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Journal of Organometallic Chemistry 641 (2002) 156–164

Journal of Organo metallic Chemistry

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Reactions of methyl(phenyl)silylene with CO and PH_3—the formation of acid–base complexes

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Received 17 July 2001

This work is dedicated to Professor Rolf Gleiter on the occasion of his 65th birthday

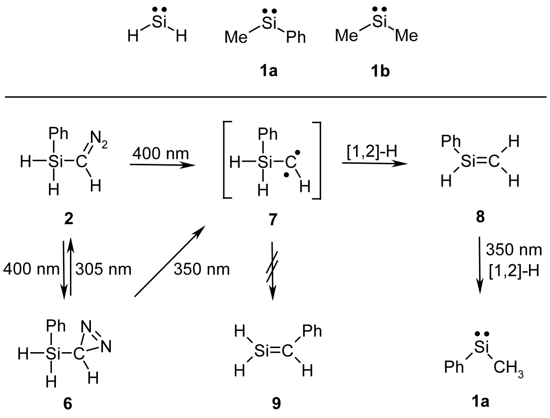
Abstract

The thermal reaction of methyl(phenyl)silylene **1a** with CO and PH_3, respectively, was investigated using matrix isolation spectroscopy in combination with DFT calculations. The silylene **1a** was produced by UV irradiation ($\lambda > 400$ nm followed by $\lambda > 350$ nm) of (phenyl)silyldiazomethane **2** in high yields. The thermal reaction of **2** with CO in CO-doped argon matrices produces the acid–base adduct **3** which was identified by IR and UV spectroscopy. The analogous reaction with PH_3 produced the acid–base adduct **4**. Complex **4** is photolabile and on irradiation with UV light ($\lambda > 350$ nm) rearranges to methylphenyl(phosphino)silane **5**, the product of the insertion of the silicon atom into a PH bond. © 2002 Published by Elsevier Science B.V.

Keywords: Silylene; Silaketene; Carbon monoxide; Phosphane; Matrix isolation; IR spectroscopy; DFT calculation

1. Introduction

Silylenes **1** are highly reactive intermediates of key importance in many reactions. The reactivity of silylenes is linked to the presence of both a lone pair and a vacant p-orbital at the silicon atom [1–3]. Thus, silylenes undergo reactions both with Lewis-acids and -bases. The formation of complexes with Lewis-bases has been used to stabilize silylenes and tame its reactivity [3–6]. Recently we reported on the synthesis of methyl(phenyl)silylene **1a** in solid argon at 10 K in high yields by irradiation of the diazo compound **2** (Scheme 1) [7]. We were also able to investigate the thermal reaction of **1a** with molecular oxygen in O_2-doped argon matrices at temperatures between 35 and 40 K. At these temperatures, the mobility of small trapped molecules is high enough to allow bimolecular reactions, as long as the activation barriers are essentially zero [8].



Scheme 1.

The reaction of dimethylsilylene **1b** with CO in low-temperature matrices was described by Arrington. In the IR spectrum an intense absorption at 1962 cm^{-1} was assigned to the adduct of **1b** with CO. A comparison of the IR spectrum with semiempirical and RHF ab-initio calculations did not allow to determine the structure—linear ketene versus a bent complex. In a 3-methylpentane glass a UV absorption with a maximum at 342 nm was assigned to the reaction product. Similar UV maxima in solid 3-methylpentane were also described by Pearsall and West [9]. The structure of the

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0022-328X/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0022-328X(01)01363-8

Table 1
IR spectroscopic data for methyl(phenyl)silylene–CO adduct **3**

Argon, 10 K			DFT (B3LYP/6-311++G(2d,p))				Assignment [c]
ν (cm^{-1})	I [a]	ν_i/ν [b]	No.	ν (cm^{-1})	I [a]	ν_i/ν [b]	
3074.9	1	1.000	48	3185	2	1.000	C–H str
3061.3	2	1.000	47	3174	3	1.000	C–H str
3018.3	1	1.000	43	3107	1	1.000	CH_3 asym. str
3001.2	1	1.000	42	3093	1	1.000	CH_3 asym. str
2909.4	2	1.000	41	3027	1	1.000	CH_3 sym. str
1992.1	100	0.978	40	2058	100	0.977	CO str
1988.7		0.978					
1984.8		0.978					
1484.6	3	1.000	37	1518	1	1.000	Skel. ring, in pl. C–H
1431.6	13	1.000	36	1470	1	1.000	HCH bend
1411.9	12	1.000	35	1464	1	1.000	HCH bend
			34	1463	1	1.000	HCH bend, ring str
1241.1	4	1.000	31	1285	1	1.000	CH_3 sym. bend
1086.2	3	1.000	28	1102	2	1.000	In pl. C–H bend
783.9	10	1.000	20	808	3	1.000	CH_3 rock
			19	799	1	0.999	CH_2 twist
737.3	8	1.000	18	752	4	1.000	C–H wag
699.4	27	1.000	17	713	4	1.000	C–H wag
691.6	6	0.999	16	699	1	1.000	Ring breathing
			12	468	1	0.993	Si–CO str, CH_3 def

[a] Relative intensity based on the strongest peak.

