The scavenging experiment with benzoic acid had to be carried out in aerated solution, because the reaction stops at a cyclohexadienyl radical in the absence of oxygen. The luminescence was measured with a Perkin-Elmer LS50B spectrometer (excitation wavelength, 300 nm).

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Characterization and Photochemistry of the Silane–Aluminum Complex Al·SiH_4 and Its Photoproducts $HAlSiH_3$ and $AlSiH_3$ in a Solid Argon Matrix**

Benjamin Gaertner and Hans-Jörg Himmel*

The activation of C–H or Si–H bonds is an area of both fundamental and industrial interest.[1] The first transition metal complex with an η^2-bound SiH_4 group, *cis*-[Mo(η^2-SiH_4)(CO)($R_2PC_2H_4PR_2$)$_2$] (**1**; R = Ph, *i*Bu, Et),[2] was synthesized in 1995. Remarkably, in solution **1** is in equilibrium with its tautomer [$MoH(SiH_3)(CO)(Et_2PC_2H_4PEt_2)_2$], which features a seven-coordinate Mo center, as evidenced by the results of variable-temperature ^{1}H and ^{31}P NMR spectroscopy. Since then other systems have been found such as [$(PR_3)_2H_2Ru(SiH_4)RuH_2(PR_3)_2$] (R = Cy, *i*Pr), in which the SiH_4 ligand bridges two dihydridobis(phosphane)ruthenium units.[3]

On the basis of these remarkable experimental results, such silane complexes have also attracted attention from theorists.[4] It is commonly agreed that the silane–metal bond comprises a dative bond involving the σ(Si–H) orbital and a vacant metal orbital of appropriate symmetry and a d(M) → σ*(Si–H) back donation (M = transition metal). However, for main group elements like Al such an interaction is not plausible; here only participation of p orbitals can be considered, and therefore one expects a much weaker bond between the metal atom and ligand. However, preliminary experiments suggested that such a complex might be of sufficient strength to allow its generation and investigation in solid inert gas matrices at temperatures near 10 K.[5] Here we report on the results leading to the detailed characterization of Al·SiH_4 (**A**) and its photoproducts, the Al^{II} species $HAlSiH_3$ (**B**) and the Al^{I} species $AlSiH_3$ (**C**) in a solid Ar matrix at 12 K.

Al atoms generated in a Knudsen cell at 1100 °C were codeposited with argon gas doped with 0.1–5 % SiH_4 on a polished copper block kept at 12 K. The matrix was subsequently exposed to several photolysis cycles at different wavelengths and IR spectra were recorded before and after each photolysis. Since some of the observed product absorptions lie close to those of SiH_4, it proved important to run experiments with very low concentrations of SiH_4 in the matrix (0.1 % SiH_4 in Ar, Figure 1) to narrow widths of the SiH_4 bands. As low concentrations, however, lead to weak signals, experiments were also carried out with high (1.5 % SiH_4 in Ar, Figure 2) concentrations of SiH_4.

In addition to absorptions of SiH_4,[6] the spectrum taken upon deposition displayed bands of a spontaneously formed product **A** of the reaction of Al atoms with SiH_4 (Figure 1). These bands were located at 2181.1, 2174.5, 2131.4, 901.7, and 892.4 cm^{-1} (most intense). Some of these absorption bands are not visible in the original spectra because they are masked by SiH_4 absorptions; however, they are clearly visible in the difference spectra shown in Figure 1b. Photolysis at $\lambda \approx$ 410 nm resulted in the rapid disappearance of these bands, and the appearance of several new absorption bands at 2158.4, 2127.6, 2113.3, 1780.9, and 846.2 cm^{-1}, which all belong to a single second reaction product **B**. The strongest absorption at 1780.9 cm^{-1} lies in a region characteristic of ν(Al–H) stretching modes in Al^{II} species ($HAlNH_2$ 1761.1,[7] $HAlCH_3$ 1764/1746,[8] HAlH 1806.3/1769.5,[9] and $HAlPH_2$ 1768.2 cm^{-1}[10]). The absorption at 846.2 cm^{-1} lies in the expected region for δ(SiH_3) deformation modes ($HHgSiH_3$ 867.8/871.4 cm^{-1}[11]).[12]

Photolysis at $\lambda \approx$ 580 nm resulted in the disappearance of the absorptions of **B** and the reappearance of those of **A**. Renewed photolysis, at $\lambda \approx$ 410 nm, caused the absorptions of **A** to vanish again and those of **B** to regain most of their initial intensity. Thus **A** and **B** can be interconverted almost reversibly.

