H, Me₂Si); 2.18 (d. 3 H, MeC, ³J_{HP} = 20.1 Hz); 7.05-8.06 (m. 15 H, Ar). ¹³C NMR (C₆D₆), δ : 6.51 (d. Me₂Si, ³J_{CP} = 2.7 Hz); 15.93 (d. <u>Me</u>C, ²J_{CP} = 2.8 Hz); 5.58 (d. P=C, ¹J_{CP} = 94.9 Hz); 128.28 (d. C_m, ³J_{CP} = 11.0 Hz); 130.89 (d. C_p, ⁴J_{CP} = 2.6 Hz); 132.29 (d. C_n, ¹J_{CP} = 82.6 Hz); 134.47 (d. C_p, ²J_{CP} = 9.1 Hz). ³¹P NMR (C₆D), δ : 21.18 (²L₀ = 29.8 Hz).

9.1 Hz). ³¹P NMR (C_6D_6), & 21.18 (${}^2J_{PS1} = 29.8$ Hz). Isomerization of 2-methyl-1-triphenylphosphonio-2-silapropane-2-thiolate, Ph₃P+CH₂SiMe₂S⁻ (3b) (vacuum method). The ²⁹Si NMR spectrum of a solution of betaine 3b in THF-d₈ has signals at δ 2.73 (d, ${}^2J_{SiP} = 6.5$ Hz), 2.17 (d, ${}^2J_{SiP} = 16.4$ Hz), and 7.42 (d, ${}^2J_{SiP} = 11.8$ Hz) along with signals of 3b at δ -0.67 (d, ${}^2J_{SiP} = 6.3$ Hz).

Isomerization of 2-phenyl-1-triphenylphosphonio-2-silapropane-2-thiolate, $Ph_3P^+CH_2SiMePhS^-$ (3c) (vacuum method). The ¹H and ¹³C NMR spectra of a solution of betaine 3c in THF-d_s have signals of betaine 3c and $Ph_3P=CHSiMePhSH$ (16c) in a ratio of 1 : 3.8. Compound 16c. ¹H NMR (THF-d_s), δ : 0.26 (s. MeSi); 0.73 (d. P=CH, ²J_{HP} = 8.7 Hz). ¹³C NMR (THF-d_s), δ : 5.19 (d. MeSi, ³J_{CP} = 7.7 Hz); 2.08 (d. P=C. ¹J_{CP} = 94.2 Hz); 128.17 (d. Ph_3P-C_m, ³J_{CP} = 11.5 Hz); 133.27 (d. Ph_3P-C_m, ²J_{CP} = 9.9 Hz); 150.61 (d. PhSi-C_h, ³J_{CP} = 2.9 Hz). Other signals were not observed because they overlap with signals of betaine 3c.²

Reaction of betaine 3a with MeOD (vacuum method). When betaine 3a (0.3 g, 0.79 mmol) was dissolved in methanol-d₁ (2 mL), a moderately exothermic reaction proceeded. The color of the solution rapidly changed from brightorange to lemon-yellow. According to the ¹H, ¹³C, and ³¹P NMR spectra measured after several hours, the colorless solution contained Me₂Si(OMe)₂ (the yield was 80%) and salts 18a, viz. [Ph₃P⁺CH₂Me]X⁻ (-30%; δ_{31p} 25.03), [Ph₃P⁺CHDMe]X⁻ (-30%; δ_{31p} 24.97), and [Ph₃P⁺CD₂Me]X⁻ (-40%; δ_{31p} 24.90), where X = HS⁻ or DS⁻.

Reaction of betaine 3b with MeOD (vacuum method). When betaine 3b was dissolved in dry methanol- d_1 , a lightyellow solution was obtained. This solution turned colorless in ~45 min. According to the ¹H, ¹³C, and ³¹P NMR spectra, the solution contained Me₂Si(OMe)₂ (90%), isopropyl(triphenyl)phosphonium thiolate, [Ph₃P⁺Me]X⁻, (**18a**) (-14%; δ_{31P} 21.22), and products of its partial deuteration, *viz.*, [Ph₃P⁺CH₂D]X⁻, (~14%; δ_{31P} 21.14), [Ph₃P⁺CHD₂]X⁻ (~31%; δ_{31P} 21.05), and [Ph₃P⁺CD₃]X⁻ (~41%; δ_{31P} 20.98), where X = HS⁻ or DS⁻.