[b] Ratio of the frequencies of the ^{13}CO versus ^{12}CO isotopomers.

[c] The assignment of experimental and calculated IR absorption is based on peak position and peak intensities and for the weak absorptions only tentative.

SiH_2–CO adduct was investigated by Hamilton and Schaefer using ab-initio theory [10]. These authors predicted a weakly bound non-planar structure whereas the linear ketene structure was calculated to be a transition state. More recently Maier et al. was able to generate the adduct of the parent silylene SiH_2 with CO in an argon matrix [11]. By comparison of the experimental with DFT calculated IR spectra these authors could show that the adduct has a bent and not a linear ketene type structure. Beccera and Walsh were able to demonstrate that SiH_2 reacts with CO in the gas phase essentially without an activation barrier [12].

The stabilization of silylenes **1** by the formation of an adduct with amines has been demonstrated in a number of examples [13]. However, reactions of **1** with phosphanes have not been reported. Due to the weaker P–H bond, compared to the N–H bond, insertion reactions could provide alternative reaction channels in these cases.

Here we describe thermal reactions of silylene **1a** with CO and PH_3 under the conditions of matrix isolation. This technique allows to cleanly prepare and characterize the silylenes. In a second step, the thermal reaction with CO and PH_3, respectively, is induced by annealing the matrix at a temperature where diffusion of small molecules becomes rapid.

2. Results and discussion

2.1. Reaction of **1a** with CO

Photolysis ($\lambda > 400$ nm followed by $\lambda > 350$ nm) of (phenyl)silyldiazomethane **2** in an 0.5% CO-doped argon matrix at 10 K resulted in high yields of methyl(phenyl)silylene **1a**. Annealing of the matrix for several min at 35 K results in the formation of ca. 50% of a new product **3**. Most characteristic in the IR spectrum of **3** is a very strong and broad absorption at 1988 cm^{-1} (Table 1, Fig. 1). If ^{13}CO is used in the experiment this absorption is red-shifted by 45 cm^{-1}, while the other IR bands of **3** exhibit only very small or no shifts. This allows to assign the 1988 cm^{-1} absorption to the CO stretching vibration of the adduct of **1a** and CO, **3** (Scheme 2).

The carbonylation reaction of **1a** to give **3** was also followed by UV spectroscopy. Irradiation of **2** results in the characteristic 260 and 482 nm absorptions of silylene **1a** and an additional broad band with $\lambda_{max} =$ 348 nm (Fig. 2). The latter absorption strongly grows during the thermal reaction and is consequently assigned to adduct **3**. Simultaneously, the bands of **1a** decrease in intensity. The formation of **3** is reversible, and photolysis ($\lambda > 375$ nm) of the CO adduct **3** results in the partial recovery of **1a**.

The structures and relative energies of the products of the carbonylation were calculated using DFT methods (B3LYP/6-311 + + G(2d,p) including zero point energy ZPE) (Scheme 3). The reaction of methyl(phenyl)silylene **1a** with CO to give **3** is calculated to be exothermic by 11.5 kcal mol^{-1}. Its planar isomer, the methyl(phenyl)silaketene, proved to be no minimum on the potential energy surface. Instead, a transition state **TS** is found, in agreement with calculations published by Hamilton and Schaefer [10] and Maier et al. [11]. **TS** is 10.5 kcal mol^{-1} higher in energy than adduct **3** and connects the two rotational conformers of **3**.

2.2. Reaction of **1a** with PH3

Irradiation ($\lambda > 400$ nm followed by $\lambda > 350$ nm) of diazo precursor **2** in an 0.25% PH_3-doped argon matrix at 10 K resulted also in high yields of methyl(phenyl)silylene **1a**. Annealing of this matrix for a few minutes at 35 K leads to the disappearance of ca. 30% of **1a** and the formation of a new compound **4** exhibiting strong IR absorptions at 2301 and 984 cm^{-1} (Table 2, Fig. 3). These bands are due to P–H stretching and deformation vibrations, respectively, but cannot be assigned to PH_3 (monomer or aggregates). The comparison of the experimental IR spectrum with calculations at the B3LYP/6-311 + + G(2d,p) level of theory allows the assignment of the newly formed compound to methyl(phenyl)silylene-PH_3 adduct 4 (Scheme 4).