Photolysis of the matrix with broadband UV/Vis (λ = 200–800 nm) resulted in the decay of the absorptions of **B**. An increase in the concentration of **A** was not observed here, instead two new absorptions appeared at 836.2 and 2151.3 cm^{-1} (Figure 2), which can be assigned to the photo-

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[*] Dr. Dr. H.-J. Himmel, Dipl.-Chem. B. Gaertner
Institut für Anorganische Chemie
Universität Karlsruhe (TH)
Engesserstrasse, Geb. 30.45, 76128 Karlsruhe (Germany)
Fax: (+49) 721-608-4854
E-mail: himmel@achpc9.chemie.uni-karlsruhe.de

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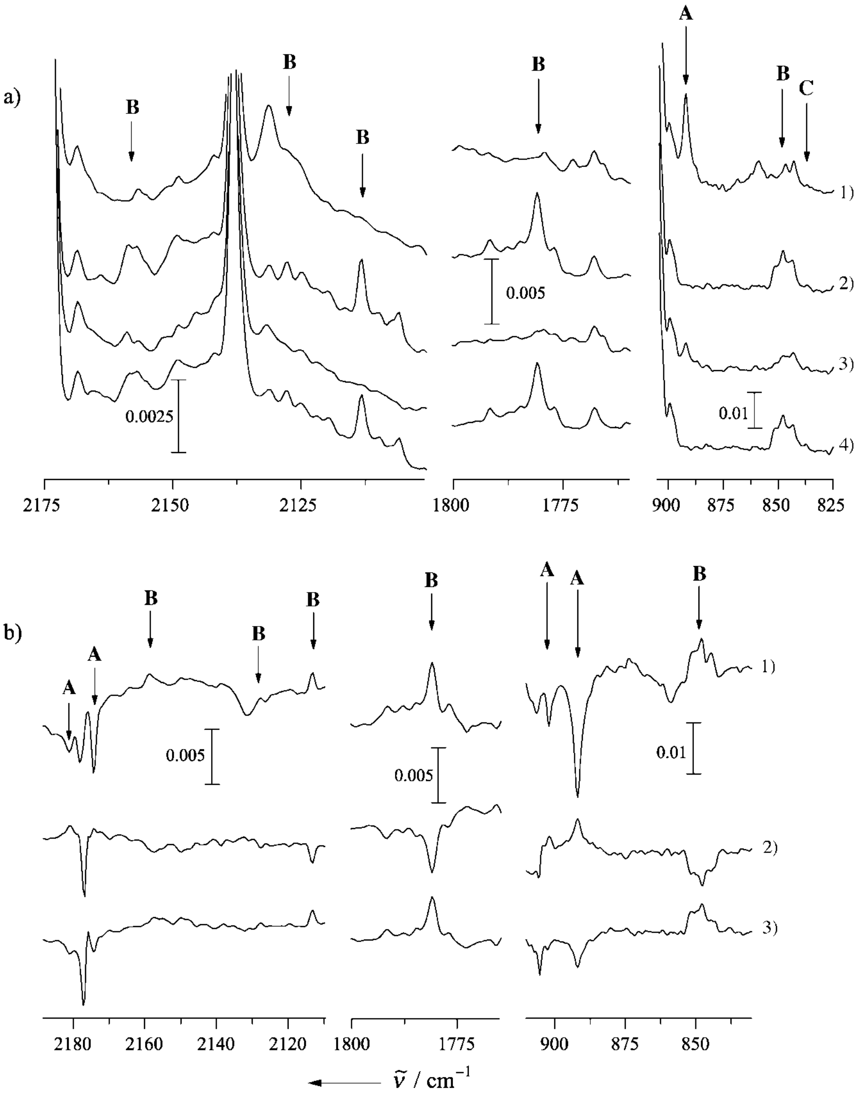

