Organometallic Chemistry

Reactions between germylenes (silylenes) and phosphaalkenes: an experimental and theoretical study. Preparation of the first representative of germaphosphacyclopropanes*

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Reactions of a number of germylenes and dimethylsilylene with a phosphaalkene, 2,2-bis(trimethylsilyl)-1-phenyl-1-phosphaethene (**1**), were studied. The reaction of short-lived dimethylgermylene with **1** produced a phosphagermirane **3** (the first representative of a new class of heterocyclic compounds). Compound **3** was characterized in solution by ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectroscopy. Subsequent reaction of **3** with dimethylgermylene results in 2,2,3,3-tetramethyl-4,4-bis(trimethylsilyl)-1-phenyl-2,3-digerma-1-phosphacyclobutane **4**, which has not been reported so far. In order to rationalize different reactivities of germylenes towards alkenes and phosphaalkenes, the addition products of GeH_2 to ethylene and phosphaethene ($HP{=}CH_2$) were studied using the G2 computational scheme and DFT PBE technique. The adducts of $GeMe_2$ ($GeCl_2$) with $HP{=}CH_2$ and of $GeMe_2$ with $PhP{=}C(SiH_3)_2$ were also calculated by the DFT PBE method. According to calculations, the exothermicity, ΔE, of cycloaddition of GeH_2 and $GeMe_2$ to the phosphaalkenes $HP{=}CH_2$ and $PhP{=}C(SiH_3)_2$ (43.5—39.7 kcal mol^{-1}) is nearly twice as high as the exothermicity of cycloaddition of these germylenes to ethylene. In addition to the minimum corresponding to the three-membered cycle, a number of minima corresponding to quite stable donor-acceptor complexes in which the Ge atom is coordinated by the lone electron pair of the P atom in the phosphaalkene molecule were located on the potential energy surface of the germylene—phosphaalkene system. The complexation energy of the complex of GeH_2 ($GeMe_2$) with phosphaethene is 25.0 (16.9) kcal mol^{-1}. For $GeCl_2$, the exothermicity of cycloaddition to $HP{=}CH_2$ decreases to 7.6 kcal mol^{-1} and the complexation energy decreases to 8.2 kcal mol^{-1}.

Key words: germylenes, silylenes, phosphaalkenes, phosphagermacyclopropanes, 1,2,3-phosphadigermethanes, coordination complexes, quantum-chemical calculations, G2 computational scheme, density functional theory.

Cycloaddition of carbene analogs (silylenes, germylenes, and stannylenes) to unsaturated compounds is a typical reaction of these species, which is thought to have a great synthetic potential.[2] This reaction has been studied in detail for substrates with the carbon—carbon, carbon—oxygen, and carbon—sulfur multiple bonds.

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Cycloaddition of carbene analogs to the carbon—phosphorus multiple bonds has been much less studied. To date, only one example of the addition of germylene[3] and silylene[4] to phosphaalkyne to give germa- and silaphosphacyclopropenes, respectively, was reported. The aim of this work was to carry out an experimental and quantum-chemical study of the reactions between germylenes with different structure and phosphaalkenes and to find synthetic routes to phosphagermacyclopropane derivatives that have been unknown so far.

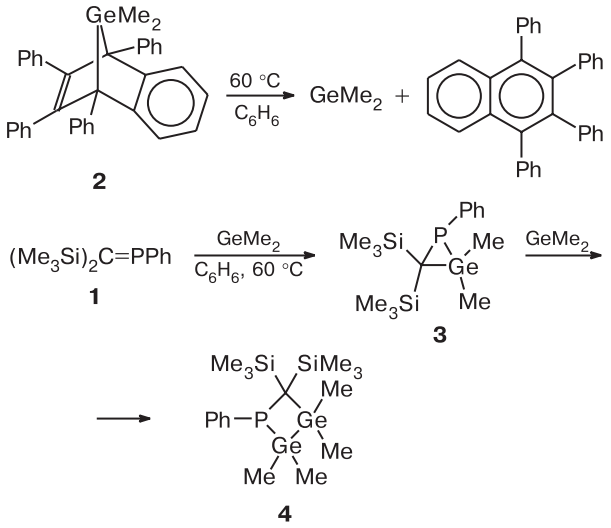
Results and Discussion

We studied the reactions of germylenes and dimethylsilylene with 1-phenyl-2,2-bis(trimethylsilyl)-1-phosphaethene (**1**).[5] It was found that both stable germylene $[(Me_3Si)_2N]_2Ge$ and GeI_2 did not react with phosphaalkene **1** (C_6H_6, 20—80 °C). No reaction was also observed between the $GeCl_2 \cdot$dioxane complex and phosphaalkene **1** at 20 °C, while heating of the reaction mixture to 80 °C led to the oxidation products of alkene **1**.