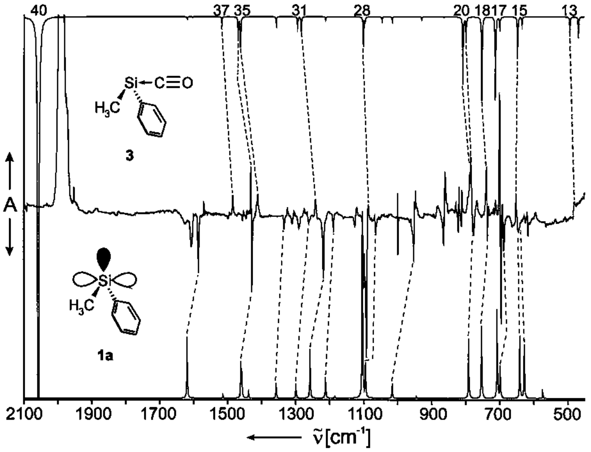
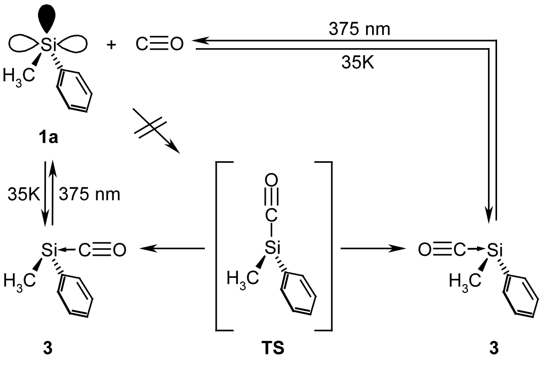


Fig. 1. Center: difference IR spectrum showing the thermally induced reaction of methyl(phenyl)silylene **1a** and CO. Bands pointing downwards are disappearing during the process of annealing and assigned to **1a**, bands pointing upwards are appearing and mainly assigned to the methyl(phenyl)silylene–CO adduct **3**. Bottom: IR spectrum of **1a**, calculated at the B3LYP/6-311 + + G(2d,p) level of theory. Top: IR spectrum of **3**, calculated at the B3LYP/6-311 + + G(2d,p) level of theory.



Scheme 2.

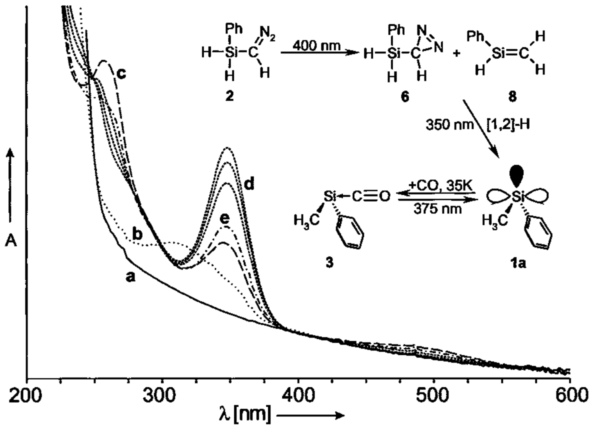
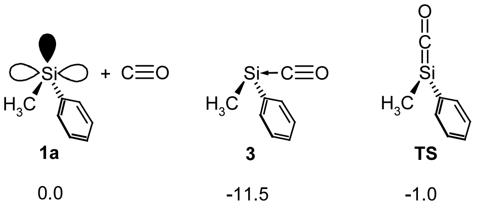


Fig. 2. UV–vis spectra showing the photochemistry of (phenyl)silyldiazomethane (**2**) and the bimolecular reaction of methyl(phenyl)silylene **1a** and CO: (a) spectrum of **2**, matrix-isolated in argon at 12 K containing 0.5% CO; (b) same spectrum after 400 nm irradiation. The major constituent is now a mixture of 1-phenylsilene and (phenyl)silyldiazirine; (c) same spectrum after 350 nm irradiation. The major constituent is now silylene **1a**; (d) same spectra after annealing for 2, 5 and 10 min. The major constituent is now adduct **3**; (e) same spectrum after 375 nm irradiation. The major constituent is now a mixture of **1a** and **3**.



Scheme 3.

The bimolecular reaction between **1a** and PH_3 was again followed by UV spectroscopy. On annealing the matrix the characteristic silylene absorptions disappear, whereas the adduct **4** does not show any strong UV absorptions.

Methyl(phenyl)silylene-PH_3 adduct **4** is photochemically unstable. On UV irradiation ($\lambda > 350$ nm) all bands of **4** completely disappear and a set of absorptions assigned to a new compound **5** is growing in. The most intense absorption of **5** is found at 2135 cm^{-1}, typical of a Si–H stretching vibration. A characteristic absorption splitted into two components at 2327 and 2323 cm^{-1} indicates the presence of P–H bonds (Table 3, Fig. 4). The most reasonable photochemical reaction of **4** is the insertion of the silicon center into a PH bond (Scheme 5). This assumption could be verified by comparison of the experimental IR spectrum with IR data of methyl(phenyl)phosphinosilane **5**, calculated at the (B3LYP/6-311 + + G(2d,p)) level of theory.