Figure 1. a) IR spectra for the reaction of Al atoms with 0.1 % SiH_4 in an Ar matrix: 1) following deposition; 2) following photolysis at $\lambda \approx 410$ nm; 3) following photolysis at $\lambda \approx 580$ nm, and 4) following renewed photolysis at $\lambda \approx 410$ nm. b) IR difference spectra for the reaction of Al atoms with 0.1 % SiH_4 in an Ar matrix: 1) spectrum following photolysis at $\lambda \approx 410$ nm minus the spectrum following deposition; 2) spectrum following photolysis at $\lambda \approx 580$ nm minus spectrum following photolysis at $\lambda \approx 410$ nm, and 3) spectrum following renewed photolysis at $\lambda \approx 410$ nm minus spectrum following photolysis at $\lambda \approx 580$ nm.

stable product **C**. The more intense of these two absorptions (at 836.2 cm^{-1}) occurs in a region typical for $\delta(SiH_3)$ deformation modes.

Experiments were performed with SiD_4 or SiD_3H in place of SiH_4, and with different concentrations of SiH_4 and Al in the matrix. The effects of photolysis were similar to those reported for Al/SiH_4, but the IR absorptions of the products were shifted. In the experiments with SiD_4, **A** and **B** absorb at 1580.5, 661.2 (most intense), 639.7, 623.6, and 1543.7, 1297.8, 630.8 cm^{-1}, respectively, in experiments with SiD_3H at 2171.9, 2128.8, 1577.7, 818.1, 813.8, 665.2, 640.8, and 2109.1, 1781.1, 1297.4, 810.4, 631.0 cm^{-1}, respectively.

The experimental results together with the results of detailed quantum-chemical calculations allow us to identify product **A** as the complex $Al\cdot SiH_4$ and product **B** as its tautomer $HAlSiH_3$.[13] The reaction $\mathbf{A} \rightleftarrows \mathbf{B}$ is photolytically reversible [Eq. (1)].

$$Al\cdot SiH_4 \underset{\lambda \approx 580\,nm}{\overset{\lambda \approx 410\,nm}{\rightleftharpoons}} HAlSiH_3^{\bullet} \qquad (1)$$

Product **C** most likely is the simple Al^I species $AlSiH_3$. It has been shown in other cases that aluminum hydrides decompose on photolysis with broadband UV/Vis with the loss of H atoms, although this process is endothermic (ca. 220 kJ mol^{-1} for the decomposition of $HAlSiH_3$ to $AlSiH_3$ and H atoms). Thus, for example, AlH_2[9] and $HAlNH_2$[7] decompose photolytically at $\lambda = 200-800$ nm to give AlH and $AlNH_2$, respectively.

The experiments also provide evidence for structural details of these species, and these are again consistent with the results of detailed quantum-chemical calculations. The complex $Al\cdot SiH_4$ has C_{2v} symmetry with the Al atom placed near one of the edges of the slightly distorted SiH_4 tetrahedron resulting in η^2 coordination (Figure 3). In Table 1 the observed wavenumbers are compared with the calculated values. The positions of the ν(Si–H) stretching fundamentals contain additional, though only qualitative, structural information. Thus two of the ν(Si–H) modes are red-shifted, and the other two blue-shifted with respect to the asymmetric ν(Si–H) stretching fundamental in free SiH_4. The obvious inference is that the Si–H bonds directly engaged in the bonding are elongated, while the Si–H