In contrast to this, the interaction of short-lived $GeMe_2$ generated by thermolysis of 7-germanorbornadiene derivative **2** (C_6H_6, 60 °C) with phosphaalkene **1** (at **1** : **2** = 1 : 1 mole ratio) resulted in the only product **3** (Scheme 1). The ^{31}P NMR spectrum of **3** exhibited a singlet at δ −137.1 in the region characteristic of phosphiranes (from δ −120 to −150).[6] The ^1H NMR spectrum of the reaction product exhibited two groups of signals with a 3 : 1 intensity ratio, corresponding to protons of the $(Me_3Si)_2C$ (a singlet at δ −0.05 and a doublet at δ 0.28; $^4J_{P,H}$ = 2.2 Hz) and $GeMe_2$ groups (a singlet at δ 0.70 and a doublet at δ 0.62; $^3J_{P,H}$ = 3.3 Hz). The signals of phenyl protons of phosphagermirane **3** are overlapped with the proton signals of four Ph substituents in 1,2,3,4-tetraphenylnaphthalene (a stable thermolysis product of 7-germanorbornadiene **2**). The ^{13}C NMR spectrum of phosphagermirane **3** exhibited a signal of the quaternary C atom (a doublet at δ 23.0 with $^1J_{P,C}$ = 69 Hz) in the region characteristic of the C atoms of phosphiranes[7] and the signals of nonequivalent Me groups at the Ge atom (doublets with phosphorus coupling constants, see Experimental). We failed to assign the signals of C atoms of the Me_3Si groups, since they are overlapped with the signals of $(Me_2Ge)_n$ polymer in the region from δ −5 to +5. The ^{29}Si NMR spectrum (two doublets at δ 0.29 and 0.93 with $^2J_{P,Si}$ = 21.4 and 4.8 Hz, respectively) also indicated inequivalence of the two Me_3Si groups.

Thus, the spectral data obtained unambiguously indicate that the reaction of $GeMe_2$ with phosphaalkene **1** results in 2,2-dimethyl-3,3-bis(trimethylsilyl)-1-phenyl-1-phospha-2-germacyclopropane (**3**), which is the first representative of phosphagermiranes.

Scheme 1



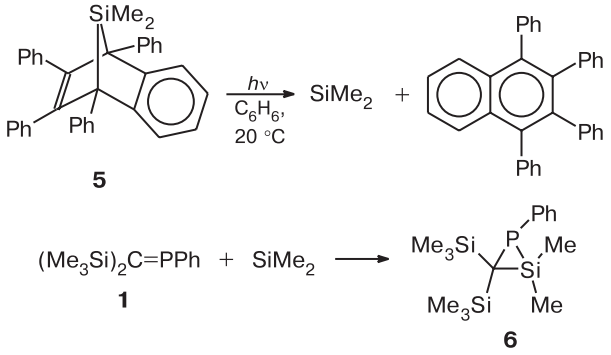
Phosphagermirane **3** was found to be a highly labile compound which instantly decomposes after exposure to dioxygen and atmospheric moisture. Our attempts at isolating this compound in individual form failed.

Phosphagermirane **3** enters into the reaction with the second equivalent of $GeMe_2$, which is generated from 7-germanorbornadiene **2** in an analogous manner (C_6H_6, 60 °C), and quantitatively forms an insertion product of $GeMe_2$ into the Ge—P bond, namely, 2,2,3,3-tetramethyl-4,4-bis(trimethylsilyl)-1-phenyl-2,3-digerma-1-phosphacyclobutane (**4**), which has not been reported so far. The ^1H NMR spectrum of compound **4** exhibits a singlet from two Me_3Si groups and two signals of Me groups (one of them is a doublet with $^3J_{P,H}$ = 5.5 Hz), while its ^{31}P NMR spectrum exhibits a signal at δ +3.2 in the region characteristic of phosphacyclobutanes.[8]

