

The (Chloromethyl)dihalosilanes X_2HSiCH_2Cl ($X = F, Cl, Br, I$): Synthesis, Multinuclear NMR Spectroscopy and Rotational Isomerism Examined by Raman Spectroscopy

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(Chloromethyl)diphenylsilane Ph_2HSiCH_2Cl (**1**) was prepared from Ph_2SiHCl and $LiCH_2Cl$, in situ, and was then treated with $CF_3SO_3H/LiCl$ and $CF_3SO_3H/LiBr$ to give the (chloromethyl)dihalosilanes Cl_2HSiCH_2Cl (**2**) and Br_2HSiCH_2Cl (**3**). I_2HSiCH_2Cl (**4**) was formed quantitatively in a protodearylation reaction between liquid hydrogen iodide and **1**. Fluorination of **4** with ZnF_2 gave F_2HSiCH_2Cl (**5**), albeit in low yields. Compounds **1**–**5** were characterised by multinuclear NMR spectroscopy (^{29}Si , ^{13}C , ^{19}F) and vibrational spectroscopy. The temperature-dependent vibrational Raman spectra of **2**, **3** and **4** prove that they are mixtures of

gauche and *anti* rotamers in the liquid state. Enthalpy differences, $\Delta H (H_{anti} - H_{gauche})$, were determined for the liquids by applying the van't Hoff relation, with the *gauche* rotamer being lower in energy for **3** and **4**, and the *anti* rotamer for **2**. The vibrational spectra were assigned with the help of ab initio calculations of equilibrium geometries and harmonic fundamental frequencies. Harmonic symmetry force constants and potential energy distributions were calculated from the ab initio Hessian matrices.

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Introduction

α -(Halomethyl)silanes are versatile starting materials for the synthesis of organosilicon compounds such as silylmethylolithium derivatives or main-group derivatives $M-CH_nX_{2-n}SiR_3$, where X is a halogen.^[1] However, only a handful of methods, each one with its own limitations, can be used for their preparation. These comprise the direct chlorination of methylsilanes, $MeSiR_3$ with Cl_2 ^[2] or Cl_2SO_2 ,^[3] a method which does not tolerate silyl, vinyl or aryl groups as the R substituent. Another synthetic approach uses silyllithiums, $LiSiR_3$ as precursors, treating them with, for instance, CH_2Cl_2 to form CH_2ClSiR_3 .^[4] However, this method is not widely applicable due to a lack of suitable silyllithiums. A third method with a wider range of applications is the alkylation of chlorosilanes by a (halomethyl)lithium $X_nH_{3-n}CLi$ ($n = 1, 2, 3$; $X = \text{halogen}$), which is usually generated in situ. Pannell and co-workers have prepared a considerable number of (chloromethyl)silanes with this method that contain functionalities such as SiH , $SiCl$, $SiSi$, Si -vinyl, Si -allyl and Si -phenyl.^[5] The introduction of these functional groups was a major step forward, as they can be replaced by other substituents without affecting the halomethyl functionality.

We are interested in the synthesis and spectroscopic properties of silaethanes, silapropanes and disilapropanes

bearing no other substituents but hydrogen and halogen atoms. They can be considered as the link between halogenated hydrocarbons and their heavier analogues the halogenated disilanes and trisilanes. The chemical behaviour of both the Si–Si bond and the Si–C bond is strongly influenced by the substituents at the molecular skeleton. Numerous experimental investigations show a weakening of the Si–C bond of carbosilanes (a term coined by Fritz^[6] for compounds in which the molecular framework is exclusively built up by Si–C bonds) upon chlorination at the carbon atom, whereas chlorination at the silicon atom has the opposite effect, causing a bond strengthening. Ab initio studies of chlorinated silaethanes confirm these effects.^[7] For instance, the bond dissociation energies of $SiCl_3CH_3$, SiH_3CH_3 , and SiH_3CCl_3 were calculated as 392, 369 and 314 kJ/mol, respectively. With disilanes, the bond strengths decrease in the order $SiCl_3SiCl_3 > SiH_3SiCl_3 > SiH_3SiH_3$, which is supported by experimental and ab initio Si–Si force constants and ^{29}Si , ^{29}Si coupling constants, for instance.^[8] The effect of Si chlorination can be rationalised by Bent's rule,^[9] which states that bonds to electronegative substituents possess more p-character, thereby increasing the s-character of the bonds to electropositive atoms; more s-character usually means a stronger bond. Upon C-chlorination, Bent's rule should also be at work, but the effect is overridden by the repulsive force between the positive charges at the Si and C atoms due to the short Si–C distance. Moreover, the steric repulsion between the chlorine atoms at carbon — the $Cl\cdots Cl$ distance is in fact considerably shorter than the van der Waals distance — is reduced

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in the free CCl_3 radical upon dissociation. This reduction of intramolecular repulsion energy certainly provides a further contribution to the weakening of the bond.