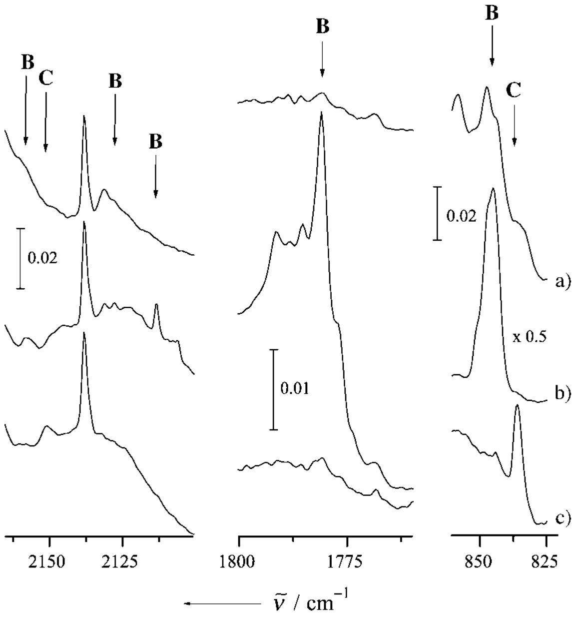

Figure 2. IR spectra for the reaction of Al atoms with 1.5 % SiH_4 in an Ar matrix: a) following deposition; b) following photolysis at $\lambda \approx 410$ nm; c) following photolysis at $\lambda = 200-800$ nm.

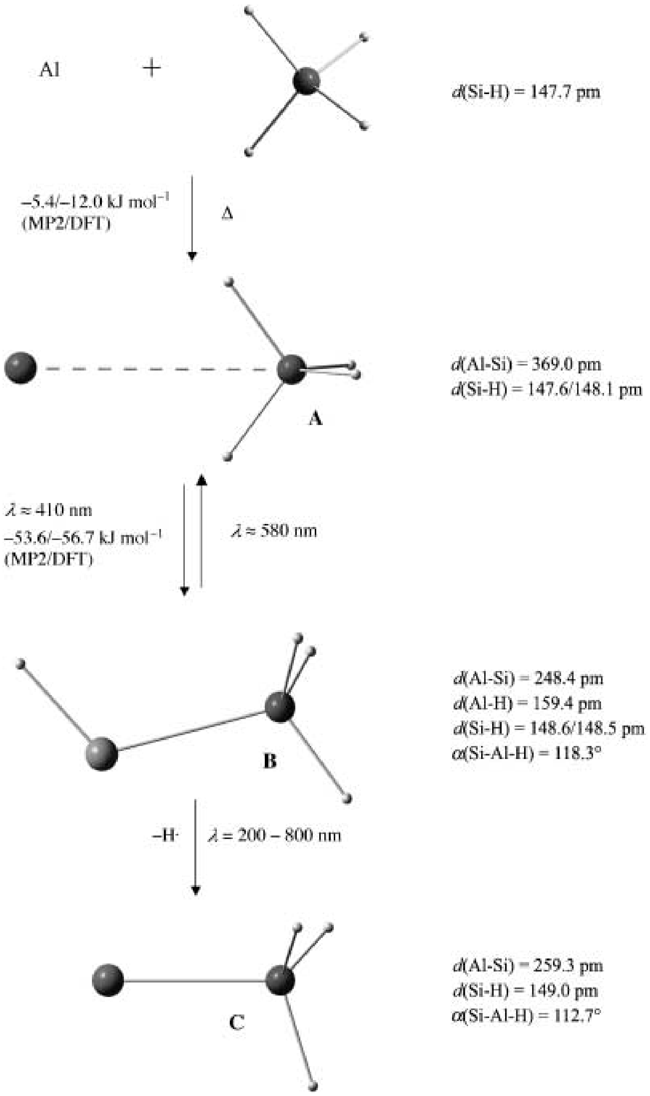

Figure 3. Photolysis of Al atoms with SiH_4 leading to the formation of $Al \cdot SiH_4$, $HAlSiH_3$, and $AlSiH_3$; the calculated structural parameters are given in each case.

bonds pointing away from the aluminum center are shortened because of either a small transfer of charge in the direction $SiH_4 \rightarrow Al$ or polarization effects. However, this charge transfer, if there is any at all, must be much smaller than in the $Al \cdot NH_3$ complex, for which it was clearly evidenced by the results of IR[7] and ESR[14] studies.[15]