For the reaction of the parent silylene SiH_2 with PH_3 some thermodynamic data were calculated by Raghavachari et al. at the MP4SDTQ/6-31(d,p)//6-31G(d) level of theory [14]. According to these calculations the SiH_2–PH_3 complex is stabilized by 17.5 kcal mol^{-1} and the corresponding insertion product by 53.1 kcal mol^{-1}. The activation barrier for the rearrangement was determined to 19.7 kcal mol^{-1}. In addition a second transition state with a large barrier of 37.0 kcal mol^{-1} was located.

The relative stabilities and structures of the products of the reaction of **1a** with PH_3 were calculated using B3LYP/6-311 + + G(2d,p) + ZPE theory (Scheme 6). To compare these results with the data published by Raghavachari et al [14]. we also calculated the SiH_3 + PH_3 reaction at the same level of theory. The formation of the SiH_2–PH_3 adduct is exothermic by 19.3 kcal mol^{-1} in good agreement with the published data. The phosphinosilane is stabilized by 52.4 kcal mol^{-1}, and the activation barrier for this rearrangement is calculated to 16.7 kcal mol^{-1}, again in agreement with the MP4 data.

The formation of the methyl(phenyl)silylene–PH_3 adduct **4** is predicted to be only slightly exothermic by 7.0 kcal mol^{-1}, while the PH insertion product **5** is 41.0 kcal mol^{-1} more stable than **4**. For the Cs-symmetrical PH_3 adduct of **1a** a transition state is calculated which connects both rotamers of **4** and is 28.2 kcal mol^{-1}

Table 2
IR spectroscopic data for methyl(phenyl)silylene–PH_3 adduct **4**

Argon, 10 K		DFT (B3LYP/6-311+ +G(2d,p))			Assignment [b]
ν (cm^{-1})	I [a]	No.	ν (cm^{-1})	I [a]	
3081.6	4	54	3181	14	C–H str
3065.2	10	53	3169	17	C–H str
		52	3161	2	C–H str
		51	3151	1	C–H str
3052.7	5	50	3132	3	C–H str
3017.1	5	49	3080	8	CH_3 asym. str
2995.3	4	48	3068	5	CH_3 asym. str
2954.9	12	47	3006	10	CH_3 sym. str
		46	2477	5	P–H str
2399.0	5	45	2452	16	P–H str
2300.7	100	44	2322	100	P–H str
1478.4	4	41	1516	1	Skel. ring, in pl. C–H
1424.1	1	40	1469	3	HCH bend
1417.4	2	39	1463	4	HCH bend
1409.5	4	38	1461	4	HCH bend, in pl. C–H bend
1325.3	3	37	1357	2	In pl. C–H bend
1255.5	2	36	1292	3	In pl. C–H bend, ring str
1230.2	2	35	1274	5	CH_3 sym. bend
		34	1211	1	In pl. C–H bend
1135.5	4	32	1121	6	HPH bend
1096.1	17	31	1108	13	HPH bend
1084.0	15	30	1095	10	In pl. C–H bend, Si–C str
		29	1094	1	In pl. C–H bend
984.3	58	27	1017	21	PH_3 sym. bend, ring breathing
977.6	14	26	1015	48	PH_3 sym. bend
773.0	15	21	791	13	CH_2 twist
746.2	4	20	764	5	CH_3 rock
735.3	21	19	750	14	C–H wag
699.6	18	18	713	17	C–H wag
675.5	3	17	689	3	
630.2	8	15	615	13	Si–CH_3 str
504.3	22	14	509	15	PH_3 def, C–H wag
		13	443	8	PH_3 rock, CH_3 def
		12	431	1	PH_3 rock, C–H wag

[a] Relative intensity based on the strongest peak.

[b] The assignment of experimental and calculated IR absorption is based on peak positions and peak intensities and for the weak absorptions only tentative.

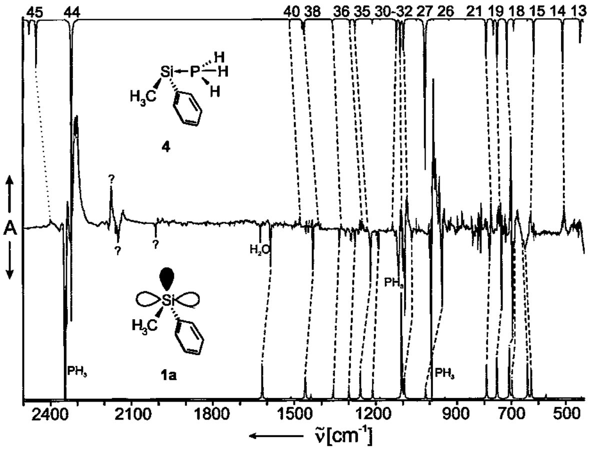
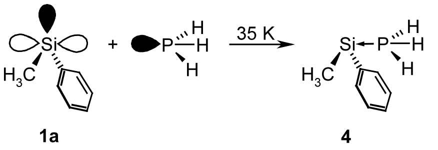