After successful synthesis of the first phosphagermirane it was reasonable to synthesize the first representative of phosphasiliranes. To this end, we studied the interaction of phosphaalkene **1** with $SiMe_2$ that was photochemically generated from 7,7-dimethyl-7-silanorbornadiene derivative **5** (C_6H_6, 20 °C) (Scheme 2). The ^{31}P NMR spectrum of the reaction mixture exhibited a signal at δ −132.4 which can be attributed to the cycloaddition product, namely, phosphasilirane **6**. However, monitoring by ^{31}P NMR spectroscopy showed that the reaction occurring under the specified conditions resulted in not only the desired phosphasilirane **6** but also a large number of other phosphorus-containing products that were formed by phototransformations of the initial phosphaalkene **1**. Because of this, a correct assignment of the signals in the ^1H and ^{13}C NMR spectra of the reaction mixture to phosphasilirane **6** was impossible.

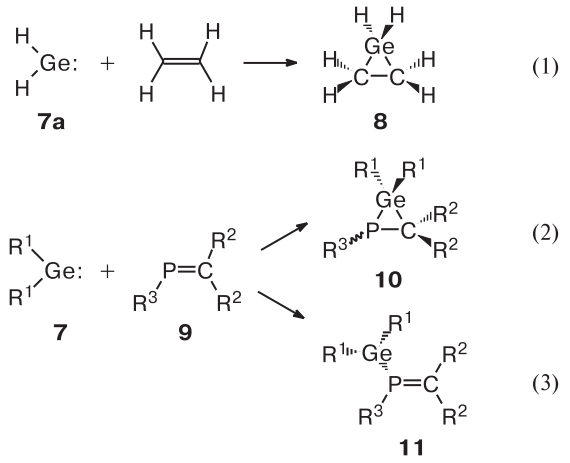
Thus, we demonstrated the possibility of cycloaddition of the short-lived dimethylgermylene to the C=P

Scheme 2



bond of phosphaalkene **1** and synthesized the first representative of germaphosphacyclopropanes. In this connection it is noteworthy that $GeMe_2$ and most of other germylenes[2,9] do not form stable germacyclopropanes. In order to rationalize different reactivity of alkenes and phosphaalkenes toward germylenes, we performed a quantum-chemical study of several model addition reactions of germylenes to the C=C and C=P bonds. To the best of our knowledge, no quantum-chemical studies of the reactions of germylenes with the C=P bond have been reported so far.

Quantum-chemical study of cycloaddition reaction of germylenes to ethylene and phosphaethene. The energies of reagents and products of the reactions of GeH_2 with ethylene (reaction (1)) and phosphaethene CH_2=PH (reaction (2)) were calculated in the framework of the Gaussian-2 (G2) approach.[10] Using this precision computational scheme allowed us to compare the thermal effects associated with different pathways of germylene transformations and to estimate the stability of germacyclopropane and its phosphorus-containing analog in the framework of a unified theoretical approach.



7, 9—11: $R^1 = R^2 = R^3 = H$ (**a**)
R^1 = Me, $R^2 = R^3$ = H (**b**)
R^1 = Cl, $R^2 = R^3$ = H (**c**)
R^1 = Me, $R^2 = SiH_3$, R^3 = Ph (**d**)

The G2 approach can be used only for calculations of relatively small systems.[10] To study the effects of substituents in the germylene and phosphaalkene molecules on the stability of corresponding products, we performed quantum-chemical calculations of the initial reagents and products of the reactions of germylenes **7a—c** and phosphaalkenes **9a,c,d** by the DFT PBE method.[11] Theoretical estimates of the energies of the structures in question allowed rationalization of some trends observed in our experiments.

