The AlB_2 hexagonal disilicides can be divided into two groups. The Gd–Ho and yttrium compounds are stable only at relatively low temperatures, while in the case of Er–Lu compounds, the hexagonal structure is the stable one up to 1600°.

Atomic size and composition appear to be the main factors in the formation of the AlB_2-type structure found for the lanthanide disilicides. In Table III interatomic distances found for the hexagonal disilicides are given. Table III shows that only when the ratio r_{Si}/r_M is more than 0.579 can the AlB_2-type structure be formed (Dy being an exception) while the $ThSi_2$ phase is formed at lower ratios. Since in this structure metal atoms form intermediate layers between the silicon sheets, metal atoms with too large size cannot be placed between the silicon sheets, and their disilicides do not crystallize in the hexagonal structure. The Gd–Ho and yttrium compounds appear to form an intermediate group according to their size where the structure equilibrates between a low-temperature hexagonal and high-temperature orthorhombic form. It is noteworthy that in the hexagonal–orthorhombic dimorphism, the orthorhombic version is always the stable one at high temperatures, having also the higher melting point as was found for the orthorhombic version of USi_2. Er–Lu disilicides having the smallest metal atoms among the lanthanides crystallize in the hexagonal structure at low as well as at high temperatures.

TABLE III

	Interatomic dist, A		Atomic radii, A		
	M–Si	M–M	r_M	r_{Si}	r_{Si}/r_M
Gd	3.054	3.867	1.934	1.120	0.579
Tb	3.036	3.843	1.922	1.114	0.580
Dy	3.022	3.829	1.915	1.107	0.578
Ho	3.003	3.800	1.900	1.103	0.581
Er	2.990	3.783	1.892	1.098	0.580
Tm	2.980	3.770	1.885	1.095	0.581
Lu	2.963	3.748	1.874	1.089	0.581
Y	3.030	3.834	1.917	1.113	0.581

The Gd–Ho disilicides crystallize in the hexagonal form also when heated to high temperature,[10] provided there is an average composition of M_3Si_5, thus indicating that when vacancies are present in the silicon layer, the AlB_2-type structure can be obtained at these conditions (high temperature).

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Halogenation of Silanes by Silver Chloride and Silver Bromide

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Halosilanes can be prepared by the reaction between silane and the appropriate hydrogen halide over an aluminum halide catalyst at 100°.[2] Chlorodisilane has been prepared in about a 3% yield from disilane at room temperature in 8 hr while bromodisilane was obtained in an 18% yield in only 5 min at −78°.[3] A large excess of silane or disilane is required to minimize the formation of the polyhalo derivatives.

Recently, chlorogermane and bromogermane have been obtained in 71 and 30% yields by the reaction between germane and silver chloride or bromide at 250–260°. Similarly, chlorodigermane and bromodigermane were prepared in 26 and 40% yields by reactions with digermane at 90°. In all of these reactions, the germanes were pumped over the appropriate silver salt in a heated tube.[4]

The liquid–solid phase reaction between diethylsilane and silver chloride to produce diethylchlorosilane has also been observed.[5]

In this Note we report our results on the gas–solid phase reactions between silanes and silver chloride or bromide.

Experimental Section

These reactions were carried out with standard high vacuum techniques. Separations were made by trap to trap distillations through traps cooled by standard slush baths. Silane, disilane, and the methylsilanes were prepared by reduction of the corresponding chloro compounds with lithium aluminum hydride.[6] The starting materials were treated with wet 1,2-dimethoxyethane to remove the last traces of HCl.

The reaction vessel consisted of a 100-ml bulb sealed to a Pyrex tube (18 mm o.d.) with a constriction 13 cm above the bulb. A glass wool plug at the constriction retained the silver salt which was held in five layers by glass wool plugs. The salt was heated by a heating tape wrapped around the reaction tube. A standard taper joint, 21 cm above the constriction, connected the reaction system to the vacuum line through a stopcock located above the joint. The temperatures were measured by a standard thermometer in a glass well located between the heating tape and the outer insulation.

The products and reactants were identified and checked for purity by infrared and vapor pressure measurements. The hydrogen chloride fractions (passing a trap cooled to −130° and condensed in a trap cooled to −160°) were considered pure when no Si–H stretching frequency (~2180 cm^{-1}) was observed. The final separation of hydrogen chloride from silane or disilane was carried out in wet 1,2-dimethoxyethane. The small fractions retained in this solvent were assumed to be hydrogen chloride.

Proton nmr spectra were obtained on neat samples with $Si(CH_3)_4$ at 0.00 as an external standard. Absorptions with a minus (−) sign were downfield.

(1) **SiH_4–AgCl Reaction.**—Silane (1.02 mmoles) was distilled through 22.5 g of silver chloride, heated to 260°, and condensed in the bulb with liquid nitrogen. The volatile fraction was then redistilled through the heated salt and condensed into a trap in the vacuum system with liquid nitrogen. The volatile fraction now consisted of silane (0.59 mmole), 0.38 mmole of chlorosilane (vapor pressure 55 torr at −78°, lit.[2] 56 torr), dichlorosilane (0.075 mmole), and hydrogen chloride (0.54 mmole).

(2) **Si_2H_6–AgCl Reaction.**—Disilane (2.46 mmoles) was passed through the reaction tube (at room temperature) and condensed

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[1] To whom inquiries concerning this Note should be sent.