Fig. 3. Center: difference IR spectrum showing the thermally induced reaction of methyl(phenyl)silylene **1a** and PH_3. Bands pointing downwards are disappearing during the process of annealing and assigned to **1a**, bands pointing upwards are appearing and mainly assigned to the methyl(phenyl)silylene–PH_3 adduct **4**. Bottom: IR spectrum of **1a**, calculated at the B3LYP/6-311 + + G(2d,p) level of theory. Top: IR spectrum of **4**, calculated at the B3LYP/6-311 + + G(2d,p) level of theory.



Scheme 4.

higher in energy. The barrier for the [1,2]-H migration from phosphorous to silicon is also 28.2 kcal mol^{-1}, and thus high enough to prevent the direct formation of **5** under matrix isolation conditions. The activation barrier of the thermal reaction of **1a** with PH_3 leading to **4** is essentially zero or extremely small (less than 1–2 kcal mol^{-1}), otherwise this reaction would not be rapid at temperatures as low as 35 K.

Thus, compared to SiH_2 the formation of acid–base complexes of **1a** with CO or PH_3 results in a smaller stabilization. This is rationalized by the stabilizing interaction between the vacant p-orbital at the silicon atom and the π system of the phenyl substituent, resulting in a lower affinity to external electron donors.

2.3. *Calculated structures of silylene adducts 3 and 4*

The fully geometry optimized structure of adduct **3** is very similar to the parent SiH_2–CO adduct calculated by Maier et al. [11]. At the B3LYP/6-311 + + G(2d,p) level of theory the dihedral angle of the silylene moiety and CO is calculated to 103.7°, clearly indicating the bonding interactions between the HOMO of CO and the LUMO the silylene (Fig. 5). The Si–C bond length of 1.887 Å is within the normal range of Si–C single bonds. With 1.144 Å the C–O distance is slightly elongated compared to uncomplexed CO. The Si–C–O bond angle is calculated to 161.8°. Compared to **1a** the change of the structural parameters of the silylene moiety of **3** is negligibly small [7].

As expected, the transition state structure of methyl(phenyl)silaketene (**TS**) shows Cs symmetry. The Si–C distance is with 1.743 Å considerably shorter than in **3**, but ca. 0.040 Å longer than calculations predict for Si–C bonds of different silenes [15,16]. Thus, with 1.167 Å the C–O bond is elongated compared to **3** and shows a double bond character. The Si–C(Ph) bond length is calculated to 1.845 Å clearly indicating π-delocalization of the silaketene moiety and the phenyl substituent.

The geometry of methyl(phenyl)silylene-PH_3 adduct **4** was also optimized by the same DFT method (Fig. 6). The calculation predicts a dihedral angle (C(Me)–Si–C(Ph)–P) of 96.8° which is significantly smaller than in the adduct **3** and fits better to the idealized model of Lewis acid–base complexes. The Si–P distance is calculated to 2.404 Å which is in excellent agreement with the value predicted by Raghavachari et al. [14] for the parent system at the MP4SDTQ/6-31G(d,p)//6-31(d) level of theory (also 2.404 Å), but is definitely elongated regarding the normal range of Si–P single bond (d(Si–P) of **5**: 2.290 Å). In spite of that, with 1.934 Å, respectively, the Si–C bonds due to both substituents are slightly longer than calculated for **3**.

The C(Me)–Si–C(Ph)–P dihedral angle of the transition state structure connecting adduct **4** and methyl(phenyl)phosphinosilane **5** is calculated to 126.0° and thus is already as large as predicted for **5**. The Si–P distance is with 2.257 Å even smaller than in silane **5**.

3. Experimental

3.1. *Calculations*

The density functional theory calculations were carried out using the GAUSSIAN 98 suite of programs [17] on a Silicon Graphics Origin 2000 R10000 or a Power Challenge R12000 workstation. Geometry optimizations and frequency calculations of the singlet species were performed at the B3LYP [18] level of theory with 6-31G(d,p) and 6-311 + + G(2d,p) basis sets.

3.2. *Materials and general methods*

^1H- and ^{13}C-NMR spectra were taken at 200.1 and 50.3 MHz, respectively (Bruker AM 400), in $CDCl_3$ as solvent. Mass spectra (EI, 70 eV) were taken on a Varian MAT CH7 instruments. All reactions involving moisture-sensitive silicon reactants were performed under an atmosphere of dry argon. Precursor **2** for matrix experiments was purified by preparative scale GLC using a Siemens RGC 202 gas chromatograph.

