Heteroorganic betaines
4.* Photolysis and thermolysis of betaines containing the $^+$P—C—Si—S$^-$ structural fragment

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Photolysis and thermal decomposition of betaines R_3P—CR^1R^2—SiR^3R^4—S$^-$ (1) follows two main pathways: (a) a Corey—Chaykovsky type reaction with elimination of Ph_3P and generation of silathiirane R^1R^2C—SiR^3R^4—$\underline{S}$ (2) and (b) a retro-Wittig type reaction accompanied by elimination of R_3P=CR^1R^2 and generation of silanethione R^3R^4Si=S (3). Highly reactive compounds 2 and 3 undergo subsequent transformations to give derivatives of tetrahydro-1,4-dithia-2,5-disilin, 1,3-dithia-2,4-disilolane, and phosphonium salts of *symm*-tetraorganodisilthiane dithiolates $[Ph_3P^+CHR^1R^2]_2[(R^3R^4SiS^-)_2S]$. The structures of the compounds obtained were established by X-ray diffraction analysis and multinuclear NMR spectroscopy.

Key words: Wittig reaction, Corey—Chaykovsky reaction, betaines, photolysis, thermal decomposition, silathiiranes, silanethiones, NMR spectroscopy, X-ray diffraction analysis.

The reaction of thiocarbonyl compounds with phosphorus ylides proceeds through the intermediate formation of betaines[1—4] and/or thiaphosphetanes.[5] The decomposition of these intermediates can follow three pathways: elimination of phosphine to give thiiranes[6,7] (a Corey—Chaykovsky type reaction) (*a*); dissociation into the initial components[8] (a retro-Wittig type reaction) (*b*); and elimination of phosphine thiooxide to give olefins[2,3b,5—11] (a Wittig type reaction) (*c*) (Scheme 1).

Previously, we reported the synthesis,[4] structure,[12] and reactions[1] of organosilicon-phosphorus betaines with a thiolate center $R^1{}_3P^+$—CR^2R^3—SiR^4R^5—S$^-$. In this study, we demonstrated that photo and thermal decomposition of betaines of this type with phenyl groups at the phosphorus atom** Ph_3P^+—CR^1R^2—SiR^3R^4—S$^-$ (1) follow pathways *a* and *b* with the intermediate formation of silathiiranes R^1R^2C—SiR^3R^4—$\underline{S}$ (2) and

silanethiones R^3R^4Si=S (3), respectively. The generation of silathiiranes by this method is the first example of synthesis of organoelement compounds according to a Corey—Chaykovsky type reaction.

Results and Discussion

Photodecomposition of betaines 1. UV irradiation stimulates intramolecular S$^-$ → P$^+$ charge transfer. When a suspension of $Ph_3P^+CMe_2SiMe_2S^-$ (1a) in benzene is exposed to the radiation of a medium-pressure mercury lamp at 20 °C, the compound decomposes by the Corey—Chaykovsky reaction pattern to give silathiirane (2a) and Ph_3P (Scheme 2).

Silathiirane 2a, like other sterically nonhindered thiiranes of Group 14 elements[13—16] and unlike the carbon analog, forms a cyclodimer, tetrahydro-2,2,3,3,5,5,6,6-octamethyl-1,4-dithia-2,5-disilin (4a, yield 57%) or undergoes other transformations.

The intermediate formation of silathiirane 2a was confirmed by trapping agents. For this purpose, photolysis of 1a (suspension in C_6H_6) in the presence of Me_2CO was performed. According to GC/MS analysis, in addition to dimer 4a (major product), the reaction mixture contained 2,2,4,4,5,5-hexamethyl-3-oxa-1-thia-4-sil-
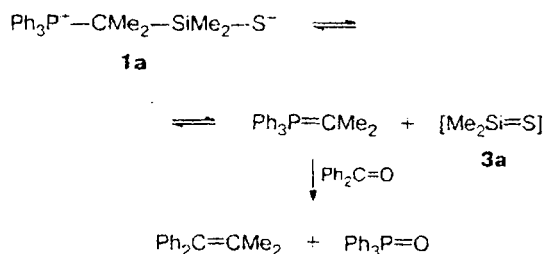
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* For part 3, see Ref. 1.

** The betaines $Et_3P^+CHMeSiMe_2S^-$ and $Et_3P^+CHMeSiPh_2S^-$ with alkyl groups at the phosphorus atom are distinguished by high thermal stability; their spectral characteristics do not change during storage of solutions of these compounds in pyridine-d_5 or metastable solutions in benzene-d_6 for 1—2 years at ~20 °C in sealed evacuated tubes or on heating (150 °C) for 15 h.

Scheme 1

$$[R_3\overset{+}{P}-CR^1R^2-CR^3R^4-S^-] \xrightarrow{a} R_3P + R^1R^2C\underset{S}{\diagdown\diagup}CR^3R^4$$

$$R_3P{=}CR^1R^2 \quad + \quad R^3R^4C{=}S \quad \underset{b}{\rightleftharpoons}$$

$$\left[\begin{array}{c} R_3P{-}CR^1R^2 \\ | \quad\quad | \\ S{-}CR^3R^4 \end{array}\right] \xrightarrow[{-R_3P=S}]{c} R^1R^2C{=}CR^3R^4$$

$$\downarrow -R_3P{=}S$$

Scheme 2

$$Ph_3\overset{+}{P}-CMe_2-SiMe_2-S^- \xrightarrow{h\nu} Ph_3P + \left[Me_2C\underset{S}{\diagdown\diagup}SiMe_2\right]$$

1a   **2a**

$$Me_2C{-}SiMe_2$$ ... $$Me_2Si{-}CMe_2$$ (with S, S) **4a**

$$-[Me_2C{=}SiMe_2] \quad \textbf{9a}$$

$$Ph_3P{=}S$$

$$Me_2C{-}CMe_2 \quad / Me_2Si \diagdown_S\diagup SiMe_2 \quad \textbf{7a}$$

$$Me_2CO$$

$$Me_2C{-}SiMe_2 \quad S \diagdown_C\diagup O \quad Me_2 \quad \textbf{5a}$$

$$Ph_3P{=}CMe_2 + Me_2C\underset{S}{\diagdown}{-}SiMe_2 \quad\underset{S}{\diagup}\quad \underset{Si}{\ }\quad Me_2 \quad \textbf{6a}$$

$$\longleftarrow [Ph_3\overset{+}{P}-CMe_2-SiMe_2-S-SiMe_2-CMe_2-S^-]$$

8a

olane (**5a**), resulting from the reaction of silathiirane **2a** with acetone, 2,2,4,4,5,5-hexamethyl-1,3-dithia-2,4-disilolane (**6a**), and 2,2,3,3,4,4,5,5-octamethyl-1-thia-2,5-disilolane (**7a**). Most likely, under heterogeneous conditions, disilolane **6a** is formed upon the reaction of silathiirane **2a** with the starting **1a**. Betaine **8a** thus formed decomposes to give predominantly $Ph_3P{=}CMe_2$ and **6a**. A much smaller amount of **8a** decomposes to give Ph_3PS (yield ~14%) and thiadisilolane **7a**. Compound Ph_3PS might arise from desulfurization of silathiirane **2a** to silaethylene **9a** by the action of Ph_3P, although we have not studied this decomposition route.

Unlike photolysis under heterogeneous conditions, in the photolysis of **1a** in a pyridine solution, the formation of disilolane **6a** becomes the predominant process because the starting betaine is present in a fairly high concentration and can act as a trapping agent with respect to silathiirane **2a**. The yield of compound **6a** increases to 57%, while the yield of cyclodimer **4a** decreases to 24%.

The structure of tetrahydro-2,2,3,3,5,5,6,6-octamethyl-1,4-dithia-2,5-disilin (**4a**) was proved by X-ray diffraction analysis (Fig. 1). A notable structural feature of compound **4a** is the *trans*-effect, which was discovered previously[17] for peroxide and ether molecules and manifests itself as a distortion of the tetrahedral coordination of carbon atoms bound to oxygen. In molecule **4a** (Table 1), the C(4)—Si(1)—S(1) and C(2)—C(1)—S(1)

bond angles, occurring in the *trans*-positions with respect to the corresponding opposing bonds of the S atom, decrease with respect to the ideal tetrahedral angle (109.5°) to 102.35(4)° and 104.64(6)°, respectively. The ring has a nearly ideal chair conformation (the torsion angles range from 60.4 to 61.7°).

Thermal decomposition of betaines 1. Thermolysis of betaines **1** under various conditions was studied in detail using betaine **1a** as an example. Heating solutions of **1a** in

Fig. 1. General view of molecule **4a**.

Table 1. Bond lengths (d) and bond angles (ω) in the structure of **4a**

Bond	$d/\text{Å}$	Bond	$d/\text{Å}$
S(1)—C(1)	1.8606(9)	Si(1)—C(5)	1.865(1)
S(1)—Si(1)	2.1494(4)	C(1)—C(2)	1.540(1)
Si(1)—C(1)*	1.890(1)	C(1)—C(3)	1.533(1)
Si(1)—C(4)	1.863(1)		

Angle	ω/deg	Angle	ω/deg
C(1)—S(1)—Si(1)	109.07(3)	C(3)—C(1)—C(2)	109.86(8)
C(4)—Si(1)—C(1)*	110.22(4)	C(2)—C(1)—S(1)	104.64(6)
C(5)—Si(1)—C(1)*	110.38(4)	C(3)—C(1)—S(1)	111.00(6)
C(4)—Si(1)—C(5)	109.29(5)	C(2)—C(1)—Si(1)*	110.44(6)
C(1)*—Si(1)—S(1)	110.02(3)	C(3)—C(1)—Si(1)*	112.58(6)
C(4)—Si(1)—S(1)	102.35(4)	S(1)—C(1)—Si(1)*	108.03(4)
C(5)—Si(1)—S(1)	114.29(4)		

* $-x, -y + 2, -z$.