Reaction of betaine 1a with MeOD in C5D5N (vacuum method). A solution of betaine 1a (0.06 g, 0.15 mmol) in a 1 : 1 C₅D₅N-MeOD mixture was kept in a sealed NMR tube at ~20 °C for 5 months. The course of the reaction was monitored by ¹H, ¹³C, and ³¹P NMR spectroscopy. After 24 h, 7 days, 70 days, and 150 days, the conversion of the betaine was 38.7, 49.1, 82.7, and 100%, respectively, and the yield of MerSi(OMe)2 was <5, 9.7, 30, and 90%, respectively. The yield of [Ph3P+CDMe2]SD- (19a) was 96%. 2-Deuteroprop-2-yl(triphenyl)phosphonium deuterothiolate (19a). ¹H NMR $(C_5D_5N-MeOD (1 : 1)), \delta: 1.49 (d, 6 H, CDMe_2, {}^3J_{PH} =$ 18.7 Hz). ¹³C NMR (C₅D₅N-MeOD (1 : 1)), δ : 16.78 (d. CDMe₂, ²J_{PC} = 2.1 Hz); 21.99 (dt. CDMe₂, ¹J_{PC} = 48.0 Hz; ${}^{1}J_{CD} = 19.8$ Hz). The signals in the aromatic region of the NMR spectrum⁹ and the signals of Me₂Si(OMe)₂ ³² correspond to the literature data. Volatile products and the solvent were removed in vacuo, and the residue was crystallized from pyridine.

Reaction of betaine 2 with MeOD (vacuum method). No changes were observed upon dissolution of betaine 2 (0.28 g, 1.19 mmol) in methanol- d_1 . According to the data of ¹H, ¹³C, and ²⁹Si NMR spectroscopy, the conversion of the initial betaine was -56.3% and 100% after 3 and -30 days, respec-

Compound	5	18a	19a <i>a</i>
Formula	C ₆ H ₁₀ O ₂ SSi	[C ₂₀ H ₂₀ P] ⁺ · ·[SH] [−]	$\frac{[C_{21}H_{22}P]^{+}}{\cdot [SH]^{-} \cdot C_{5}H_{5}N}$
М	174.29	324.4	417.52
Crystal system	Ortho- rhombic	Monoclinic	Ortho- rhombic
Space group	Pnma	C2/c	Pnma
a/A	8.834(2)	14.162(3)	18.460(5)
b/Å	7.361(2)	12.545(3)	18.850(5)
c/À	13.454(2)	19.819(5)	13.558(2)
α/deg	90	90	90
β/deg	90	92.26(2)	90
γ/deg	90	90	90
$V/Å^3$	874.9(3)	3518(1)	4718(2)
Ζ	4	8	8
<i>T</i> ∕°C	-120(2)	-120(2)	-120(2)
$d_{\rm calc}/{\rm g~cm^{-3}}$	1.323	1.225	1.176
θ_{max}/deg	28	25	23
N _{refl} /N' _{refl} ^b	994/980	3244/3056	2532/2488
$(c l \ge 2\sigma(l))$			
R	0.033	0.054	0.068
wR ₂	0.107	0.100	0.202

Table 2. Principal crystallographic data for compound 5 and salts 18a and 19a

^a Solvate with pyridine.

 ${}^{b}N_{refl}$ and N'_{refl} are the number of the measured reflections and the number of reflections used in the structure refinement, respectively.

tively. The yields of Me₂Si(OMe)₂, $[Et_3P^+CHDMe]X^-$ (19b), and $[Et_4P^+]SH^-$, where X = HS⁻ or DS⁻, were 75%, -95% (δ_{31P} 40.91), and ~5% (δ_{31P} 41.01), respectively.

X-ray diffraction study. The unit cell parameters of the compounds under study and intensities of independent reflections were measured on an automated four-circle Siemens P3/PC diffractometer (λ (Mo-K α) radiation, graphite monochromator, $\theta/2\theta$ scanning technique). In the case of compound 5, the crystal was placed into a glass (Pyrex) tube filled with argon. The tube was evacuated to 10^{-3} Torr and sealed. All structures were solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. Molecule 5 was located in a special position on a mirror plane. In the crystal of compound 19a. two pyridine molecules of solvation, which occupy special positions on mirror planes, were revealed. Two SHT anions also occupy special positions on mirror planes. All hydrogen atoms of compounds 5 and 18a and the hydrogen atoms of the SH⁻ anions of compound 19a were located from the difference Fourier syntheses and refined isotropically. The remaining hydrogen atoms of compound 19a were calculated from geometric considerations and were included in the refinement with fixed positional (the riding model) and thermal parameters in the isotropic approximation. All calculations were carried out on an IBM PC/AT-486 computer using the SHELXTL PLUS program package (PC Version 5.0).³³ The principal characteristics of X-ray diffraction studies are given in Table 2. The complete tables of the bond lengths and bond angles, the atomic coordinates, and the thermal parameters have been deposited with the Cambridge Structural Database.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 96-03-33188a and 00-15-97359).