3.3. Phenylsilyl trifluoromethanesulfonate

The triflate was prepared in analogy to a procedure by Bassindale and Stout [19] for the synthesis of dimethylsilyl triflate. Trifluoromethanesulfonic acid (36 mmol, 3.2 ml) was added dropwise to neat diphenylsilane (36 mmol, 6.6 g) at room temperature. After complete addition, benzene (formed as coproduct) was slowly removed under vacuum. The yield of phenylsilyl triflate was quantitatively. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.32–7.67 (m, 5H, Ph), 5.25 (s, 2H, SiH_2). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 135.79, 133.32, 129.21, 128.74, 126.52, 121.90, ^1J(C,F) 314 Hz.

3.4. (Phenyl)silyldiazomethane (**2**)

Compound **2** was synthesized in analogy to a procedure by Martin [20] for the synthesis of (trimethylsilyl)diazomethane. Freshly prepared phenylsilyl trifluoromethanesulfonate (36 mmol, 9.3 g) was added dropwise to equimolar quantities of diazomethane (36 mmol, 1.5 g in 100 ml of diethyl ether) and ethyldiiso-

Table 3
IR spectroscopic data for methyl(phenyl)phosphinosilane **5**

Argon, 10 K		DFT (B3LYP/6-311++G(2d,p))			Assignment [b]
ν (cm^{-1})	I [a]	No.	ν (cm^{-1})	I [a]	
3093.4	5	54	3185	10	C–H str
3076.6	8	53	3174	15	C–H str
		52	3165	1	C–H str
3060.8	5	51	3153	2	C–H str
		50	3150	3	C–H str
3029.1	9	49	3102	4	CH_3 asym. str
		48	3096	4	CH_3 asym. str
2977.6	11	47	3026	3	CH_3 sym. str
2326.7	22	46	2371	27	PH_2 asym. str
2322.8	25	45	2363	24	PH_2 sym. str
2134.8	100	44	2201	55	Si–H str
1498.5	5	41	1523	1	Skel. ring, in pl. C–H
1436.3	3	40	1465	5	In pl. C–H, HCH bend
		39	1464	1	HCH bend
1433.4	4	38	1460	4	HCH bend
1334.2	3	37	1362	2	Skel. ring, in pl. C–H
1252.2	26	36	1298	6	In pl. C–H, ring str
		35	1294	5	CH_3 sym. bend
		34	1214	1	In pl. C–H bend
1116.1	43	32	1127	19	In pl. C–H bend, Si–C str
1060.0	13	31	1099	6	HPH bend, in pl. C–H
		30	1096	3	HPH bend, in pl. C–H
877.5	66	24	902	48	Si–H def, CH_3 rock
874.1	37				
836.2	76	22	852	100	Si–H def, CH_3 def, PH_2 twist
832.3	55				
825.1	21				
756.2	5	21	788	1	Si–H def, CH_3 rock, PH_2 def
743.5	15	20	760	8	PH_2 def, C–H wag
726.8	22	19	747	25	
702.3	18	18	714	27	Si–H def, C–H wag
		17	709	1	
672.5	4	16	681	7	PH_2 twist, Si–H def
		15	658	2	Si–CH_3 str, PH_2 def
588.3	14	13	597	18	Si–H def, CH_3 def, PH_2 def
468.7	8	12	475	7	Si–PH_2 str, C–H wag
463.3	7				
		11	436	9	

[a] Relative intensity based on the strongest peak.

[b] The assignment of experimental and calculated IR absorption is based on peak positions and peak intensities and for the weak absorptions only tentative.

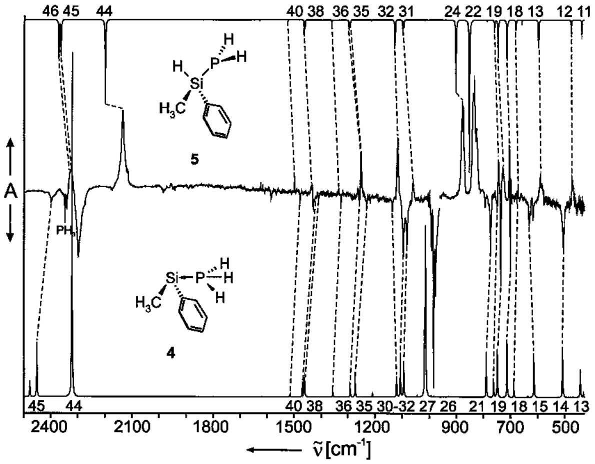
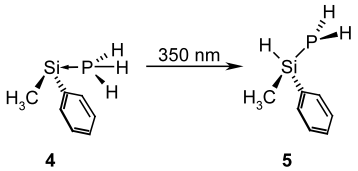
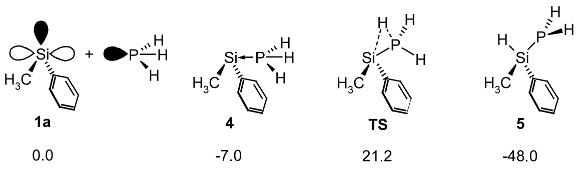


Fig. 4. Center: difference IR spectrum showing the photochemistry (375 nm irradiation) of methyl(phenyl)silylene–PH_3 adduct **4**. Bands pointing downwards are disappearing during the irradiation and assigned to **4**, bands pointing upwards are appearing and mainly assigned to methyl(phenyl)phosphinosilane (**5**). Bottom: IR spectrum of **4**, calculated at the B3LYP/6-311++G(2d,p) level of theory. Top: IR spectrum of **5**, calculated at the B3LYP/6-311++G(2d,p) level of theory.