Ab initio MP2/6-31G(d) calculations of the potential energy surface (PES) of reaction (1) revealed that this reaction occurs barrierlessly. According to the G2 calculations, the exothermicity, ΔE, of the cycloaddition reaction (1) is 21.1 kcal mol^{-1} (Table 1). This value is in good agreement with the results of a recent investigation[12] of the reaction (1) by the DFT B3LYP/6-31G(d) method ($\Delta E = -27.4$ kcal mol^{-1}). In study[12] it was found that cycloaddition of GeH_2 and $GeMe_2$ to the double bond of ethylene molecule involves the formation of a π-complex followed by its rearrangement into germirane with a rather low activation barrier (<2 kcal mol^{-1}). Similarly, our DFT PBE calculations also predict the formation of a π-complex between GeH_2 and ethylene ($\Delta E = -21.8$ kcal mol^{-1}) in the first stage and subsequent transformation of the complex into germirane **8** with an activation barrier of 1.6 kcal mol^{-1}. Thus, the MP2 calculations predict a barrierless cycloaddition (see reaction (1)), whereas both versions of DFT calculations imply the formation of a π-complex. DFT calculations also showed that the π-complex should be of extremely low stability toward rearrangement into germirane (the activation barrier is at most 2 kcal mol^{-1}). Taking into account these results, possible role of the π-complex in reaction (1) can be ignored.

Similarly to the reaction with ethylene, the most stable product of the reaction of germylene **7a** with phospha-

Table 1. Total energies (E) and the Gibbs free energies (G) of structures **7a**, C_2H_4, **8**, and **9a—11a** and thermodynamic characteristics (ΔE, ΔG, ΔH) of reactions (1)—(3) calculated by the G2 method

Structure	$-E$ [a]	$-G$ [b]	ΔE	ΔG [c]	ΔH [c]
	a.u.		kcal mol^{-1}		
7a	2076.57212	2076.59333	—	—	—
C_2H_4	78.41593	78.43809	—	—	—
8	2155.02173	2155.04873	−21.1	−10.9	−22.7
9a	380.69211	380.71555	—	—	—
10a	2457.32903	2457.35715	−40.7	−30.3	−42.0
11a	2457.29287	2457.32377	−18.0	−9.3	−18.4

[a] Calculated for 0 K.
[b] Calculated for 298 K.
[c] Calculated for p = 1 atm and T = 298 K.

Table 2. Total energies* (E_0), dipole moments, and geometric parameters (bond lengths (d) and bond angles (ω)) of reagents and products of reactions (1)—(3) calculated by the DFT PBE method

Structure	$-E_0$/a.u.	Dipole moment/D	d/Å					ω/deg
			C—P	C—Ge	P—Ge	Ge—$R^{1'}$	Ge—$R^{1''}$	R^1—Ge—R^1
C_2H_4	78.4527	0.00	—	—	—	—	—	—
8	2156.3522	0.19	—	1.966	—	1.531	1.531	117.9
9a	381.0037	0.96	1.683	—	—	—	—	—
9d	1192.8425	2.24	1.695	—	—	—	—	—
7a	2077.8623	0.22	—	—	—	1.610	1.610	90.0
7b	2156.3751	0.83	—	—	—	2.015	2.015	95.6
7c	2996.9035	2.37	—	—	—	2.221	2.221	100.9
10a	2458.9354	1.32	1.921	1.956	2.322	1.534	1.533	116.4
10b	2537.4456	2.31	1.934	1.957	2.329	1.966	1.966	116.6
10c	3377.9194	1.95	1.979	1.932	2.297	2.168	2.168	109.4
10d	3349.2809	2.85	1.953	1.988	2.318	1.968	1.967	114.3
11a	2458.9059	2.31	1.676	3.717	2.359	1.591	1.594	97.1
11b	2537.4057	0.78	1.688	3.686	2.388	2.016	2.020	102.8
11c	3377.9202	4.98	1.679	3.734	2.649	2.263	2.249	101.7
11d	3349.2509	2.56	1.701	3.646	2.343	2.002	2.009	105.7

* Calculated with inclusion of zero-point vibrational energy correction ($E_0 = E$ + ZPE).

ethene **9a** is a three-membered cycloadduct, namely, phosphagermirane **10a** (see reaction (2)). Yet another, unexpectedly stable product is acyclic structure **11a** which has no analogs in the reactions with olefins. This structure can be considered as either a donor-acceptor complex in which germylene is coordinated by the lone electron pair of the P atom or as an ylide (reaction (3)). The total energies of structures **7a**, **8**, and **9a—11a** calculated by the G2 and DFT PBE methods are listed in Tables 1 and 2, respectively. Table 2 also includes the principal geometric parameters of the reagents and products of reactions (1)—(3) obtained from the DFT PBE calculations.