C_5D_5N above 80 °C brings about a dark-claret color, typical of phosphorus ylide, whose formation was detected by NMR spectroscopy. In the presence of an equivalent amount of Ph_2CO, the reaction carried out for 10 min at 100 °C gives 1,1-dimethyl-2,2-diphenylethylene and Ph_3PO in a yield of 53% with respect to the theoretical yield. This indicates that decomposition of **1a** in solution follows a retro-Wittig type pathway (Scheme 3).

Scheme 3

$$Ph_3P^+ - CMe_2 - SiMe_2 - S^- \ \rightleftharpoons$$

1a

$$\rightleftharpoons \ Ph_3P = CMe_2 \ + \ [Me_2Si = S]$$

3a

$$\Big| Ph_2C = O$$

$$Ph_2C = CMe_2 \ + \ Ph_3P = O$$

An increase in the solution temperature shifts the equilibrium to the right (see Scheme 3). When betaine **1a** is dissolved in C_5D_5N at room temperature, the ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra of the solution exhibit only the signals due to the starting betaine. After heating of this solution (90 °C, ~30 min) in the NMR spectrom-

eter probe, doublets at δ 2.00 ($^3J_{PH}$ = 16.5 Hz) and δ 20.9 ($^2J_{CH}$ = 13.6 Hz), characteristic of the Me groups in $Ph_3P = CMe_2$, appear in the ^1H and ^{13}C NMR spectra and a singlet at δ 10 appears in the ^{31}P NMR spectrum. All signals corresponding to phosphorus ylide are broadened. The **1a** : $Ph_3P = CMe_2$ molar ratio is 0.8 : 1. When the temperature decreases to 50 °C, the ratio increases to 2.9 : 1, while subsequent repeated heating to 75 °C diminishes this ratio to 1.46 : 1. The ^1H and ^{29}Si NMR spectra contain somewhat broadened signals due to cyclooligomers $(Me_2SiS)_n$ at about 0.7—1.0 ppm and at ~21.0 ppm (n = 3) and ~16 ppm (n = 2), respectively. Since the irreversible processes considered below occur in parallel, the concentrated ratios presented here cannot be regarded as being equilibrium values.

Thermolysis of **1a** at higher temperatures follows simultaneously the Corey—Chaykovsky and retro-Wittig reaction routes. The ratio of the two processes depends on the temperature. This is confirmed by pyrolysis of **1a** in alcohol. Betaine **1a** is fairly stable with respect to alcohols; it can be recrystallized from hot methanol or ethanol.[4] However, keeping its solution in ethanol at 150 °C for 4 h gives rise to 2,3-dimethyl-3-ethoxy-3-silabutane-2-thiol (**10a**) and $Me_2Si(OEt)_2$ in 1 : 1 ratio as well as to Ph_3P and **11a** in the same ratio (Scheme 4).

Evidently, the arising silathiirane **2a** and silanethione **3a** immediately react with ethanol to give silylated mercaptan **10a** and $Me_2Si(OEt)_2$. The molar ratios of the products imply that the rates of the Corey—Chaykovsky type and the retro-Wittig type decomposition pathways are roughly equal. The former process starts to predominate at 245 °C (the **10a** : $Me_2Si(OEt)_2$ molar ratio is 3 : 1).

In the pyrolysis of **1a** (150 °C) in a suspension in benzene, in a melt, or in a pyridine solution, the yield of disilolane **6a** amounts to 30—48%, while the yield of cyclodimer **4a** does not exceed 12%. Decomposition of betaines $Ph_3P^+CMe_2SiMePhS^-$ (**1b**) and $Ph_3P^+CHMeSiMe_2S^-$ (**1c**) in benzene follows a similar route. The yields of 2,4,5,5-tetramethyl-2,4-diphenyl-1,3-dithia-2,4-disilolane (**6b**) and 2,2,4,4,5-pentamethyl-1,3-dithia-2,4-disilolane (**6c**) are 78 and 46%, respectively.

In all cases, silanethiones $[R^3R^4Si=S]$ (**3**) and ylides $Ph_3P = CR^1R^2$ formed upon pyrolysis of betaines **1** undergo further transformations, resulting in the phosphonium *symm*-tetraorganodisilthianedithiolates $[Ph_3P^+CHR^1R^2]_2[(R^1R^2SiS^-)_2S]$ (**12**). For instance, a

Scheme 4

$$Ph_3P^+ - CMe_2 - SiMe_2 - S^- \ \xrightarrow{t} \ Ph_3P \ + \ \left[Me_2C - SiMe_2 \atop \diagdown_S\diagup \right] \ \xrightarrow{EtOH} \ Me_2Si - CMe_2 - SH$$
$$\text{1a} \qquad\qquad\qquad \text{2a} \qquad \overset{|}{OEt}$$
$$\text{10a}$$

$$\Big\Updownarrow t$$

$$Ph_3P = CMe_2 \ + \ [Me_2Si = S] \ \xrightarrow{EtOH} \ Me_2Si(OEt)_2 \ + \ [Ph_3P^+ - CHMe_2]SH^-$$
$$\text{3a} \qquad\qquad\qquad\qquad \text{11a}$$
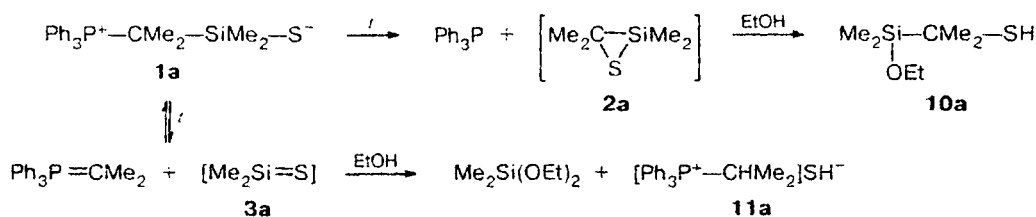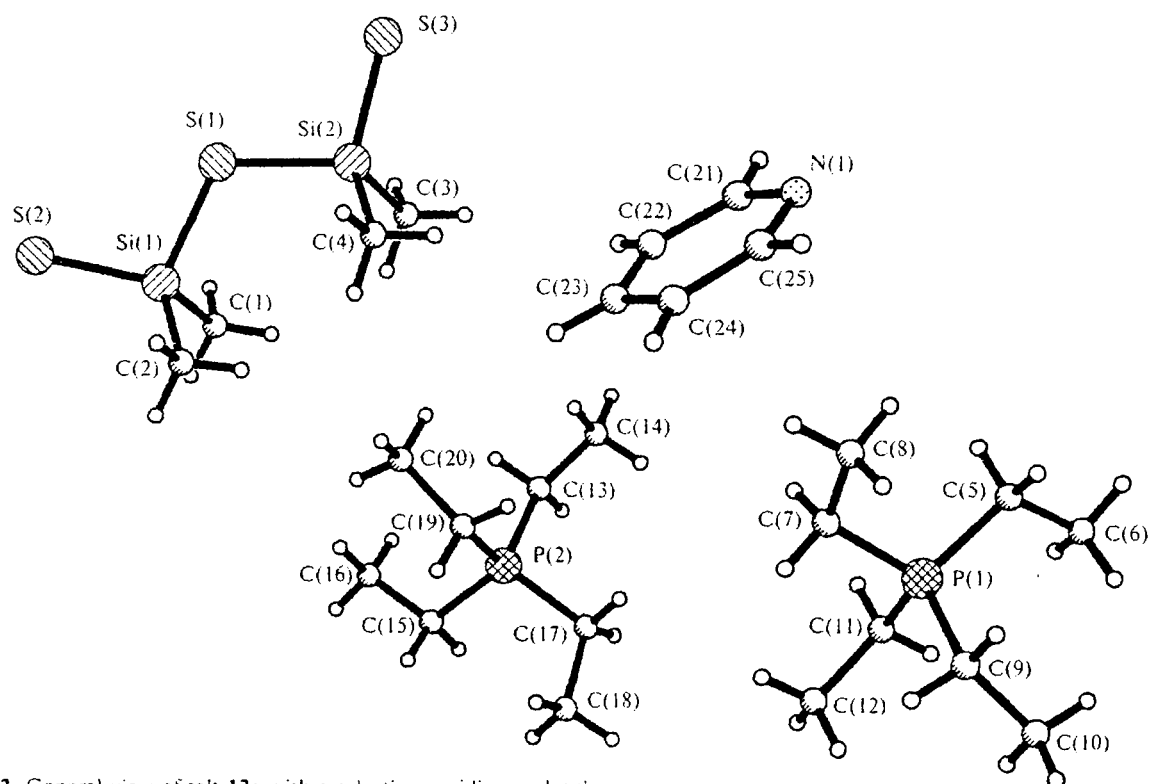
Fig. 2. General view of salt **13a** with a solvation pyridine molecule.

foam-like highly voluminous yellowish substance **12a**, readily decomposing in air, was isolated upon the pyrolysis of betaine **1a**. The NMR spectra of compound **12a** in C_5D_5N exhibit signals for the $[Ph_3P^+CHMe_2]$ cation with a markedly broadened multiplet for the CH protons (^1H NMR spectrum)

and highly broadened signals due to the anionic moiety at about 0.8—1.1 ppm (^1H NMR), ~14 ppm (^{13}C NMR), and ~11 ppm (^{29}Si NMR). Methanolysis of **12a** yields equimolar amounts of $[Ph_3P^+CHMe_2]SH^-$ (**11a**) and $Me_2Si(OMe)_2$; treatment with phosphorus ylide $Et_3P=CHMe$ (which is more