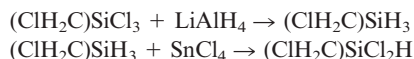
If chlorine is replaced by other halogens, the relative contributions of these two effects will certainly vary. Fluorine substitution is expected to increase the positive charge on the carbon atom, thereby also increasing the Si–C repulsion. Conversely, the nonbonding halogen–halogen repulsion will decrease. Substitution with bromine should decrease the positive charge and increase the nonbonding interactions, an effect which will be even more pronounced with iodine. For instance, no (triiodomethyl)silanes have been reported in the literature so far. C_2I_6 is also unstable and has not been prepared yet.

These properties of the Si–C bond should also influence the barriers to internal rotation and conformer stabilities. Our attention, therefore, is mainly focussed on silaethanes and silapropanes that can display rotational isomerism. The existence of at least two different conformers in silaethanes and silapropanes demands the presence of EH_2X or EHX_2 groups (X = halogen, E = C or Si) in the molecule. A literature search revealed that only a handful of these compounds have been prepared so far, such as $\text{ClH}_2\text{CSiCl}_2\text{H}$ ^[10] and $\text{ClH}_2\text{CSiH}_2\text{X}$ (X = F, Cl, Br),^[11] no such compounds with iodine have been described. Moreover, the literature search revealed a complete absence of general procedures for the preparation of (halomethyl)silanes with SiH_2X or SiHX_2 groups. We have therefore set out to develop general synthetic methods suitable for the preparation of a wide range of (halomethyl)dihalosilanes.

Results and Discussion

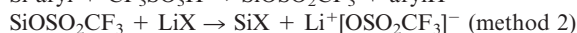
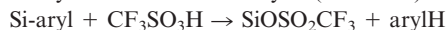
Syntheses

Tetrachlorosilaethane, $\text{CClH}_2\text{SiCl}_3$, is readily obtained by direct chlorination of trichloromethylsilane with Cl_2 .^[12] However, it is difficult to transform it into $\text{CClH}_2\text{SiCl}_2\text{H}$ or $\text{CClH}_2\text{SiClH}_2$, as it is not easy to achieve a selective chlorination of the SiH_3 group. Recently, a two-step reaction sequence was reported^[10] involving a reduction with LiAlH_4 and subsequent chlorination with SnCl_4 .



Dichloro(chloromethyl)silane was prepared for vibrational spectroscopic purposes. No NMR shifts and physical data were reported, and the synthesis seems inappropriate for the preparation of larger quantities due to the volatility of $(\text{ClH}_2\text{C})\text{SiH}_3$.

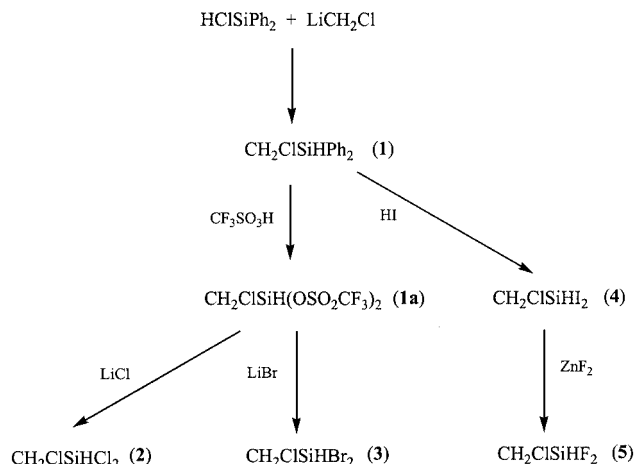
The introduction of aryl substituents into (chloromethyl)silanes offers the possibility to replace them with Cl, Br or I by using either liquefied hydrogen halides HX or trifluoromethanesulfonic acid in combination with the lithium halides LiX . Both methods tolerate chloromethyl groups as well as Si–H and Si–Si functionalities, give good to excellent yields, and are widely applicable.



Method 1 usually gives better overall yields than 2.

From our experience with these two methods we expect that they can also be used successfully with (bromomethyl)-, (iodomethyl)- and even (fluoromethyl)silanes, though we have not yet tested them with these substrates.