The geometric parameters of structures **7a**, **8**, and **9a—11a** calculated by the MP2/6-31G(d) method incorporated into the G2 computational scheme are close to those obtained using the DFT PBE approach. The C—C bond lengths differ by less than 0.01 Å. The differences between the C—P, C—Ge, and P—Ge bond lengths in the three-membered cycles calculated by different methods amount 0.03 Å and have a systematic character, that is, the MP2 calculations give shorter bond lengths (*i.e.*, more compact cycles). The P—Ge distance in structure **11a** is 2.368 (MP2) and 2.359 Å (PBE), respectively. By and large, the geometric parameters of structures **7a**, **8**, and **9a—11a** calculated by both quantum-chemical methods are in good agreement.

Calculations of the energy characteristics by the G2 method (see Table 1) showed that cycloaddition of GeH_2 to phosphaethene **9a** is much more energetically favorable than its cycloaddition to ethylene ($\Delta E = -40.7$ and -21.1 kcal mol^{-1}, respectively). The lack of experimental data allows these values to be considered as realistic theoretical estimates of the relative stabilities of germirane **8** and phosphagermirane **10a**. The known values of the enthalpies, ΔE, of cycloaddition of GeH_2 to ethylene calculated for $T = 0$ K are as follows: -18.3 kcal mol^{-1} (CCSD/DZ+d//HF/DZ+d calculations[13]) and -27.4 kcal mol^{-1} (DFT B3LYP/6-31G(d) calculations[12]). Our DFT PBE calculations of the same reaction gave a ΔE value of -23.3 kcal mol^{-1} (Table 3), which is much closer to the result obtained using the most accurate G2 approach. This is clearly due to both the accuracy of the method based on the PBE functional[14] and the fact that our calculations were carried out with a much more flexible basis set compared to those used in other studies.[12,13]

Table 3. Total energy differences (ΔE_0) and the Gibbs free energy differences* (ΔG) for reactions (1)—(3) obtained from G2 and DFT PBE calculations

Reagents	Products			
	Three-membered cycle **8** or **10**		Complex **11**	
	ΔE_0	ΔG	ΔE_0	ΔG
	kcal mol^{-1}			
7a + C_2H_4	−23.3	−8.9	—	—
7a + **9a**	−43.5	−28.6	−25.0	−12.7
7b + **9a**	−41.8	−26.0	−16.9	−3.6
7c + **9a**	−7.6	6.2	−8.2	2.8
7a + **9d**	−39.7	−23.6	−20.8	−7.0

* Calculated for $p = 1$ atm and $T = 298$ K.

The ΔE values calculated earlier[12,13] characterize the stabilities of the three-membered rings toward their retrodecomposition at 0 K. More realistic estimates of the stability under normal conditions are provided by the Gibbs free energies (ΔG) calculated for $T = 298$ K. Based on the ΔG values obtained by both methods (see Tables 1 and 3), at $T = 298$ K the difference in stability of phosphagermirane **10a** and germirane **8** should be even greater, namely, −10.9 *vs.* −30.3 kcal mol^{-1} (G2) or −8.9 *vs.* −28.6 kcal mol^{-1} (PBE), respectively. It is noteworthy that the energies calculated using the G2 and PBE methods are also rather close. It should be noted that our PBE calculations predict a barrierless cycloaddition of GeH_2 to phosphaethene **9a**, which does not involve the formation of a π-complex as is the case of the reaction with ethylene.[12]

The thermodynamic stability of the donor-acceptor complex of GeH_2 with phosphaethene (**11a**) is close to that of the three-membered cycle formed in the reaction of GeH_2 with ethylene (see Table 1). Similarly to germirane, complex **11a** seems to be hard to isolate under normal conditions. Despite insignificant discrepancies, all computational methods employed predict a charge transfer from phosphaethene to germylene in complex **11a**. The degree of charge transfer depends on the method and to the greatest extent on the basis set employed and varies from 0.094 au (MP2/6-311G+(3df,2pd)) to 0.263 a.u. (QCISD(T)/6-311G(d,p)). The dipole moment of complex **11a** (3.62 or 2.31 D according to the MP2/6-311G+(3df,2pd) or PBE calculations, respectively) is much larger than those of the starting reagents or phosphagermirane **10a** (1.54 D (MP2/6-311G+(3df,2pd)) and 1.32 D (PBE)). Therefore, one can expect that solvation will favor additional stabilization of structure **11a**.