Table 2. Bond lengths (d) and bond angles (ω) in the structure of **13a**

Bond	d/Å	Bond	d/Å	Bond	d/Å	Bond	d/Å
S(1)—Si(1)	2.176(2)	P(2)—C(13)	1.805(4)	N(1)—C(21)	1.332(10)	C(15)—C(16)	1.534(6)
S(1)—Si(2)	2.180(2)	P(2)—C(15)	1.796(4)	N(1)—C(25)	1.319(9)	C(17)—C(18)	1.526(6)
S(2)—Si(1)	2.055(2)	P(2)—C(17)	1.802(4)	C(5)—C(6)	1.515(6)	C(19)—C(20)	1.526(5)
S(3)—Si(2)	2.051(2)	P(2)—C(19)	1.792(3)	C(7)—C(8)	1.540(6)	C(21)—C(22)	1.345(11)
P(1)—C(5)	1.795(4)	Si(1)—C(1)	1.886(4)	C(9)—C(10)	1.500(7)	C(22)—C(23)	1.398(11)
P(1)—C(7)	1.806(4)	Si(1)—C(2)	1.873(5)	C(11)—C(12)	1.491(6)	C(23)—C(24)	1.379(10)
P(1)—C(9)	1.811(5)	Si(2)—C(3)	1.878(5)	C(13)—C(14)	1.523(6)	C(24)—C(25)	1.334(9)
P(1)—C(11)	1.797(4)	Si(2)—C(4)	1.883(4)				

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Si(1)—S(1)—Si(2)	117.52(5)	C(19)—P(2)—C(13)	111.1(2)	C(3)—Si(2)—S(1)	108.6(2)	C(14)—C(13)—P(2)	113.8(3)
C(5)—P(1)—C(7)	109.5(2)	C(19)—P(2)—C(15)	111.7(2)	C(3)—Si(2)—S(3)	114.7(2)	C(16)—C(15)—P(2)	116.1(3)
C(5)—P(1)—C(9)	106.9(2)	C(19)—P(2)—C(17)	107.3(2)	C(4)—Si(2)—S(1)	108.6(2)	C(18)—C(17)—P(2)	114.0(3)
C(5)—P(1)—C(11)	112.6(2)	C(1)—Si(1)—S(1)	109.3(2)	C(4)—Si(2)—S(3)	114.3(2)	C(20)—C(19)—P(2)	116.0(3)
C(7)—P(1)—C(9)	110.5(2)	C(1)—Si(1)—S(2)	113.5(2)	S(3)—Si(2)—S(1)	105.30(7)	N(1)—C(21)—C(22)	124.7(8)
C(11)—P(1)—C(7)	112.2(2)	C(2)—Si(1)—S(1)	109.0(2)	C(25)—N(1)—C(21)	115.1(7)	C(21)—C(22)—C(23)	119.4(8)
C(11)—P(1)—C(9)	104.9(2)	C(2)—Si(1)—S(2)	115.1(2)	C(6)—C(5)—P(1)	114.1(3)	C(24)—C(23)—C(22)	115.5(7)
C(15)—P(2)—C(13)	109.6(2)	C(2)—Si(1)—C(1)	104.8(2)	C(8)—C(7)—P(1)	115.4(3)	C(25)—C(24)—C(23)	120.3(7)
C(15)—P(2)—C(17)	109.9(2)	S(2)—Si(1)—S(1)	105.13(7)	C(10)—C(9)—P(1)	113.2(4)	N(1)—C(25)—C(24)	125.0(8)
C(17)—P(2)—C(13)	107.2(2)	C(3)—Si(2)—C(4)	105.2(2)	C(12)—C(11)—P(1)	116.6(3)		

basic than $Ph_3P=CMe_2$) gave rise to the crystalline salt $[Et_4P^+]_2[^-S-SiMe_2-S-SiMe_2-S^-]$ (**13a**) and $Ph_3P=CMe_2$ in 1 : 1 ratio as the major products.

The structure of **13a** was established by X-ray diffraction analysis (Fig. 2). According to X-ray diffraction data (Table 2), the $(Me_2SiS^-)_2S$ dianion in **13a** has a nearly planar W conformation. The Si—S distances are 2.140(2) and 2.141(2) Å, which is in good agreement with the statistical mean value,[18] equal to 2.145 Å. The terminal Si—S$^-$ bonds (2.051(2) and 2.055 Å) are somewhat shorter than the single Si—S bond but longer than the Si—S$^-$ bond in betaines **1**.[12]

In addition to the signals due to the Et_4P^+ cation, the NMR spectra of **13a** exhibit singlets at 1.17 ppm (^1H NMR), 14.45 ppm (^{13}C NMR, $J_{CSi} = 53.2$ Hz), and 11.68 ppm (^{29}Si NMR) due to the $(Me_2SiS^-)_2S$ dianion.

The results obtained strongly indicate that the starting salt **12a** has the structure $[Ph_3P^-CHMe_2]_2[(Me_2SiS^-)_2S]$. The reactions of this compound with methanol and $Et_3P=CHMe$ are presented in Scheme 5.

Scheme 5

$2 [Ph_3P^+CHMe_2]SH^-$ $+$ $2 Me_2Si(OMe)_2$

11a

$\downarrow$ MeOH

$[Ph_3P^+CHMe_2]_2 \begin{bmatrix} ^-S \overset{Me_2}{\underset{}{Si}} S \overset{Me_2}{\underset{}{Si}} S^- \end{bmatrix}$

12a

$Et_3P=CHMe \downarrow$

$Ph_3P=CMe_2$ $+$ $[Et_4P^+]_2 \begin{bmatrix} ^-S \overset{Me_2}{\underset{}{Si}} S \overset{Me_2}{\underset{}{Si}} S^- \end{bmatrix}$

13a
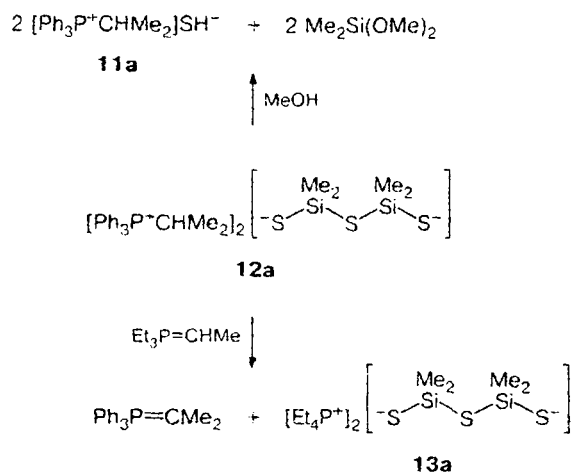
The substantial broadening of the resonance signals of the dianion of salt **12a** in the ^1H, ^{13}C, and ^{29}Si NMR spectra is apparently due to reversible deprotonation of the $Ph_3P^+CHMe_2$ cation by the strongly basic dianion; this results in a set of equilibria (Scheme 6) which are rather fast on the NMR time scale. Indeed, upon the addition of 0.5 equiv. of $[Ph_3P^+CHMe_2]Br^-$ to a solution of salt **13a** in pyridine, the relatively narrow singlet of the $(Me_2SiS^-)_2S$ dianion and the multiplet of the CH group in the $Ph_3P^+CHMe_2$ cation in the ^1H NMR spectrum are broadened and look like those in the corresponding spectrum of **12a**. Deprotonation of the $Ph_3P^+CHMe_2$ cation of **12a** with transfer of the proton to the thiolate center is similar to that observed previously[19] in the reaction of CS_2 with phosphorus ylides.

Thermolysis of betaine **1a**, prepared in the presence of $LiBr$,[4] gives disilolane **6a** (22%) and the salt

Scheme 6

$\begin{matrix} ^-S \overset{Me_2}{\underset{Si}{}} S \overset{Me_2}{\underset{Si}{}} S^- \\ Ph_3P^+CHMe_2 Ph_3P^+CHMe_2 \end{matrix}$ $\rightleftharpoons$

12a

$\rightleftharpoons$ $HS \overset{Me_2}{\underset{Si}{}} S \overset{Me_2}{\underset{Si}{}} S^-$ $+$ $Ph_3P=CMe_2$

      $Ph_3P^+CHMe_2$

$\updownarrow$

$Ph_3P^--CMe_2-SiMe_2-S^-$ $+$ $Ph_3P^+CHMe_2$

1a $HS \overset{Me_2}{\underset{Si}{}} S^-$
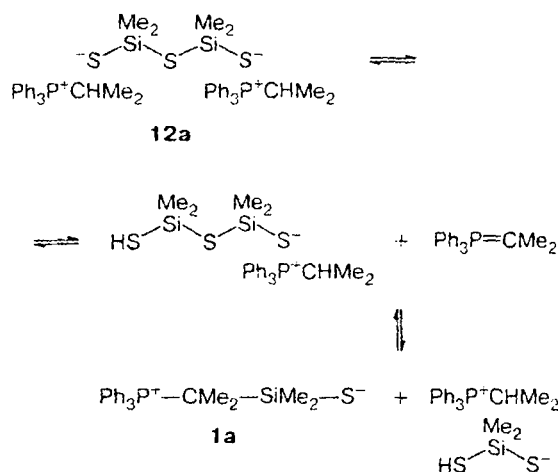
$LiS-SiMe_2-S-SiMe_2-SLi$ (46%). In solutions of this salt, contact ion pairs are apparently formed, in which the negative charge on the sulfur atoms decreases due to strong interaction with the lithium cations. Consequently, the ability of the dianion to deprotonate the $Ph_3P^+CHMe_2$ cations decreases and the rate of proton exchange also decreases. This shows itself as sharp signals in the ^1H and ^{13}C NMR spectra of the dianionic moiety of the molecule (unlike the broadened signals in the spectrum of phosphonium salt **12a**).