Scheme 5.



Scheme 6.

propylamine (40 mmol, 5.2 g) at −65 °C. After complete addition the mixture was slowly warmed to 0 °C and the white precipitate was removed by rapid filtration through a frit. The yellow solution was concentrated in a first step at −50 °C in vacuo in order to remove excess diazomethane. In a second step, **2** (0.8 g, 15%) was obtained after distillation of the residue under reduced pressure (~30 °C/0.2 mbar). The yellow distillate was finally purified by preparative GLC (OV 101, 0.5 m, 60 °C, detector/injector 80 °C). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.60–7.65 (m, 2H, Ph), 7.40–7.42 (m, 3H, Ph), 4.77 (d, 2H, SiH_2), 2.87 (t, 1H, CHN_2). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 135.11, 130.40, 128.26, 15.47. EIMS (*m/e* (%)): 148 (26) [M^+], 120 (18) [$M^+ - N_2$], 119 (38) [$M^+ - (N_2 + H)$], 105 (100), 93 (28), 91 (19). IR (argon, 10 K): 3063.1 (1), 2195.3 (2), 2180.0 (2), 2154.6 (3), 2134.0 (7), 2093.0 (14), 2088.2 (100), 2082.9 (51), 1433.0 (5), 1274.0 (2), 1265.8 (8), 1158.0 (2), 1119.3 (11), 951.5 (2), 940.4 (9), 862.2 (100), 860.3 (5), 856.8 (87), 853.7 (9), 851.1 (11), 847.7 (1), 779.1 (3), 746.4 (2), 709.8 (6), 699.0 (2), 587.0 (4), 507.0 (1), 495.6 (3), 451.9 (1) cm^{-1} (relative intensity). UV (argon, 12 K): $\lambda_{max} = 220, 228$ nm.

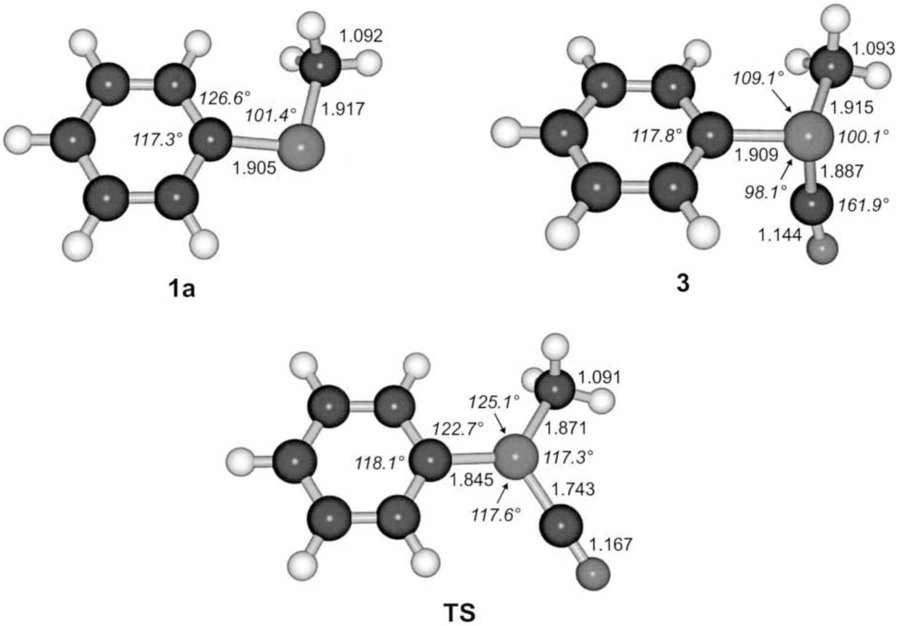
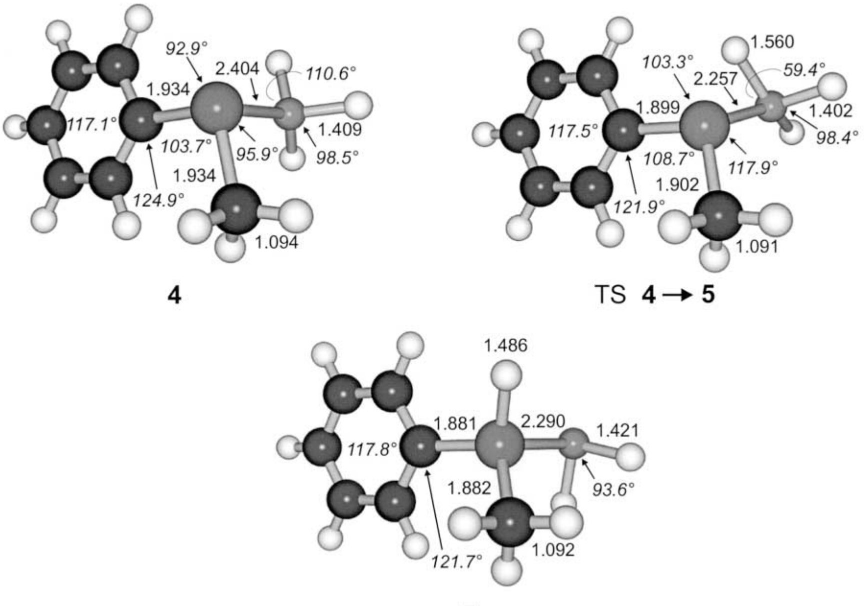