The P—Ge distance in complex **11a** is 2.368 (MP2) or 2.359 Å (PBE), which is appreciably shorter than in the crystalline complex $GeCl_2 \cdot PPh_3$ (2.51 Å).[15] This is an argument in favor of the ylide character of complex **11a**. For comparison, mention may be made that the length of the covalent P—Ge bond in phosphagermirane **10a** obtained from our calculations lies between 2.294 and 2.322 Å (see Table 2).

The influence of substituents on the geometry and stability of products **10** and **11** can be traced by analyzing the data listed in Tables 2 and 3. Passage from germylene to dimethylgermylene has little effect on the geometry of the three-membered cycle **10** (see Table 2). The C—P and P—Ge bonds are lengthened by 0.014 and 0.007 Å, respectively. The cycloaddition energies, ΔE_0 and ΔG, of $GeMe_2$ are somewhat lower (by 1.6 and 2.6 kcal mol^{-1}, respectively) than the corresponding parameters of GeH_2 (see Table 3). Earlier B3LYP calculations[12] also revealed that the enthalpies of cycloaddition of GeH_2 and $GeMe_2$ to ethylene are nearly equal. Thus, attachment of Me groups to the Ge atom has virtually no effect on the stability of the corresponding three-membered cycles.

To a greater extent the Me groups affect the ability of germylene to undergo complexation. On going from **11a** to **11b** the stability of the complex reduces by 8.1 kcal mol^{-1} (ΔE_0) and 9.1 kcal mol^{-1} (ΔG). At the same time, the P—Ge distance in **11b** (2.359 Å) is lengthened by 0.029 Å as compared to **11a**.

According to calculations, the reactions (2) and (3) involving $GeCl_2$ are much less energetically favorable than similar processes with participation of GeH_2 or $GeMe_2$. The PES minima corresponding to adducts **10c** and **11c** were located. On going from **10a** to **10c** the C—P bond is shortened by 0.058 Å while the C—Ge and P—Ge bonds are lengthened by nearly the same value (0.025 Å). This indicates that the cycle in structure **10c** is less stable and more prone to retrodecomposition into **9a** and $GeCl_2$. The energies of the corresponding reactions (see Table 3) also confirm this conclusion. According to PBE calculations, 2,2-dichlorophosphagermirane **10c** can exist only at very low temperatures (ΔE_0 = −7.6 kcal mol^{-1}), while its formation in the reaction (2) under normal conditions is energetically unfavorable (ΔG = 6.2 kcal mol^{-1}). Introduction of two Cl atoms into the germylene molecule affects its ability to undergo complexation with **9a** to somewhat lesser extent. However, the P—Ge distance in complex **11c** is lengthened by 0.290 Å compared to complex **11a** and by 0.352 Å compared to the cycle **10c** (see Table 2). Clearly, structure **11c** is a conventional donor-acceptor complex (a typical[16] product of the reactions involving $GeCl_2$). Complex **11c** is much less stable (ΔE_0 = −8.2 kcal mol^{-1}, ΔG = 2.8 kcal mol^{-1}) compared to complex **11a**; however, it is more stable than germirane **10c** (see Table 3). Thus, the results of calculations show that cycloaddition of $GeCl_2$ to phosphaalkene **1** under normal conditions is thermodynamically unfavorable.

To assess the influence of substituents in the phosphaalkene molecule on the stability of the cycloadduct, we studied the reaction of phosphaalkene $(H_3Si)_2C{=}PPh$ (**9d**) with $GeMe_2$ resulting in compounds **10d** and **11d**. According to calculations, the reaction products **10d** and **11d** are characterized by nearly the same stabilities as their respective analogs **10b** and **11b** formed by phosphaethene. The stability of phosphagermirane **10d** is 2.1 kcal mol^{-1} (ΔE_0) and 2.4 kcal mol^{-1} (ΔG) lower compared to **10b**, while complex **11d** is 4.0 kcal mol^{-1} (ΔE_0) and 3.4 kcal mol^{-1} (ΔG) more stable than **11b**. Nevertheless, phosphagermirane **10d** remains much more stable toward elimination of germylene than complex **11d** and even more stable than germirane. This indicates that the substituents (silyl groups at the C atom and the Ph group at the P atom) favor the formation of phosphagermirane.