When pathways to salt **12a** are considered, the main question is what is the source of the proton. To clarify this point, selectively deuterated betaines $Ph_3P^+CMe_2Si(CD_3)_2S^-$ (**1a'**), $Ph_3P^+C(CD_3)_2SiMe_2S^-$ (**1a''**), and $Ph_3P^+C(CD_3)_2Si(CD_3)_2S^-$ (**1a'''**) were synthesized and thermal decomposition of compounds **1a—1a'''** was studied under strictly identical temperature conditions.

When either nondeuterated betaine **1a** is pyrolyzed in pyridine-d_5 or selectively deuterated analogs-d_6 **1a'** and **1a''** are pyrolyzed in nondeuterated pyridine, phosphonium cations of the resulting salts **12a** contain both protium and deuterium. The same result is obtained in the pyrolysis of betaine-d_{12} **1a'''** in pyridine-d_5. It follows from the ratio of nondeuterated and deuterated phosphonium cations (Table 3) that both pyridine and all the substituents in betaine **1a** serve as sources of protons in the formation of salt **12a**. The possibility of participation of the hydrogen atoms of the phenyl groups at phosphorus in the reactions of the ylide $Ph_3P=CMe_2$ has been noted previously.[20] The methyl groups at the silicon atom are deprotonated to the greatest extent. The enhanced acidity of the MeSi groups was demonstrated[21,22] by performing reactions of various methylsilanes with RLi.

The thermolysis (150 °C, 5 h, suspension in C_6H_6) of betaine $Ph_3P^+CMe_2SiMePhS^-$ (**1b**), containing only one Me group at the silicon atom, gives salt $[Ph_3P^+Pr^i]_2[(MePhSiS^-)_2S]$ (**12b**) in a yield not exceed-

Table 3. Ratio of the $Ph_3P^+CHMe_2$ and Ph_3P^+CDMe cations formed upon thermal decomposition* of betaines **1a**, **1a'**, **1a"**, and **1a'''** in C_5D_5N and C_5H_5N (in parentheses)

Betaine	Relative yield (%)	
	$Ph_3P^+CHMe_2$	$Ph_3P^+CDMe_2$
$Ph_3P^+CMe_2SiMe_2S^-$ (**1a**)	64 (100)	36 (0)
$Ph_3P^+CMe_2Si(CD_3)_2S^-$ (**1a'**)	35 (57)	65 (43)
$Ph_3P^+C(CD_3)_2SiMe_2S^-$ (**1a"**)	46 (58)	54 (42)
$Ph_3P^+C(CD_3)_2Si(CD_3)_2S^-$ (**1a'''**)	36	64

* Reaction conditions: 100 °C, 5 h, degree of conversion ~80%.

ing 4%, whereas salt $[Ph_3P^+Pr^i]_2[(MeBzSiS^-)_2S]$ (**12d**) is formed in a yield of up to 50% even during the synthesis[4] (20 °C) of the betaine $Ph_3P^+CMe_2SiMeBzS^-$ (**1d**), containing a benzyl group at the silicon atom, which is more acidic than the Me group. These results confirm the importance of the acidity of the substituents at silicon for the formation of salts **12**.

The betaine $Ph_3P^+CHMeSiMe_2S^-$ (**1c**) contains an "acidic" hydrogen atom in the α-position to the phosphonium center; the yield of salt $[Ph_3P^+Et]_2[(Me_2SiS^-)_2S]$ (**12c**) formed upon its thermolysis (150 °C, 5 h, suspension in C_6H_6) increases to 49%, whereas in the case of betaine **1a**, the yield of **12a** does not exceed 35%. The NMR spectra of compound **12c** exhibit rather sharp signals for both cationic and anionic moieties of the molecule.

Pyrolysis of betaine **14** (150 °C, 5 h, suspension in C_6H_6) gives, according to NMR spectra, ~70% of salt **12c** and 5.5% of disilolane **6c**. Thus, apart from the acidity of substituents in the molecule of the starting betaine, betaines of type **14** evidently play an important role in the synthesis of salts **12** but they make an insignificant contribution to the formation of dithiadisilolanes **6** (Scheme 7).

The results of the study indicate that thermal decomposition of betaines **1** involves a complex set of reversible processes with participation of phosphorus ylides, silanethiones **3**, their cyclodimers, and intermediate betaines containing the $^+P—C—(SiS)_nSi—S^-$ fragment ($n = 1, 2$). We will illustrate these processes in relation to thermal decomposition of betaine **1a**. It is clear that silanethione **3a**, formed in the first stage, dimerizes to give tetramethylcyclodisilathiane. The thermal nu-

cleophilic cleavage of its ring by the starting betaine **1a**, present in the reaction mixture, gives the intermediate betaine, 2,4,4,6.6.7-hexamethyl-2,4,6-trisila-3,5-dithiaoctane-7-triphenylphosphonio-2-thiolate (**15**) (Scheme 8). The phosphorus ylide arising simultaneously with silanethione **3a** can cleave any Si—S bond in molecule **15**. The attacks on the Si(4)—S(5) and Si(2)—S(3) bonds lead to the same products, a pair of betaines (**1a** and **16**), while the attack on the Si(6)—S(5) or Si(4)—S(3) bond affords **17** or **18**, respectively. Betaine **16**, the anion of salt **17**, and the cation of salt **18** can enter into subsequent reactions with $Ph_3P=CMe_2$ at the Si—S bonds. Thus, salt **19** should be the final product of thermal decomposition of betaine **1a**. The dianions $[SiMe_2S_2]^{2-}$, which are strong nucleophiles, are able to cleave the fairly labile C—Si bond in $(Ph_3P^+CMe_2)_2SiMe_2$ thus making the interconversion **16** + $Ph_3P=CMe \rightleftharpoons$ **19** reversible. Since all the steps in the set of equilibria shown in Scheme 8 are reversible, salt **19**, which has not been detected among the reaction products, would undergo subsequent transformations and the actual composition of the reaction products would be controlled by their thermodynamic stability. It is evident that the $[SiMe_2S_2]^{2-}$ dianion can efficiently trap the short-lived silanethiones $Me_2Si=S$ (**2a**), arising upon the retro-Wittig decomposition of betaine **1a**, to give the dithiolate anions $(Me_2SiS^-)_2S$.

During thermal decomposition, the $Ph_3P=CMe_2$ formed acts as a deprotonating reagent with respect to **1a** and the solvent. These deprotonation reactions giving rise to $Ph_3P^+CHMe_2$ cations are irreversible because the carbanions thus formed rapidly enter into subsequent reactions. Thus, the greater part of $Ph_3P=CMe_2$, resulting from the retro-Wittig decomposition pathway, comes out during the pyrolysis as $Ph_3P^+CHMe_2$, which is the reason why the set of equilibria (see Scheme 8) shifts toward the formation of the final salts. We intend to study these processes in more detail in the future.
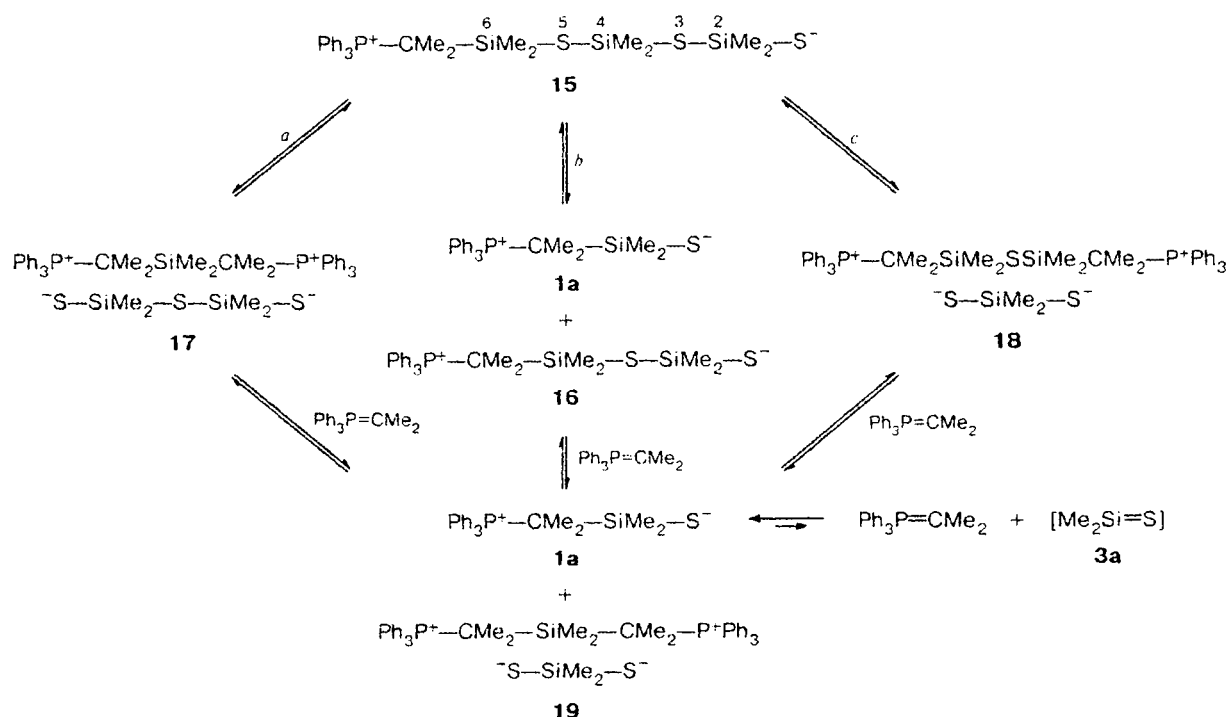
Experimental