The choice of which of the two methods to apply for a specific problem is dictated by practical considerations. If the desired carbosilane has a boiling point which is near that of the hydrocarbon arylH formed (which is the case for benzene and $\text{CClH}_2\text{SiCl}_2\text{H}$), purification becomes difficult. If one wishes to apply method 1 a larger aryl group can be introduced; for instance, phenyl groups can be replaced by tolyl or mesityl groups. Method 2 offers the advantage that phenyl groups still can be used as substituents, because benzene is easily separated from the trifluoromethanesulfonyloxysilane by evaporation in vacuo. Thus, commercially available phenylsilanes can be used as starting materials, reducing the time needed for the synthesis. As shown in Scheme 1, chlorodiphenylsilane was treated with CH_2ClLi , generated in situ from bromochloromethane and lithium at low temperatures,^[13] forming (chloromethyl)diphenylsilane **1**. When a solution of **1** in toluene was treated with two equivalents of trifluoromethanesulfonic acid, the two phenyl groups were cleaved off, giving benzene and (chloromethyl)bis(trifluoromethanesulfonyloxy)silane (**1a**) without noticeable side reactions. Toluene and benzene were then removed by evaporation in vacuo, giving the pure (chloromethyl)sulfonyloxysilane as a colourless oily liquid. Upon addition of LiCl or LiBr , the (halomethyl)silanes **2** and **3** were formed in yields not exceeding 30%, presumably due to Si–C cleavage.



Scheme 1. Synthesis of (chloromethyl)dihalosilanes

Compound **4** was prepared by method 1, treating **1** with liquid HI . Dry gaseous hydrogen iodide was easily obtained from tetrahydronaphthalene and iodine as described in the literature,^[14] and purified by trap-to-trap condensation. Scheme 1 summarises the syntheses of **1–5**. Fluorination

of **4** with various fluorinating agents such as ZnF_2 turned out to be difficult due to extensive Si–C bond cleavage. The yields achieved were so small that only the NMR spectra of **5** could be obtained, albeit in good quality. We will therefore report on the fluorination of **5** in conjunction with the synthesis of (bromomethyl)halosilanes and (iodomethyl)halosilanes.

NMR Spectroscopy

Compounds **2–5** were characterised by multinuclear NMR spectroscopy (^{13}C , ^{19}F , ^{29}Si), and **1** by ^{29}Si NMR only. Table 1 summarises the chemical shifts and coupling constants that were obtained. In the proton-coupled ^{29}Si NMR spectra of **2**, **3** and **4**, the signal of the Si nucleus is split into a doublet of triplets due to one- and two-bond Si–H coupling. The ^{13}C NMR signal splits into a triplet of doublets. The ^{29}Si and ^{13}C NMR spectra of **5** are presented in Figure 1. The unusual appearance of the ^{29}Si NMR spectrum, which consists of two triplets and two quadruplets, results from the near equality of $^1J_{\text{Si,H}}$ and $^1J_{\text{Si,F}}$ the difference being almost equal to $^2J_{\text{Si,H}}$. Each quadruplet is therefore an overlap of two triplets. The ^{13}C NMR spectrum is composed of six triplets, as expected for a first-order spec-

Table 1. Chemical shifts^[a] (ppm) and coupling constants (Hz) for the (chloromethyl)dihalosilanes **1–5**

	$\delta(^{29}\text{Si})$	$\delta(^{13}\text{C})$	$\delta(^{19}\text{F})$	$^1J_{\text{Si,H}}$	$^2J_{\text{Si,H}}$	$^1J_{\text{C,H}}$	$^2J_{\text{C,H}}$	$^2J_{\text{C,F}}$	$^1J_{\text{Si,F}}$
1	–17.6			204.9	4.3				
1a	–30.3			335.6					
2	+0.9	29.9		300.0	4.3	144.0	16.0		
3	–13.4	29.6		299.0	4.3	146.0	15.0		
4	–85.2	28.1		292.0	4.3	146.0	11.0		
5	–29.1	23.8	–141.5	301.0	4.8	141.0	23.5	18.3	305.0

^[a] $\delta(^{29}\text{Si})$ and $\delta(^{13}\text{C})$ are referenced against TMS; $\delta(^{19}\text{F})$ is referenced against CCl_3F .

The ^{29}Si NMR chemical shifts of **1–5** do not follow a linear dependence on the electronegativities of the directly bonded halogens, which is not surprising, as it is known that ^{29}Si chemical shifts depend on the sum of the electronegativities of the substituents in a nonlinear manner.^[15] The shift maximum for **2** can easily be explained on that basis.