Experimental and Calculation Procedure

All reactions were carried out in a dry argon atmosphere using anhydrous solvents prepared following standard procedures. Phosphaalkene **1**,[5] stable germylene $[(Me_3Si)_2N]_2Ge$,[17] complex $GeCl_2 \cdot$dioxane,[18] GeI_2,[19] 7-germanorbornadiene **2**,[20] and 7-silanorbornadiene **5** [21] were obtained following the known procedures. The reactions of phosphaalkene **1** with germylenes were studied using tubes for NMR spectroscopy. The reactions were monitored by NMR spectroscopy with anhydrous C_6D_6 as solvent.

NMR spectra were recorded on Bruker AC-200 (200 MHz for ^1H and 50 MHz for ^{13}C nuclei), Bruker AM-300 (300 MHz for ^1H, 75 MHz for ^{13}C, 121.5 MHz for ^{31}P, and 59.6 MHz for ^{29}Si nuclei), and Bruker DRX-500 (125 MHz for ^{13}C) instruments.

2,2-Dimethyl-1-phenyl-3,3-bis(trimethylsilyl)-1-phospha-2-germacyclopropane (3). Phosphaalkene **1** (85 mg, 0.32 mmol), C_6D_6 (1.0 mL), and 7-germanorbornadiene **2** (172 mg, 0.32 mmol) were placed in an NMR tube. The reaction mixture was heated at 60 °C directly inside the probe of the NMR spectrometer. The reaction was monitored by ^{31}P NMR spectroscopy by tracing a decrease in the intensity of the signal of the initial phosphaalkene (δ +376.0) and the appearance of a signal of compound **8** (δ −137.1). The reaction completed after 3 h. ^1H NMR (δ, *J*/Hz): −0.05 (s, 9 H, Me_3Si); 0.28 (d, 9 H, Me_3Si, $^4J_{P,H}$ = 2.2); 0.62 (d, 3 H, Me, $^3J_{P,H}$ = 3.3); 0.70 (s, 3 H, Me). ^{31}P NMR (δ): −137.1 (s). ^{13}C NMR (δ, *J*/Hz): −2.02 (d, Me, $^2J_{P,C}$ = 8.9); −1.36 (d, Me, $^2J_{P,C}$ = 80.4); 23.0 (d, $C(SiMe_3)_2$, $^1J_{P,C}$ = 68.9). ^{29}Si NMR (δ, *J*/Hz): 0.29 (d, $^2J_{P,Si}$ = 21.4); 0.93 (d, $^2J_{P,Si}$ = 4.8).

2,2,3,3-Tetramethyl-1-phenyl-4,4-bis(trimethylsilyl)-2,3-digerma-1-phosphacyclobutane (4). Phosphaalkene **1** (85 mg, 0.32 mmol), C_6D_6 (1.0 mL), and 7-germanorbornadiene **2** (344 mg, 0.64 mmol) were placed in an NMR tube. The reaction mixture was heated at 60 °C directly inside the probe of the NMR spectrometer. The reaction was monitored by ^{31}P NMR spectroscopy; the formation of phosphagermirane **3** (a singlet at δ −137.1) in the first stage was followed by its transformation into 2,3-digerma-1-phosphacyclobutane **4** (a singlet at δ +3.2). The reaction completed after 6 h. ^1H NMR (δ, *J*/Hz): 0.24 (s, 18 H, 2 Me_3Si); 0.74 (s, 6 H, 2 Me); 0.82 (d, 6 H, 2 Me, $^3J_{P,H}$ = 5.5). ^{31}P NMR (δ): +3.2 (s).

Quantum-chemical calculations in the framework of the G2 computational scheme were carried out using the GAUSSIAN-94 program suite.[22] Energy calculations in the framework of the G2 approach[10] involve several stages which include optimization of the geometry at the MP2/6-31G(d) level of theory and calculations of the energy by the QCISD, MP4, and MP2 methods with different basis sets. The final energy value obtained from G2 calculations is an approximation of the results of QCISD(T)/6-311G+(3df,2pd) calculations for structures with the geometries optimized at the MP2-FU/6-31G(d) level of theory with inclusion of the zero-point vibrational energy correction, ZPE, calculated at the HF/6-31G(d) level of theory.