Scheme 7

Scheme 8

$$\overset{6}{\text{Ph}_3\text{P}^+}\text{—CMe}_2\text{—}\overset{5}{\text{SiMe}_2}\text{—}\overset{4}{\text{S}}\text{—SiMe}_2\text{—}\overset{3}{\text{S}}\text{—}\overset{2}{\text{SiMe}_2}\text{—S}^-$$

15

a   *b*   *c*

Ph$_3$P$^+$—CMe$_2$SiMe$_2$CMe$_2$—P$^+$Ph$_3$
$^-$S—SiMe$_2$—S—SiMe$_2$—S$^-$

17

Ph$_3$P$^+$—CMe$_2$—SiMe$_2$—S$^-$

1a

+

Ph$_3$P$^+$—CMe$_2$—SiMe$_2$—S—SiMe$_2$—S$^-$

16

Ph$_3$P$^+$—CMe$_2$SiMe$_2$SSiMe$_2$CMe$_2$—P$^+$Ph$_3$
$^-$S—SiMe$_2$—S$^-$

18

Ph$_3$P=CMe$_2$ Ph$_3$P=CMe$_2$ Ph$_3$P=CMe$_2$

Ph$_3$P$^+$—CMe$_2$—SiMe$_2$—S$^-$ ⇌ Ph$_3$P=CMe$_2$ + [Me$_2$Si=S]

1a   **3a**

+

Ph$_3$P$^+$—CMe$_2$—SiMe$_2$—CMe$_2$—P$^+$Ph$_3$
$^-$S—SiMe$_2$—S$^-$

19

Note. a. Attack of the Si(6)—S(5) bond by phosphorus ylide; *b.* Attack of the Si(4)—S(5) bond by phosphorus ylide; *c.* Attack of the Si(4)—S(3) bond by phosphorus ylide.

^{13}C nuclei of the deuterated solvents were used as internal standards in ^{13}C NMR spectra (C$_6$D$_6$: 7.25 (^{1}H) and 128 (^{13}C) ppm; C$_5$D$_5$N: 8.71 (^{1}H) and 139 (^{13}C) ppm). Tetramethylsilane and 80% aqueous H$_3$PO$_4$, respectively, were used as external standards for ^{29}Si and ^{31}P NMR spectroscopy.

Mass spectra were recorded on a Varian MAT 44-5 spectrometer. GC/MS analysis was carried out on a Varian MAT-112S mass spectrometer (EI, 70 eV) connected to a Varian 3700 gas chromatograph (a 60-m DB-1 column, temperature range 40—250 °C) and on an Engine HP GS-MS instrument. GLC analysis was performed on an LKhM-80 instrument with a heat-conductivity detector (a 1-m long column 3 mm in diameter, Chromosorb G, silanized 5% SE-30, helium as the carrier gas, column temperature 50—290 °C).

All operations were carried out under dry argon purified from traces of oxygen using standard Schlenk equipment, in a dry inert box or *in vacuo* (10^{-3} Torr). The reactions were performed in seamless vessels using the compartments and tubes breaking technique. The synthesis and NMR spectral parameters of betaines **1a—d** and **14** were described previously.[1] Procedures proposed for nondeuterated analogs were used to prepare (CD$_3$)$_2$SiCl$_2$,[23,24] [(CD$_3$)$_2$SiS]$_n$,[25] Ph$_3$P$^+$CH(CD$_3$)$_2$Br$^-$,[26] and Ph$_3$P=C(CD$_3$)$_2$[27] from commercial CD$_3$I or (CD$_3$)$_2$CO (Merck). Betaines **1a—a'''** were synthesized by procedures described previously.[4]

3-Methyl-2-trideuteriomethyl-3-triphenylphosphonio-1,1,1-trideuteriomethyl-2-silabutane 2-thiolate, Ph$_3$P$^+$CMe$_2$Si(CD$_3$)$_2$S$^-$ (1a'), was prepared by mixing Ph$_3$P=CMe$_2$ (5.74 g, 18.88 mmol) with [(CD$_3$)$_2$SiS]$_n$ (1.87 g, 19.47 mmol of the monomer units (CD$_3$)$_2$SiS) in 50 mL of Et$_2$O. Yield 6.87 g (91.0%). According to the data of the

^{1}H NMR spectra, the degree of deuteration at the Si(CD$_3$)$_2$ groups was at least 99.8%.

4,4,4-Trideuterio-2-methyl-2-trideuteriomethyl-3-triphenylphosphonio-2-silabutane 2-thiolate, Ph$_3$P$^+$C(CD$_3$)$_2$SiMe$_2$S$^-$ (1a''), was prepared from Ph$_3$P=C(CD$_3$)$_2$ (3.43 g, 11.1 mmol) and (Me$_2$SiS)$_n$ (1.00 g, 11.1 mmol of Me$_2$SiS units) in 30 mL of C$_6$H$_6$. Yield 3.47 g (78.3%). According to ^{1}H NMR spectra, the degree of deuteration in relation to C(CD$_3$)$_2$ was ≥99%.

1,1,1,4,4,4-Hexadeuterio-2,3-di(trideuteriomethyl)-3-triphenylphosphonio-2-silabutane 2-thiolate, Ph$_3$P$^+$C(CD$_3$)$_2$Si(CD$_3$)$_2$S$^-$ (1a'''), was prepared from Ph$_3$P=C(CD$_3$)$_2$ (1.35 g, 4.4 mmol) and [(CD$_3$)$_2$SiS]$_n$ (0.6 g, 6 mmol of (CD$_3$)$_2$SiS units) in 20 mL of C$_6$H$_6$. Yield 1.53 g (86.4%).

According to the data of ^{1}H NMR spectra, the degree of deuteration relative to the C(CD$_3$)$_2$ groups was ≥98.1%; that relative to the Si(CD$_2$)$_2$ groups was ≥99.8%.

Photolysis of betaine 1a in C$_6$H$_6$. A suspension of betaine **1a** (4.73 g, 120.1 mmol) in C$_6$H$_6$ (60 mL) was irradiated for 13 h at ~20 °C with a medium-pressure mercury lamp in a quartz reactor with a magnetic stirrer. The resulting homogeneous solution was concentrated at 20 °C (1 Torr). Pentane (50 mL) was added to the oily residue and the precipitate was filtered off and thrown away. The pentane was removed from the filtrate at 20 °C (1 Torr). Three rectystallizations of the residue (−20 °C) from hexane gave tetrahydro-2,2,3,3,5,5,6,6-octamethyl-1,4-dithia-2,5-disilin (**4a**) (0.6 g, 38%), m.p. 142—143 °C. Found (%): C, 45.39; H, 9.14; S, 24.24; Si, 21.23. C$_{10}$H$_{24}$S$_2$Si$_2$. Calculated (%): C, 45.21; H, 9.32; S, 24.06; Si, 21.45. ^{1}H NMR (C$_6$D$_6$), δ: 0.38 (s, 6 H, Me$_2$Si); 1.46 (s, 6 H, Me$_2$C). ^{13}C NMR (C$_6$D$_6$, δ): −1.30 (s, Me$_2$Si, $^1J_{CSi}$ =

52.6 Hz); 28.80 (s, $\underline{Me}_2C$); 30.54 (s, $Me_2\underline{C}$). ^{29}Si NMR $(C_6D_6,$ δ): +13.05.

Photolysis of betaine 1a in C_6D_6: NMR monitoring. According to ^{1}H, ^{13}C, and ^{31}P NMR spectra, the reaction mixture obtained after irradiation (for 2 h) of a suspension of betaine 1a (0.32 g, 0.81 mmol) in 3 mL of C_6D_6 under the conditions described above contained Ph₃P (yield 72%), Ph₃PS (yield 14%), silathiirane dimer 4a (yield 57%), and 2,2,4,4,5,5-hexamethyl-1,3-dithia-2,4-disilolane (6a) (yield 27%). Compound 6a. ^{1}H NMR $(C_6D_6),$ δ: 0.39 (s, 6 H, Me₂Si); 0.61 (s, 6 H, Me₂Si); 1.46 (s, 6 H, Me₂C). ^{13}C NMR $(C_6D_6),$ δ: −0.66 (Me₂Si); 7.32 (Me₂Si); 28.07 ($\underline{Me}_2C$); 39.87 (Me₂$\underline{C}$). ^{29}Si NMR $(C_6D_6),$ δ: 32.29 (Me₂Si); 35.12 (Me₂Si).