One-bond Si–H coupling constants usually increase with increasing electronegativities (sum of the electronegativities) of the substituents, which can be interpreted in terms of isovalent hybridisation. Bonds to electronegative elements possess more p-character, which is balanced by more s-character in the Si–H bond. As the Fermi contact term dominates $^1J_{\text{Si,H}}$, the coupling constant increases. Interestingly, the values of $^1J_{\text{Si,H}}$ for **2–5** show only a slight increase by no more than 9 Hz with increasing electronegativity of the halogens. For the silanes H_2SiI_2 and H_2SiF_2 , the difference is 7.4 Hz.^[15]

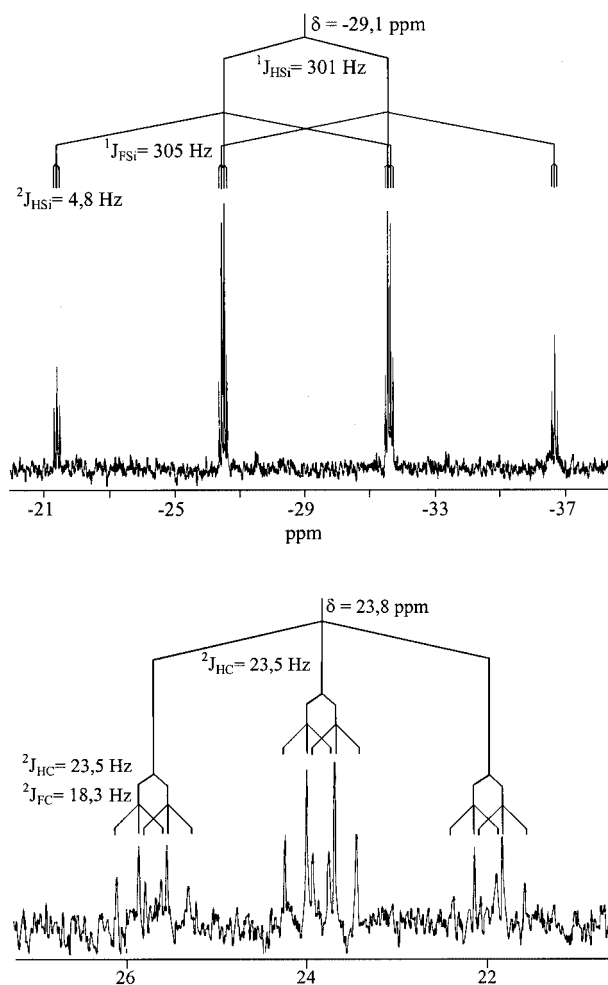


Figure 1. Splitting of the ^{29}Si (top) and the ^{13}C NMR signal (bottom) of $\text{CH}_2\text{ClSiF}_2\text{H}$ due to indirect spin–spin coupling

Raman Spectroscopy and Rotational Isomerism

At ambient temperatures, the (chloromethyl)dihalosilanes **2–5** exist as mixtures of *gauche* [C_1 symmetry, $\omega(\text{ClCSiH}) \approx 52^\circ$] and *anti* [C_s , $\omega(\text{ClCSiH}) = 180^\circ$] conformers, as illustrated in Figure 2 with the help of Newman projections.

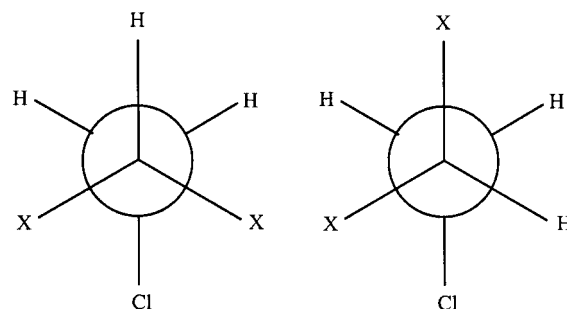


Figure 2. Newman projections of *anti* (left) and *gauche* (chloromethyl)dihalosilanes

As long as the barriers separating the two conformers are well above 2.5 kJ/mol (= RT at room temperature), they

behave as distinct vibrating entities and can be identified by their IR and Raman vibrational spectra. For Si–C and Si–Si bonds this condition is usually fulfilled. For assigning bands to individual rotamers, a normal coordinate analysis based upon ab initio calculations of vibrational frequencies and force constants is normally carried out for both conformers.

The rotational isomerism of dichloro(chloromethyl)silane has been investigated recently by FT-IR spectroscopy on solutions in liquid xenon, with the more stable form being the *gauche* conformer ($\Delta H_{\text{exp}} = 4.34 \pm 0.48$ kJ/mol).^[10] The result is consistent with ab initio calculations at the MP2/6-31G(d) level of theory, but is also reproduced correctly at the Hartree–Fock level. Values for ΔH obtained on solutions in noble gases are supposed to differ only slightly from values in the gas phase.