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in the bulb with liquid nitrogen. The salt (22.5 g) was heated to 90° and the liquid nitrogen was lowered from the bulb and replaced by a water bath at room temperature which forced the disilane to vaporize into the reaction zone. After 1 min, the volatile fraction now contained disilane (0.81 mmole) and 0.74 mmole of chlorodisilane (the proton nmr spectrum of the neat sample consisted of absorptions at −2.82 ppm (SiH_3) and at −4.26 ppm (SiH_2) with relative intensities of 3.0:1.9). The neat sample also contained dichlorosilane (4%) and chlorosilane (2%). Also present in the volatile fraction were more highly substituted chlorodisilanes (0.13 mmole), hydrogen chloride (0.86 mmole), and hydrogen (0.5 mmole).

(3) **CH_3SiH_3–AgCl Reaction.**—The methylsilane was distilled through 22.5 g of silver chloride heated to 260° and condensed in the bulb with liquid nitrogen. The dewar was removed and the methylsilane was allowed to vaporize into the heated zone. About 1 min later, the volatile fraction was condensed at −196° in the vacuum system and analyzed. When 2.17 mmoles of methylsilane reacted with 22.5 g of silver chloride, the volatile fraction contained methylsilane (0.64 mmole), methylchlorosilane (1.31 mmoles), methyldichlorosilane (0.17 mmole), hydrogen chloride (1.61 mmoles), and hydrogen (0.2 mmole). The proton nmr spectrum of the neat methylchlorosilane had a triplet at +1.03 ppm (CH_3) and a poorly defined quartet at −3.13 ppm (SiH_2) of relative intensities 3.0:2.1.

(4) **$(CH_3)_2SiH_2$–AgCl Reaction.**—The reaction between dimethylsilane and silver chloride was carried out as described for the reaction with methylsilane except that the dimethylsilane was exposed to the heated salt for 1 hr. When 1.30 mmoles of dimethylsilane was allowed to react with 22.5 g of silver chloride, the final volatile fraction contained dimethylsilane (0.46 mmole), dimethylchlorosilane (0.48 mmole), dimethyldichlorosilane (0.24 mmole), hydrogen chloride (0.89 mmole), and hydrogen (0.2 mmole). The proton nmr spectrum of the neat dimethylchlorosilane had absorptions at +0.30 ppm (2 CH_3) and at −4.04 ppm (SiH) of relative intensities 6.0:0.9.

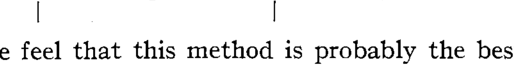
(5) **$(CH_3)_3SiH$–AgCl Reaction.**—Trimethylsilane (1.34 mmoles) was allowed to react with silver chloride at 280°. For this reaction the procedure was identical with that for methylsilane except that the trimethylsilane remained exposed to the heated silver chloride for 1.75 hr. After the reaction, the volatile fraction contained trimethylsilane (0.52 mmole), trimethylchlorosilane (0.58 mmole), hydrogen chloride (0.65 mmole), and hydrogen (0.2 mmole).

(6) **SiH_4–AgBr Reaction.**—The reaction between silane and silver bromide was carried out as described in section 4 (1 hr). When 1.30 mmoles of silane was allowed to react with 25 g of silver bromide the volatile products were bromosilane (0.41 mmole), dibromosilane (0.04 mmole), hydrogen bromide (0.02 mmole), and hydrogen (0.5 mmole), while 0.77 mmole of silane was recovered.

Discussion

These reactions can be represented by the following general equations

$$-\overset{|}{\underset{|}{Si}}-H + 2AgCl \longrightarrow -\overset{|}{\underset{|}{Si}}-Cl + HCl + 2Ag \qquad (1)$$



$$-\overset{|}{\underset{|}{Si}}-H + AgBr \longrightarrow -\overset{|}{\underset{|}{Si}}-Br + {}^1/_2\,H_2 + Ag \qquad (2)$$

We feel that this method is probably the best general method for the stepwise halogenation of the volatile silicon hydrides. We are currently extending this method to obtain and isolate the chlorodisilanes ($Si_2H_{6-x}Cl_x$ with x = 2–5).

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The Raman Spectra of Manganese and Rhenium Carbonyl Hydrides and Some Related Species

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In the determination of the manganese–hydrogen bond length of $HMn(CO)_5$ from the second moment of the broad line proton magnetic resonance spectrum,[1] it was necessary initially to assume that the hydrogen atom was located on the C_4 axis of the presumably C_{4v} molecule.[2] In view of our subsequent treatment of this and other carbonyl hydrides as effectively isolated two-spin systems,[3] this assumption was no longer necessary to establish the metal–hydrogen distance. We have therefore studied the Raman spectrum of this and several related molecules in an attempt to establish, in the absence of any direct information, the orientation of the hydrogen atom. The infrared spectral evidence for the structure is confused by C^{13}, overtone, and combination bands[4] in solution and in addition by pqr structure in the gas phase.[5]

The spectra (Figure 1 and Table I) and, in particular, the polarizations are consistent with C_{4v} symmetry for both manganese and rhenium carbonyl hydrides. The following points concerning the spectra are noteworthy. (1) The metal–hydrogen stretching mode is particularly intense, indicating a large polarizability change during vibration. A significant polarization indicates that it is a totally symmetric mode and presumably that the hydrogen is on the fourfold axis. (2) The polarization of the high-energy band shows that this also is a totally symmetric mode confirming the assignments previously made from the infrared spectra.[4] (3) The spectra of the neat liquids show considerable shifts from the position of the frequencies expected on the basis of infrared spectra taken in hydrocarbon solvents. (4) The relative intensities and the positions of the bands are markedly dependent on the nature of the metal and the X group in the $XM(CO)_5$ systems. (5) The resolution of five bands in crystalline $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ represents some activation of infrared bands in the crystal, but nevertheless is consistent with the previous assignments.[6] (6) The spectrum of solid

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