Photolysis of betaine 1a in C_6H_6 in the presence of Me₂CO: GC/MS monitoring. A suspension of betaine 1a (3.32 g, 8.43 mmol) in a mixture of benzene (60 mL) with acetone (5.06 g, 87.2 mmol) was irradiated for 9 h as described above until the betaine entirely dissolved. The volatile products were condensed in a Schlenk tube at a temperature of up to 90 °C (1 Torr) and analyzed using an Engine HP GS-MS spectrometer (a 30-m column, DB-5 phase, temperature 40—300 °C, column heating rate 7 K min⁻¹, EI, 70 eV). The main products detected in the mixture were 2,2,4,4,5,5-hexamethyl-3-oxa-1-thia-4-silolane (5a) (13.82 min), *m/z* (I_{rel}(%)): 192 [M⁺ + 2] (1.5), 191 [M⁺ + 1] (2.5), 190 [M⁺] (16), 175 [M⁺ − 15] (1), 134 [M⁺ − 56] (10), 133 [M⁺ − 57] (100), 115 [M⁺ − 75] (9.5), 75 [M⁺ − 115] (14), 61 (8.5), 57 (9); disilolane 6a (17.06 min). *m/z* (I_{rel}(%)): 224 [M⁺ + 2] (1.5), 223 [M⁺ + 1] (8.5), 222 [M⁺] (22), 207 [M⁺ − 15] (12), 180 [M⁺ − 44] (14), 165 [M⁺ − 57] (100), 133 [M⁺ − 89] (11), 92 (12), 73 (57), 59 (19); compound 7a (18.73 min), *m/z* (I_{rel}(%)): 234 [M⁺ + 2] (2), 233 [M⁺ + 1] (3.5), 232 [M⁺] (17.5), 217 [M⁺ − 15] (4), 190 [M⁺ − 42] (2), 175 [M⁺ − 57] (4.5), 161 [M⁺ − 71] (21), 149 [M⁺ − 83] (100), 133 [M⁺ − 99] (7), 111 (3), 99 (4), 85 (3.5), 73 (44), 59 (19); compound 4a (22.64 min), *m/z* (I_{rel}(%)): 266 [M⁺ + 2] (5.5), 265 [M⁺ + 1] (7), 264 [M⁺] (29), 221 [M⁺ − 43] (63), 207 [M⁺ − 57] (6), 190 [M⁺ − 74] (14), 175 [M⁺ − 89] (73), 165 [M⁺ − 99] (38), 147 [M⁺ − 117] (65), 133 (14), 117 (5.9), 100 (40), 85 (42), 84 (38), 75 (42.5), 73 (100), 59 (67).

Photolysis of betaine 1a in C_5D_5N: NMR monitoring. According to ^{1}H and ^{31}P NMR spectra, the reaction mixture obtained after irradiation (12 h) of a suspension of betaine 1a (0.36 g, 0.91 mmol) in 2.5 mL of C_5D_5N under the conditions described previously contained Ph₃P (yield 90%), Ph₃PS (yield 4%), silathiirane dimer 4a (yield 24%), and heterocycle 6a (yield 57%).

Decomposition of betaine 1a according to the retro-Wittig reaction pathway: reaction with benzophenone (vacuum method). A solution of betaine 1a (0.25 g, 0.63 mmol) and benzophenone (0.12 g, 0.63 mmol) in C_5D_5N (0.8 mL) was heated for 10 min at 100 °C in a sealed NMR tube. The mixture colored first dark claret and gradually turned yellow. According to ^{1}H, ^{13}C, and ^{31}P NMR spectra and to GLC, the solution contained Ph₃PO and Ph₂C=CMe₂. The yield of the compounds was 53% of the theoretical yield.

Decomposition of betaine 1a according to the retro-Wittig reaction pathway: NMR monitoring (vacuum method). According to ^{1}H, ^{13}C, and ^{31}P NMR spectra, a freshly prepared solution of betaine 1a (60 mg) in C_5D_5N (0.8 mL) contained at 25 °C only betaine 1a. After heating in the NMR probe at 90 °C for ~30 min, the solution contained 1a and Ph₃P=CMe₂ in 0.8 : 1 ratio and (Me₂SiS)ₙ, Ph₃P, and isopropyltriphenylphosphonium *symm*-tetramethyldisilthianedithiolate (12a). The subsequent lowering of the probe temperature to 50 °C and keeping the same sample at 50 °C for 40 min resulted in 1a and

Ph₃P=CMe₂ in 2.9 : 1 ratio; after subsequent heating of the probe to 75 °C and keeping the sample for 40 min at this temperature, the ratio of these products was 1.46 : 1. Ph₃P=CMe₂. ^{1}H NMR $(C_5D_5N),$ δ: 2.00 (br.d, Me₂C, J_{HP} = 16.5 Hz). The ^{1}H and ^{13}C NMR spectra of (Me₂SiS)ₙ and the ^{13}C and ^{31}P NMR spectra of Ph₃P=CMe₂ correspond to the published data.[28—30]

Thermolysis of betaine 1a in EtOH: NMR experiment (vacuum method). *A.* A solution of 1a (0.18 g, 0.46 mmol) in ethanol (1.8 mL) was heated for 4 h at 150 °C in a sealed 8-mm NMR tube. According to the ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra and GC/MS data, the solution contained residual 1a (1%), 1-[dimethyl(ethoxy)silyl]-1-methylethanethiol, Me₂Si(OEt)CMe₂SH, 10a (48%), Me₂Si(OEt)₂ (48%), Ph₃P (45%), [Ph₃P⁺CHMe₂]SH⁻ (45%), and Ph₃PS (9%).

B. According to ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra, heating solution 1a (0.21 g, 0.53 mmol) in EtOH (1.8 mL) in a sealed 8-mm NMR tube at 245 °C for 5 min gives 1a (10%), mercaptan 10a (67%), Me₂Si(OEt)₂ (23%), Ph₃P (89%), [Ph₃P⁺CHMe₂]SH⁻ (1%), and Ph₃PS (9%).

Silanethiol 10a. ^{1}H NMR (EtOH, C_6D_6 as the external standard), δ: 0.70 (s, 6 H, Me₂Si, $^2J_{HSi}$ = 6.0 Hz); 1.83 (s, 6 H, Me₂C); 4.28 (q, 2 H, OCH₂); the signals of the $\underline{CH}_3CH_2O$ group are covered by the solvent signals. ^{13}C NMR (EtOH, C_6D_6 as the external standard), δ: −5.19 (Me₂Si, $^2J_{CSi}$ = 69.5 Hz); 18.48 ($\underline{CH}_3CH_2O$); 27.90 (Me₂$\underline{C}$); 28.64 ($\underline{Me}_2C$); 57.71 ($\underline{CH}_2O$). ^{29}Si NMR (EtOH, C_6D_6 as the external standard), δ: 14.09. MS, *m/z* (I_{rel}(%)): 178 [M]⁺ (9), 163 [M⁺ − 15] (9), 133 [M⁺ − OEt] (1), 103, Me₂SiOEt⁺ (100), 91, Me₂SiSH⁺ (9), 75 [M⁺ − 103] (84). 73, Me₃Si (11).

Me₂Si(OEt)₂. ^{1}H NMR (EtOH, C_6D_6 as the external standard), δ: 0.61 (s, 6 H, Me₂Si, $^2J_{HSi}$ = 7.1 Hz); 1.57 (t, 6 H, $\underline{CH}_3CH_2O,$ $^3J_{HH}$ = 7.0 Hz); 4.27 (q, 4 H, $\underline{CH}_2O,$ $^3J_{HH}$ = 7.0 Hz). ^{13}C NMR (EtOH, C_6D_6 as the external standard), δ: −3.57 (Me₂Si, $^2J_{CSi}$ = 73.5 Hz); 18.51 ($\underline{CH}_3CH_2O$); 58.41 ($\underline{CH}_2O$). ^{29}Si NMR (EtOH, C_6D_6 as the external standard), δ: −3.44.

Thermolysis of betaines 1a and 1c in benzene. Heating (150—155 °C) a suspension of 1a (8.74 g, 22.2 mmol) in benzene (30 mL) for 5—6 h in a sealed evacuated tube resulted in the formation of two liquid layers. The upper layer was colored dark yellow and the lower layer was claret-yellow-colored. All the volatile products from the upper layer were condensed in a liquid nitrogen-cooled trap and the content of the trap was fractionated *in vacuo* to give disilolane 6a (0.73 g, 30%), b.p. 103—104 °C (15 Torr). Found (%): C, 37.59; H, 8.04; S, 28.74; Si, 25.73. C₇H₁₈S₂Si₂. Calculated (%): C, 37.78; H, 8.15; S, 28.82; Si, 25.25. Mass and ^{1}H, ^{13}C, and ^{29}Si NMR spectra of the product were identical to those presented above. The lower layer, a viscous reddish oil, was washed twice with benzene with decantation and subsequent recondensation of the solvent *in vacuo* (1 Torr). All the volatile products were removed at 20—25 °C (0.01 Torr) for 5—6 h to give 1.18 g (13.0% (w/w) relative to the 1a taken) of isopropyltriphenylphosphonium *symm*-tetramethyldisilthianedithiolate 12a as a solid foamed voluminous, slightly yellowish compound, which immediately decomposed in the presence of traces of air. Since the compound was extremely unstable in the presence of traces of oxygen or air moisture, we were unable to obtain reliable results of elemental analysis. Salt 12a. ^{1}H NMR $(C_5D_5N),$ δ: 0.8—1.1 (br.s, Me₂Si). ^{13}C NMR $(C_5D_5N),$ δ: 11.0—15.0 (br.s, Me₂Si). ^{29}Si NMR $(C_5D_5N),$ δ: 13—15 (br.s). The NMR spectra of the Ph₃P⁺CHMe₂ cation correspond to published data.[29,30]

Thermolysis of betaine 1c (11.21 g, 29.5 mmol) in benzene (30 mL) carried out in a similar way gave 0.73 g (23.8%) of 2,2,4,4,5-pentamethyl-1,3-dithia-2,4-disilolane 6c, b.p. 54 °C