Our results also show that the insertion product $HAlSiH_3$ contains no hydrogen bond, as one might expect, but has a structure resembling that of $HAlCH_3$ with the unpaired electron located near the Al atom (Figure 3). A normal coordinate analysis gave force constants of 182.9 and 107.0 N m^{-1} for f(Al–H) and f(Al–Si), respectively (cf. 176.3 and 214.4 N m^{-1} for f(Al–H) and f(Al–C) in $HAlCH_3$).[16] The calculated wavenumbers are in excellent agreement with the observed values (Table 1).[17] $AlSiH_3$ features only terminal Si–H bonds. A normal coordinate analysis gave a force constant of 120 N m^{-1} for f(Al-Si) (cf. 175.6 N m^{-1} for $AlCH_3$).[16] According to ab initio MP2 and DFT BP86 methods the photolysis of **A** to **B** is exothermic (–53.6 and –56.7 kJ mol^{-1}, respectively; TZVPP basis set). The formation of the Al^I species **C** as the photostable end product of the reaction is analogous to the previously described reaction of Al with H_2[9] and of Ga and In with CH_4.[18]

In summary, cocondensation of Al atoms and SiH_4 in an Ar matrix at 12 K forms spontaneously the complex $Al \cdot SiH_4$. Our experiments show, in agreement with the results of quantum-chemical calculations, that the silane molecule is η^2-coordinated to the Al atom. Photolysis at $\lambda \approx 410$ nm causes tautomerization to give the radical $HAlSiH_3$. However, the complex $Al \cdot SiH_4$ is reformed by photolysis at $\lambda \approx 580$ nm. With broadband UV/Vis light ($\lambda = 200-800$ nm) $HAlSiH_3$ decomposes to give the monovalent Al^I species $AlSiH_3$. All observed reaction products were characterized by IR spectroscopy and quantum-chemical calculations.

Experimental Section

Aluminum (Merck, purity 99.99 %) was evaporated in a boron nitride cell heated resistively to about 1100 °C. The metal vapor was codeposited with an excess of SiH_4-doped argon on a highly polished copper block cooled to 12 K by means of a closed-cycle cryostat (Leybold LB 510). Further details of the relevant matrix assemblies are given in reference [18]. The ratio SiH_4:Ar was typically 0.1:100 and 5:100, while deposition rates were about 2 mmol of matrix gas per hour, continued over a period of 1.5 h. Similar experiments were carried out with SiD_4 and SiD_3H in place of SiH_4. Materials used: SiH_4 (Linde, > 99.99 %), SiD_4 (prepared by reaction of $LiAlD_4$ with $SiCl_4$), SiD_3H (prepared by reaction of $LiAlD_4$ with $SiHCl_3$)

Table 1. Observed and calculated wavenumbers [cm^{-1}] (IR intensities [km mol^{-1}] in parentheses) for $Al \cdot SiH_4$, $HAlSiH_3$, and $AlSiH_3$.