Density functional calculations were carried out using the PRIRODA program.[23] These calculations including full geometry optimization and calculations of the vibrational frequencies were carried out with the three-exponent basis set of Gaussian functions of size (5s2p) [3s2p] for H, (11s6p2d) [6s3p2d] for C, (15s11p2d) [10s6p2d] for Si and P, and (18s14p9d) [13s10p5d] for Ge (the patterns of uncontracted and contracted basis sets are given in parentheses and brackets, respectively). The program uses the electron density expansion[24] over an auxiliary basis set of uncontracted functions of dimensions (5s2p) for H, (10s3p3d1f) for C, (14s3p3d1f1g) for Si and P, and (18s3p3d1f1g) for Ge. The characters of the stationary points located on the PES were determined by calculating the eigenvalues of the matrix of the second derivatives of energy with respect to coordinates. The thermodynamic functions were calculated in the framework of the "harmonic oscillator—rigid rotator" model.

Density functional calculations were performed on personal computers with Pentium®-II 300 and Celeron® 433 CPUs. Calculations using the GAUSSIAN-94* program suite were carried out on a SGI POWER CHALLENGE L supercomputer at the Computer Center, N. D. Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences.

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References

1. B. G. Kimel, V. V. Tumanov, M. P. Egorov, and O. M. Nefedov, *Mendeleev Commun.*, 2001, 85.
2. W. P. Neumann, *Chem. Rev.*, 1991, **91**, 311.
3. A. H. Cowley, S. W. Hall, C. M. Nunn, and J. M. Power, *J. Chem. Soc., Chem. Commun.*, 1988, 753.
4. A. Shaefer, M. Weidenbruch, W. Saak, and S. Pohl, *Angew. Chem.*, 1987, **99**, 806.
5. R. Appel, J. Peters, and A. Westerhaus, *Tetrahedron Lett.*, 1981, **22**, 4957.
6. A. Marinetti and F. Mathey, *Organometallics*, 1984, **3**, 456.
7. M. J. M. Vlaar, A. W. Ehlers, F. de Kanter, and K. Lammertsma, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 2943.
8. A. Marinetti, V. Krueger, and F.-X. Buzin, *Tetrahedron Lett.*, 1997, **38**, 2497.
9. S. P. Kolesnikov, M. P. Egorov, A. M. Gal´minas, and O. M. Nefedov, *Metalloorg. Khim.*, 1989, **2**, 1351 [*Organomet. Chem. USSR*, 1989, **2** (Engl. Transl.)].
10. L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.*, 1991, **94**, 7221.

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11. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
12. M.-D. Su and S.-Y. Chu, *J. Am. Chem. Soc.*, 1999, **121**, 11478.
13. D. A. Horner, R. S. Grev, and H. F. Schaefer, III, *J. Am. Chem. Soc.*, 1992, **114**, 2093.
14. C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158.
15. N. G. Bokii, Yu. T. Struchkov, S. P. Kolesnikov, I. S. Rogozhin, and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 812 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1975, **24** (Engl. Transl.)].
16. S. P. Kolesnikov, *Zh. Vses. Khim. O-va im. D. I. Mendeleeva*, 1979, **24**, 505 [*Mendeleev Chem. J.*, 1979, **24** (Engl. Transl.)].
17. M. J. S. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Riviere, and M. Riviere-Baudet, *J. Chem. Soc., Dalton Trans.*, 1977, 2004.
18. S. P. Kolesnikov, I. S. Rogozhin, and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 2379 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1974, **23** (Engl. Transl.)].
19. T. G. Oikova and G. G. Gospodinov, *Izv. Vuz. Khim. Khim. Tekhnol.*, 1980, **23**, 1331 [*Bull. Higher School Research USSR, Ser. Chem. Chem. Technol.*, 1980 (Engl. Transl.)].
20. W. P. Neumann and M. Schriewer, *Tetrahedron Lett.*, 1980, **21**, 3273.
21. J. A. Hawari and D. Griller, *Organometallics*, 1984, **3**, 11.
22. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *Gaussian-94, Revision D. 1*, Gaussian Inc., Pittsburgh (PA), 1995.
23. D. N. Laikov, Diss. kand. fiz.-mat. nauk [Ph.D. Thesis (Phys./Math.)], Moscow State University, Moscow, 2000 (in Russian).
24. D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.

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