(1 Torr), n_D^{20} 1.5174. Found (%): C, 34.21; H, 7.86; S, 30.62. $C_6H_{16}S_2Si_2$. Calculated (%): C, 34.57; H, 7.74; S, 30.76. ^1H NMR (C_6D_6), δ: 0.33, 0.36 (both s, each 3 H, nonequivalent Me_2Si); 0.57, 0.59 (both s, each 3 H, nonequivalent Me_2Si); 1.32 (d, 3 H, Me$\underline{C}$H, $^3J_{HH}$ = 7.5 Hz); 2.35 (q, 1 H, Me$\underline{CH}$, $^3J_{HH}$ = 7.5 Hz). ^{13}C NMR (C_6D_6), δ: −0.76, −0.47 (nonequivalent Me_2Si); 6.69, 7.87 (nonequivalent Me_2Si); 19.36 ($\underline{Me}$CH); 29.29 (Me$\underline{C}$H). ^{29}Si NMR (C_6D_6), δ: 35.10, 37.25 (both s, Me_2Si). From the lower layer, 1.29 g of ethyltriphenylphosphonium *symm*-tetramethyldisilthianedithiolate 12c (11.7%) was isolated. ^1H NMR (C_5D_5N), δ: 0.97 (s, Me_2Si, J_{CSi} = 6.5 Hz). ^{13}C NMR (C_5D_5N), δ: 11.51 (s, Me_2Si, J_{CSi} = 53.5 Hz). The NMR spectra of the $Ph_3P^+CH_2Me$ cation correspond to the published data.[29,30]

Thermolysis of betaine 1a without a solvent: NMR experiment. Thermal decomposition (150 °C, 4 h) of betaine 1a (0.1 g) in a 5-mm NMR tube sealed under argon was accompanied by melting of the compound and the appearance of a dark-claret color, whose intensity gradually decreased. After ~0.5 h, two layers formed; the upper layer was slightly yellowish and the lower layer was red. The tube was cooled down and opened under argon, and 0.8 mL of C_5D_5N was added. According to ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra, the following products were obtained (yield (mol.%)): 4a (5), 6a (18), Ph_3P (47), Ph_3PS (6), and 12a (20). The second experiment was carried out in a similar way. After opening of the tube, a solution of methanol (0.2 mL) in C_6D_6 (0.6 mL) was added. According to NMR spectra, the reaction mixture contained $Me_2Si(OMe)_2$ (68%) and $Me_2Si(OMe)CMe_2SH$ (17%), as well as Ph_3PS (5%), Ph_3P (43%), and $Ph_3P^+CHMe_2SH^-$ (11a) (42%).

Thermolysis of betaine 1a in pyridine-d_5 (150 °C): NMR monitoring (vacuum method). A solution of betaine 1a (0.1 g) in Py-d_5 was heated for 5 h at 150 °C in a 5-mm NMR tube. According to ^1H, ^{13}C, and ^{31}P NMR spectra, the solution contained Ph_3PS, Ph_3P, disilolane 6a, and salt 12a (47% of the theoretical yield) with the $Ph_3P^+CHMe_2$ and $Ph_3P^+CDMe_2$ cations in 1 : 44 : 23.5 : 25 molar ratio.

Thermolysis of betaines 1a, 1b, 1c, and 14 in benzene: NMR experiment (vacuum method). A suspension of betaine (0.7—1 mmol) in C_6D_6 (0.8 mL) was heated for 5 h at 150 °C in a 5-mm NMR tube; the mixture separated into layers. To determine the product yield, NMR spectra of the upper layer were first recorded (the lower layer, which was a viscous reddish oil, did not fall within the NMR receiver coil). The tube was opened, methanol (2.3—2.5 equiv.) was added, and multinuclear NMR spectra of the homogeneous solution were recorded once again. Analysis of both sets of NMR spectra showed that the reaction mixture contained silathiirane dimers 4, disilolanes 6, Ph_3P, and salts $[Ph_3P^+CHR^1R^2]_2[(R^3R^4SiS^-)_2S]$ (12). After methanolysis, the reaction mixtures contained $R^3R^4Si(OMe)_2$, silanethiols $R^3R^4Si(OMe)CR^1R^2SH$, Ph_3P, and salts $[Ph_3P^+CHR^1R^2]SH^-$ (11). The following products were obtained (yield (mol. %)): from 1a: disilin 4a (6.0), disilolane 6a (24), Ph_3P (56), Ph_3PS (5), and salt 12a (17.5); from 1b: 4b (0), 2,4,5,5-tetramethyl-2,4-diphenyl-1,3-dithia-2,4-disilolane (6b) (39), Ph_3P (78.3), Ph_3PS (2.3), and isopropyltriphenylphosphonium *symm*-dimethyldiphenyldisilthianedithiolate (12b) (2.0); for 1c: disilolane 6c (23), Ph_3P (44), Ph_3PS (3), and salt 12c (24.5). The following products were isolated in the case of 14 (mol. %): $(Me_2SiS)_3$ (33), disilolane 6c (5.5), Ph_3P (23.3), and salt 12c (35).

Disilolane 6b. ^1H NMR (C_6D_6), δ (since 6b contains two chiral Si atoms and exists as a mixture of two pairs of enantiomers, all the signals in the ^1H, ^{13}C, and ^{29}Si NMR spectra are doubled): 0.75, 0.80 (both s, each 3 H, MeSi); 0.91, 0.98 (both s, each 3 H, Me_2Si); 1.39, 1.46 (both s, each 3 H, Me_2C);

1.50 (s, 6 H, Me_2C); the region of PhSi is covered by the Ph_3P signals. ^{13}C NMR (C_6D_6), δ: −1.77, −1.63 (MeSi); 6.08, 6.14 (MeSi); 27.40, 27.53, 29.37, 29.42 (nonequivalent $\underline{Me}_2C$ groups); 40.54, 40.59 ($Me_2\underline{C}$); 128.17, 128.20, 128.29, 128.32 (C_m); 137.58, 137.70, 138.19, 138.29 (C_j); 134.91 (C_o); other signals are covered by the signals of Ph_3P. ^{29}Si NMR (C_6D_6), δ: 23.66, 23.92, 27.48, 27.77.

$Me_2Si(OMe)CMe_2SH$. ^1H NMR $(C_6D_6$—MeOH), δ: 0.16 (s, 6 H, Me_2Si, J_{HSi} = 6.4 Hz); 1.31 (s, 6 H, Me_2C); 3.36 (s, 3 H, MeO). ^{13}C NMR $(C_6D_6$—MeOH), δ: −5.74 $(Me_2Si$, J_{CSi} = 60.3 Hz); 28.41 $(\underline{Me}_2C)$; 28.71 (SiCS); 51.24 (OMe).

$MePhSi(OMe)CMe_2SH$. ^1H NMR $(C_6D_6$—MeOH), δ: 0.53 (s, 3 H, MeSi); 1.38, 1.43 (both s, 6 H, Me_2C); 3.44 (s, 3 H, MeO); 7.30—7.80 (m, 5 H, Ph). ^{13}C NMR $(C_6D_6$—MeOH), δ: −7.62 (MeSi, J_{CSi} = 61.4 Hz); 28.15, 28.57 (both nonequivalent $\underline{Me}_2C$ groups); 28.23 (SiCS); 51.47 (OMe); 127.99 (C_m); 130.38 (C_p); 135.22 (C_o) (the C_j signal is covered by strong signals of Ph_3P present in the reaction mixture). ^{29}Si NMR $(C_6D_6$—MeOH), δ: 3.89.

$MePhSi(OMe)_2$. ^1H NMR $(C_6D_6$—MeOH), δ: 0.39 (s, 6 H, Me_2Si); 3.50 (s, 6 H, MeO); 7.30—7.80 (m, 5 H, Ph). ^{13}C NMR $(C_6D_6$—MeOH), δ: −4.94 $(Me_2Si$, J_{CSi} = 76.1 Hz); 50.26 (OMe); 128.19 (C_m); 130.14 (C_p); 134.37 (C_o); 134.68 (C_j). ^{29}Si NMR $(C_6D_6$—MeOH), δ: −14.62.

$Me_2Si(OMe)CHMeSH$. ^1H NMR $(C_6D_6$—MeOH), δ: 0.26 (s, 6 H, Me_2Si); 1.20 (q, 1 H, CH, $^3J_{HH}$ = 7.5 Hz); 1.43 (d, 3 H, Me$\underline{C}$H, $^3J_{HH}$ = 7.5 Hz); 3.51 (s, 3 H, MeO). ^{13}C NMR $(C_6D_6$—MeOH), δ: −1.51 $(Me_2Si$, J_{CSi} = 74.1 Hz); 16.23 (Me); 29.15 (CH); 49.54 (MeO). ^{29}Si NMR $(C_6D_6$—MeOH), δ: −1.34.

The reaction of salt 12a with MeOH (vacuum method). *A.* Methanol (0.1 g, 3 mmol) was condensed *in vacuo* into a solution of salt 12a (0.64 g, 0.78 mmol) in 0.8 mL of C_5D_5N. The mixture was transferred into an NMR tube and the tube was sealed off. According to ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra, the mixture contained $Me_2Si(OMe)_2$ and $Ph_3P^+CHMe_2SH^-$ in 1 : 1 molar ratio.

B. The reaction of MeOH (4.68 mmol) with an emulsion of salt 12a (1.18 g, 1.44 mmol) in C_6D_6 gave a colorless precipitate of the salt $[Ph_3P^+CHMe_2]SH^-$ (0.93 g, 96%). NMR and GLC analysis of the C_6D_6 solution showed the presence of $Me_2Si(OMe)_2$.