	$Al \cdot SiH_4$			$HAlSiH_3$			$AlSiH_3$	
obsd	calcd[a]	assignment	obsd	calcd[b]	assignment	obsd	calcd[c]	assignment
2174.5	2173.7 (254)	$\nu_1(a_1)$	2158.4	2161.9 (79)	$\nu_1(a')$	2151.3	2093.7 (99)	$\nu_1(a_1)$
2131.4	2125.9 (49)	$\nu_2(a_1)$	2113.3	2126.7 (57)	$\nu_2(a')$	836.2	822.4 (211)	$\nu_2(a_1)$
[b]	928.5 (45)	$\nu_3(a_1)$	1780.9	1780.2 (220)	$\nu_3(a')$	[c]	308.2 (52)	$\nu_3(a_1)$
892.4	868.9 (319)	$\nu_4(a_1)$	[b]	904.9 (32)	$\nu_4(a')$	[b]	2106.1 (103)	$\nu_4(e)$
[c]	136.7 (5)	$\nu_5(a_1)$	846.2	836.5 (221)	$\nu_5(a')$	[b]	907.5 (20)	$\nu_5(e)$
[b]	827.0 (0.1)	$\nu_6(a_2)$	[b]	575.5 (48)	$\nu_6(a')$	[c]	302.7 (24)	$\nu_6(e)$
2181.1	2173.1 (71)	$\nu_7(b_1)$	[b]	412.9 (31)	$\nu_7(a')$			
[b]	748.7 (34)	$\nu_8(b_1)$	[c]	345.8 (3)	$\nu_8(a')$			
[c]	282.1 (0.3)	$\nu_9(b_1)$	2127.6	2139.7 (71)	$\nu_9(a'')$			
[c]	2125.8 (19)	$\nu_{10}(b_2)$	[b]	919.1 (28)	$\nu_{10}(a'')$			
901.7	879.3 (58)	$\nu_{11}(b_2)$	[b]	425.1 (16)	$\nu_{11}(a'')$			
[c]	343.8 (2)	$\nu_{12}(b_2)$	[c]	331.4 (9)	$\nu_{12}(a'')$			

[a] DFT calculations: BP86-methods with TZVPP basis set; $Al \cdot SiH_4$: C_{2v} symmetry, $HAlSiH_3$: C_s symmetry, C_{3v} symmetry. [b] Intensity too weak to be observed or hidden by SiH_4 absorptions. [c] Outside the range of detection.

and argon (Messer, purity 99.998%). Gas mixtures of argon with the different isotopologues of the silane were prepared by standard manometric methods.

After deposition and IR analysis of the resulting matrix, the sample was exposed to photolysis at different wavelengths and the changes were monitored by IR spectroscopy. A medium-pressure Hg lamp (Philips LP 125) operating at 70 W served as the source of photolyzing radiation. The IR radiation was absorbed by a water filter to minimize any heating effects. IR spectra were recorded in the reflection mode by using a Bruker 113v spectrometer and either a liquid N_2 cooled MCTB or a DTGS detector operating in the range 4000–400 cm^{-1}.

MP2 and DFT calculations using a TZVPP basis set were performed with the aid of the TURBOMOLE[19] program package.

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[12] IR absorptions at 2158.4, 2127.6, 2113.3, 1780.9, and 846.2 cm^{-1} were already observed and assigned to $HAlSiH_3$ in a previous work (see ref. [5]).

[13] B. Gaertner, H.-J. Himmel, unpublished results.

[14] P. Kasai, H.-J. Himmel, unpublished results.

[15] Attempts to study the complex with our UV/Vis spectrometer failed because the light of the spectrometer caused rapid decomposition of the complex as evidenced by IR spectra taken before and after 1 min of exposure to the radiation of the spectrometer. In our setup (spectrometer from Oriel, equipped with a 75 W Xe, HgXe, or Hg arc lamp and a photodiode array detector, Model 77112) the gratings are located between the matrix and the detector and the matrix is exposed to the full radiation of the lamp.

[16] The normal coordinate analysis were performed by using experimental values for the wavenumbers where available and calculated values for the rest.

[17] Additional calculations for the deuterated and partially deuterated species were performed. Observed/calculated wavenumbers [cm^{-1}] for the most intense absorptions: $Al\cdot SiD_4$: 1580.5/1567.7, 639.7/635.3, 661.2/660.6, 623.6/644.6; $Al\cdot SiD_3H$ (both isotopomers): 2171.9/2170.7, 2128.8/2127.7, 1577.7/1569.0, 818.1/818.0, 813.8/811.6, 665.2/659.5, 640.8/636.4; $DAlSiD_3$: 1543.7/1545.4, 1297.8/1282.2, 630.8/618.1; $HAlSiD_3$: 1781.1/1780.3, 631.0/618.1; $DAlSiD_2H$: 2109.1/2134.3–2160.6 (depending on the DAlSiH dihedral angle), 1297.4/1282.2, 810.4/748.7–823.8 (depending on the DAlSiH dihedral angle); $AlSiD_3$: 618.4/600.3.

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