Fig. 5. Geometries and some structural data of methyl(phenyl)silylene **1a**, its CO adduct **3** and its isomeric silaketene calculated at the B3LYP/6-311++G(2d,p) level of theory.



4

TS **4**→**5**

5

Fig. 6. Geometries and some structural data of adduct **4** and several of its isomers calculated at the B3LYP/6-311 + + G(2d,p) level of theory.

3.5. *Matrix spectroscopy*

Matrix isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed cycle helium cryostat. Matrices were produced by deposition of argon (Messer Griesheim, 99.9999%) or mixtures of argon and CO (Messer Griesheim, 99.997%), ^{13}CO (Deutero GmbH, 99.0%) or PH_3 (Messer Griesheim, 99.9%), respectively, on top of a CsI (IR) or sapphire (UV–vis) window at a rate of ca. 0.15 mmol min^{-1} at 30 K. Infrared spectra were recorded by using an Equinox 55 FTIR spectrometer with a standard resolution of 0.5 cm^{-1} in the range 400–4000 cm^{-1}. UV–vis spectra were recorded on a Hewlett–Packard 8452A diode array spectrophotometer with a resolution of 2 nm. Irradiations were carried out using Osram HBO 500 W/2 mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation from the lamps was absorbed by a 10 cm path of water. For wavelength selection dichronic mirrors ('cold mirrors') in combination with Schott cutoff filters (50% transmission at the wavelength specified) were used.

3.6. *(Phenyl)silyldiazirine (**6**)*

Irradiation of matrix-isolated (phenyl)silyldiazomethane **2** with $\lambda > 400$ nm produced (phenyl)silyldiazirine (**6**). IR (argon, 10 K): 2174.8 (13), 2171.7 (7), 2162.0 (5), 2151.7 (31), 2149.9 (6), 2147.1 (7), 1638.7 (4), 1433.4 (18), 1294.9 (5), 1191.3 (1), 1121.4 (20), 948.7 (4), 936.8 (35), 858.6 (100), 855.7 (3), 848.1 (4), 844.3 (5), 840.5(3), 838.9 (9), 701.0 (28), 590.2 (3), 582.1 (10), 470.4 (9) cm^{-1} (relative intensity).

3.7. *1-Phenylsilene (**8**)*

Irradiation of matrix-isolated (phenyl)silyldiazomethane (**2**) with $\lambda > 400$ nm produced 1-phenylsilene (**8**). IR (argon, 10 K): 2192.3 (13), 1433.4 (56), 1317.9 (3), 1282.5 (3), 1191.3 (3), 1122.4 (100), 964.5 (28), 960.9 (19), 917.7 (7), 851.7 (38), 737.6 (42), 656.7 (10), 646.2 (6), 450.7 (9) cm^{-1} (relative intensity).

3.8. *Methyl(phenyl)silylene (**1a**)*

Irradiation of matrix-isolated (phenyl)silyldiazomethane (**2**) with $\lambda > 400$ nm followed by $\lambda > 350$ nm produced methyl(phenyl)silylene **1a**. IR (argon, 10 K): 3085.7 (2), 3075.1 (15), 3055.3 (4), 3023.6 (6), 2964.9 (6), 1585.5 (33), 1496.2 (3), 1429.5 (48), 1378.4 (1), 1332.0 (5), 1260.5 (4), 1217.7 (16), 1187.8 (10), 1159.3 (2), 1091.7 (100), 953.6 (19), 777.7 (13), 735.2 (66), 695.5 (61), 686.8 (11), 666.1 (7), 657.9 (3), 649.7 (3), 575.4 (5) cm^{-1} (relative intensity). UV (argon, 12 K): $\lambda_{max} = 260$, 482 nm.

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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