The reaction of salt 12a with $Et_3P=CHMe$ (vacuum method). $Et_3P=CHMe$ (0.2 g, 1.37 mmol) was added in portions to an emulsion of salt 12a (0.53 g, 0.64 mmol) in benzene. The solution immediately developed a dark-claret color and the emulsion solidified. The mixture was allowed to stand for ~10 h. The solution was decanted from the precipitate and the precipitate was washed with benzene until complete decoloration of the decantate and dried *in vacuo* (0.01 Torr) at 50 °C to give 0.28 g (84.4%) of tetraethylphosphonium *symm*-tetramethyldisilthianedithiolate (13a) as a white powder, which was crystallized from a small amount of pyridine. The product had no clear-cut melting point and decomposed in the 60—80°C range. ^1H NMR (C_5D_5N), δ: 1.17 (s, 12 H, Me_2Si); 1.23 (dt, 24 H, $\underline{CH}_3CH_2P^+$, $^3J_{HH}$ = 7.7 Hz, $^3J_{HP}$ = 17.7 Hz); 2.74 (dq, 16 H, $CH_3\underline{CH}_2P^+$, $^2J_{HH}$ = 7.7 Hz, $^2J_{HP}$ = 13.3 Hz). ^{13}C NMR (C_5D_5N), δ: 6.12 (d, $\underline{CH}_3CH_2P^+$, $^2J_{CP}$ = 2.5 Hz); 12.13 (d, $CH_3\underline{CH}_2P^+$, $^1J_{CP}$ = 48.4 Hz); 14.45 (s, Me_2Si, J_{CSi} = 53.2 Hz). ^{29}Si NMR (C_5D_5N), δ: 11.68. ^{31}P NMR (C_5D_5N), δ: 40.24. The decanted liquid was concentrated *in vacuo* (0.01 Torr) at 50 °C and 3 mL of C_6H_6 was condensed into it. The resulting solution was transferred into an NMR tube and analyzed. According to ^1H and ^{31}P NMR spectra, the solution contained betaine 1a (8%), $Ph_3P=CMe_2$ (81.0%), and Ph_3P (10.0%).

Thermolysis of betaine 1a prepared in the presence of LiBr: NMR monitoring (vacuum method). Thermal decomposition (150 °C, 1.5 h) of betaine **1a** (0.1 g) synthesized in the presence of LiBr in C_5D_5N in a sealed evacuated 5-mm NMR tube gives, according to ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra, disilolane **6a** (yield 22%), Ph_3P (50.4%), salt $[Ph_3P^+CHMe_2]Br^-$ (47.1%), and salt $LiS-SiMe_2-S-SiMe_2-SLi$ (23%). $LiS-SiMe_2-S-SiMe_2-SLi$. ^1H NMR (C_5D_5N), δ: 1.10 (s, 12 H, Me_2Si, $^2J_{HSi}$ = 6.8 Hz). ^{13}C NMR (C_5D_5N), δ: 13.74 (Me_2Si, $^1J_{CSi}$ = 54.8 Hz). ^{29}Si NMR (C_5D_5N), δ: 13.74.

Thermolysis of betaines 1a, 1a′, 1a″, and 1a‴ in pyridine or pyridine-d_5 (100 °C, 5 h): NMR monitoring (vacuum method). Betaines **1a—a‴** (0.04 g, 0.1 mmol) were placed in a 5-mm (or 8-mm) NMR tube, the tube was evacuated and cooled with liquid nitrogen, and C_5D_5N was condensed using a vacuum line. The tube was sealed off and heated for 5 h at 100 °C. According to ^1H, ^{13}C, and ^{31}P NMR spectra, the solution contained Ph_3P, the corresponding disilolanes **6a—a‴**, and salts **12a—a‴** with the $Ph_3P^+CHMe_2$ and $Ph_3P^+CDMe_2$ cations in ~1 : 0.5 : 0.5 molar ratio. The $Ph_3P^+CHMe_2$: $Ph_3P^+CDMe_2$ ratio of the cations in salts **12a—a‴** is given in Table 3. The degree of conversion of betaines was ~80%.

X-ray diffraction study. The X-ray diffraction study of compounds **4a** and **13a** was carried out on a Siemens P3/PC automated four-circle diffractometer (−120 °C, λ-Mo-Kα, graphite monochromator, $\theta/2\theta$ scan mode, θ_{max} = 32° (**4a**) and 28° (**13a**)). The structures were solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for nonhydrogen atoms. The X-ray diffraction data were processed using an IBM PC/AT-486 and the SHELXTL PLUS program package.[31]

The crystals of **4a** are monoclinic, $C_{10}H_{23}S_2Si_2$, M = 264.59, space group $P2_1/n$; at −120 °C, a = 7.230(2) Å, b = 11.394(2) Å, c = 9.441(2) Å, β = 103.49(1)°, V = 756.3(3) Å^3, Z = 2 (the molecule occupies a partial position in an inversion center), d_{calc} = 1.162 g cm^{-3}. The hydrogen atoms, located objectively from the difference Fourier synthesis, were refined in the isotropic approximation. The final discrepancy factors were R_1 = 0.021 for 2157 reflections with $I > 2\sigma(I)$ and wR_2 = 0.055 for all 2364 independent reflections.

The crystals of **13a** (from pyridine) are orthorhombic, $[C_4H_{12}PS_3Si_2]^{2-}[C_8H_{20}P]_2^+ \cdot C_5H_5N$, M = 586.02, space group $P2_12_12_1$; at −120 °C, a = 21.654(5) Å, b = 12.645(3) Å, c = 12.806(3) Å, V = 3507(1) Å^3, Z = 4, d_{calc} = 1.110 g cm^{-3}. The hydrogen atoms in positions found from geometrical considerations were included in the refinement in the isotropic approximation with fixed positional ("rider" model) and thermal parameters. The final discrepancy factors were R_1 = 0.045 for 4135 reflections with $I > 2\sigma(I)$ and wR_2 = 0.120 for all 4514 independent reflections.

References

1. I. V. Borisova, N. N. Zemlyanskii, A. K. Shestakova, V. N. Khrustalev, Yu. A. Ustynyuk, and E. A. Chernyshev, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 935 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 933 (Engl. Transl.)].

2. I. V. Borisova, N. N. Zemlyansky, A. K. Shestakova, and Yu. A. Ustynyuk, *Mendeleev Commun.*, 1996, 90.

3. (a) C. Puke, G. Erker, N. C. Aust. E.-U. Würtheim, and R. Fröhlich, *J. Am. Chem. Soc.*, 1998, **120**, 4863;

(b) C. Puke, G. Erker, B. Wibbeling, and R. Fröhlich, *Eur. J. Org. Chem.*, 1999, 1831.

4. 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., Int. Ed.*, 2000, **49**, 920 (Engl. Transl.)].

5. S. Wilker, C. Laurent, C. Sarter, C. Puke, and G. Erker, *J. Am. Chem. Soc.*, 1995, **117**, 7293.

6. F. Duus, in *Comprehensive Organic Chemistry, Sulfur Compounds*, Ed. D. N. Jones, Pergamon Press, Oxford, 1979, **3**, p. 580.

7. E. Vedejs, D. A. Perry, and R. G. Wilde, *J. Am. Chem. Soc.*, 1986, **108**, 2985.

8. B. E. Maryanoff and A. B. Reitz, *Chem. Rev.*, 1989, **89**, 863.

9. K. Okuma, *Rev. Heteroat. Chem.*, 1992, **7**, 117.

10. G. M. Li, M. Segi, T. Kamogawa, and T. Nakajima, *Chem. Express*, 1993, **8**, 53.

11. K. Okuma, T. Ishida, S. Morita, H. Ohta, and T. Inoue, *Heteroat. Chem.*, 1995, **6**, 265.

12. 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., Int. Ed.*, 2000, **49**, 929 (Engl. Transl.)].

13. T. Tsumuraya, S. Sato, and W. Ando, *Organometallics*, 1989, **8**, 161.

14. P. Jutzi and A. Mohrke, *Angew. Chem.*, 1989, **101**, 769; *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 762.

15. J. Barrau, G. Rima, M. El. Amin, and J. Satge, *J. Organomet. Chem.*, 1988, **345**, 39.

16. J. Barrau, G. Rima, and J. Satge, *J. Organomet. Chem.*, 1983, **252**, C73.

17. Yu. L. Slovokhotov, T. V. Timofeeva, M. Yu. Antipin, and Yu. T. Struchkov, *J. Mol. Struct.*, 1984, **112**, 127.

18. F. H. Allen, O. Kennard, D. G. Watson, A. G. Orpen, L. Brammer, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.

19. H. J. Bestmann, R. Engler, H. Hartung, and K. Roth, *Chem. Ber.*, 1979, **112**, 28.

20. A. S. Batsanov, M. G. Davidson, J. A. K. Howard, S. Lamb, and C. Lustig, *Chem. Commun.*, 1996, 1791.

21. G. A. Gornowicz and R. West, *J. Am. Chem. Soc.*, 1968, **90**, 4478.

22. D. J. Peterson, *J. Organomet. Chem.*, 1967, **9**, 373.

23. M. Beltzung, C. Picot, P. Rempp, and J. Herz, *Macromolecules*, 1982, **15A**, 1594.

24. X. K. Zhang, J. O. Stuart, S. J. Clarson, A. Sabata, and G. Beaucage, *Macromolecules*, 1994, **27**, 5229.

25. M. D. Mizhiritskii and V. O. Reikhsfel'd, *Usp. Khim.*, 1988, **57**, 803 [*Russ. Chem. Rev.*, 1988, **57**, 447 (Engl. Transl.)].

26. R. Koster, D. Simic, and M. A. Grassberger, *Ann.*, 1970, **379**, 211.

27. H. J. Bestmann, W. Stransky, and O. Vostrovsky, *Chem. Ber.*, 1976, **109**, 1694.

28. E. V. van den Berghe and G. P. van der Kelen, *J. Organomet. Chem.*, 1976, **122**, 329.

29. T. A. Albright, M. Gordon, W. J. Freeman, and E. E. Schweizer, *J. Am. Chem. Soc.*, 1976, **98**, 6249.

30. T. A. Albright, W. J. Freeman, and E. E. Schweizer, *J. Am. Chem. Soc.*, 1975, **97**, 2542.

31. 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.