References

- V. N. Khrustalev, N. N. Zemlyanskii, I. V. Borisova, Yu. A. Ustynyuk, and E. A. Chernyshev, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 931 [*Russ. Chem. Bull.*, 2000, **49**, 929 (Engl. Transl.)].
- I. V. Borisova, N. N. Zemlyanskii, A. K. Shestakova, Yu. A. Ustynyuk, and E. A. Chernyshev, *Izv. Akad. Nauk. Ser. Khim.*, 2000, 922 [*Russ. Chem. Bull.*, 2000, **49**, 920 (Engl. Transl.)].
- 3. S. Scheithauer and R. Mayer, Chem. Ber., 1967, 100, 1413.
- 4. H. Schmidbaur, Acc. Chem. Res., 1975, 8, 62.
- F. H. Allen, O. Kennard, D. G. Watson, A. G. Orpen, L. Brammer, and R. Taylor, J. Chem. Soc., Perkin Trans. 2, 1987, S1.
- 6. M. G. Voronkov and S. V. Basenko, J. Organomet. Chem., 1995, 500, 325.
- Kapp, M. Remko, and P. v. R. Schleyer, J. Am. Chem. Soc., 1996, 118, 5745.
- I. Hemme and U. Klingebiel, Adv. Organomet. Chem., 1996, 39, 159.
- 9. T. A. Albright, M. Gordon, W. J. Freeman, and E. E. Schweizer, J. Am. Chem. Soc., 1976, 98, 6249.
- K. A. O. Starzewski and H. T. Dieck, *Phosphorus*, 1976.
 6, 177.
- 11. H. Schmidbaur and W. Tronich, Chem. Ber., 1967, 100, 1032.
- H. Schmidbaur, R. Pichl, and G. Muller, Chem. Ber., 1987, 120, 789.
- H. Schmidbaur, W. Richter, W. Wolf, and F. H. Kohler, Chem. Ber., 1975, 108, 2642.
- 14. H. Schmidbaur and W. Wolf, Chem. Ber., 1975, 108, 2834.
- D. Seyferth, D. P. Duncan, H. Schmidbaur, and P. Holl, J. Organomet. Chem., 1978, 159, 137.
- 16. H. Gilman and R. A. Tomasi, J. Org. Chem., 1962, 27, 3647.
- 17. H. J. Bestmann, R. Engler, H. Hartung, and K. Roth, Chem. Ber., 1979, 112, 28.
- 18. H. Schmidbaur, J. Eberlein, and W. Richter, Chem. Ber., 1977, 110, 677.
- (a) H. Schmidbaur, H. Stuhler, and W. Buchner, Chem. Ber., 1973, 106, 1238; (b) O. I. Kolodyazhnyi, in Khimiya ilidov fosfora {Chemistry of Phosphorus Ylides}, Naukova Dumka, Kiev, 1994, 244 pp. (in Russian).
- 20. K. Sasse, in *Houben-Weyl*, Thieme, Stuttgart, 1963, XXII/1, 106.
- 21. E. J. Smail and G. M. Sheldrick, Acta Crystallogr., Sect. B, 1973, 29, 2027.
- 22. A. Criado, A. Conde, E. Moreno, and R. Marquez, Z. Kristallogr., 1975, 141, 193.
- D. Mootz, D. Brodalla, and M. Wiebcke. Acta Crystallogr., Sect. C, 1990. 46, 797.
- 24. M. T. Andras, A. F. Hepp, P. E. Fanwick, R. A. Martuch, S. A. Duraj, and E. M. Gordon. Acta Crystallogr., Sect. C, 1996, 52, 1701.
- 25. O. V. Shishkin, N. N. Kolos, V. D. Orlov, V. P. Kuznetsov, and E. E. Lakin, Acta Crystallogr., Sect. C, 1995, 51, 2643.
- D. Brandes and A. Blaschette, J. Organomet. Chem., 1974, 73, 217.

- 27. V. V. Yastrebov, A. V. Krylov, G. Ya. Zueva, and O. N. Schumilov, Org. React. (Tartu), 1977, 14, 332.
- 28. J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, 1964, 20, 449.
- 29. K. A. Kocheshkov, N. N. Zemlyanskii, N. I. Sheverdina, and E. M. Panov, Metody elementoorganicheskoi khimii. Germanii. Olovo. Svinets [Methods of Heteroorganic Chemistry. Germanium. Tin. Lead], Nauka. Moscow, 1968 (in Russian).
- 30. J. Goubeau and D. Paulin, Chem. Ber., 1960, 93, 1111.
- 31. R. K. Harris, B. J. Kimber, M. D. Wood, and A. Holt, J. Organomet. Chem., 1976, 116, 291.
- 32. E. V. van den Berghe and G. P. van der Kelen, J. Organomet. Chem., 1976, 122, 329.
- 33. G. M. Sheldrick, SHELXTL PC Version 5.0. An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data, Siemens Analytical X-Ray Instruments, Inc., Madison (WI), 1994.

Received December 15, 1999