For the present study, we have recorded the Raman spectra for the liquids of **2**, **3** and **4**. Figure 3 presents the Raman spectrum of **3** at two temperatures, illustrating the variations that occur upon cooling. In all cases we only obtained glassy solids at low temperatures that contained both conformers at the temperature of liquid nitrogen. No crystallisation was observed.

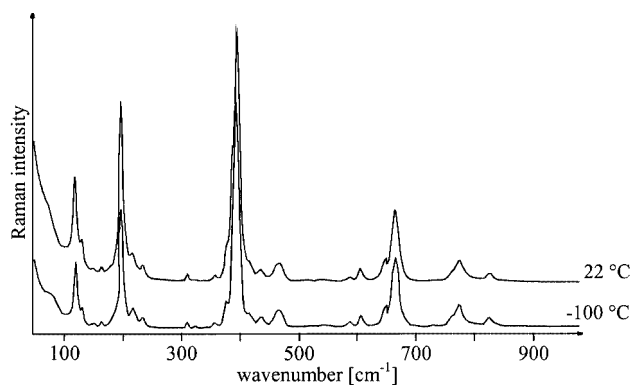


Figure 3. Raman spectrum of dibromo(chloromethyl)silane in the range 50–900 cm^{–1} at 22 °C and –100 °C.

To facilitate the identification of vibrational bands belonging to the various conformers, ab initio calculations of equilibrium geometries, harmonic frequencies and force constants (Hessian matrices) were performed at the Hartree–Fock level of theory for **2–5**. Inner filled electron shells were replaced by the electron core potentials (ECPs) reported by Stevens, Krauss and Basch.^[16] A 6-31G** double-zeta basis set was used for the valence electrons. By use of the ECPs, relativistic corrections for the heavier halogens are taken into account. Table 2 summarises the most important geometric parameters for both conformers of **2–5** — *anti* and *gauche* — as well as the relative conformational energies predicted by the ab initio calculations. The Hessian matrices, which represent the force constants defined in Cartesian coordinates, were transformed into force fields defined with symmetry coordinates which are linear combinations of bond distortions and angle distortions. With the symmetry force fields, normal coordinate analyses were carried out which allow the description of the

normal modes as group vibrations by use of the potential-energy distributions (PEDs). The program ASYM40^[17] was used for these calculations. A factor of 0.92 was used to scale the calculated frequencies, and $(0.92)^2$ to scale the force constants. Table 3 and 4 summarise the wavenumbers in the Raman and IR spectra of **3** and **4**, the scaled and unscaled ab initio wavenumbers, and the descriptions of the modes as group vibrations based on calculated PEDs. The spectra of **2** are not repeated here as they have been reported previously.^[10]

Table 2. Selected structural constants (pm, deg.) and relative energies (kJ/mol) for the conformers of **2–5** as predicted by the ab initio calculations

	CClH ₂ SiF ₂ H		CClH ₂ SiCl ₂ H		CClH ₂ SiBr ₂ H		CClH ₂ SiI ₂ H	
	<i>anti</i>	<i>gauche</i>	<i>anti</i>	<i>gauche</i>	<i>anti</i>	<i>gauche</i>	<i>anti</i>	<i>gauche</i>
CSi	187.8	187.8	188.9	188.8	189.3	189.1	189.9	189.7
SiH	147.2	146.7	147.4	146.9	147.6	147.1	147.7	147.3
SiX	158.1	158.6	205.2	206.2	222.2	223.2	245.4	246.5
		158.1		205.3		222.2		254.4
CSiH	111.5	114.2	109.3	112.4	108.8	112.3	107.9	111.5
CSiX	109.9	107.3	110.4	106.9	110.5	106.7	110.7	106.6
ClCSi	112.5	110.3	114.1	110.9	114.5	111.1	114.9	111.3
ClCSiH	180.0	52.2	180.0	52.2	180.0	52.0	180.0	52.3
<i>E</i> _{rel}	4.8	0.0	5.7	0.0	6.2	0.0	6.3	0.0

The value of the enthalpy difference can be determined from temperature-dependent vibrational spectra by applying the van't Hoff relationship, which is derived under the assumption that ΔH is independent of temperature

$$\ln(I_a/I_g) = -\Delta H/RT + \text{const.}$$

where I_a and I_g are the intensities of the Raman or IR bands for rotamer a and g, respectively. Plotting $\ln(I_a/I_g)$ versus $1/T$ thus results in a straight line whose slope is equal to $-\Delta H/R$. ΔH values were obtained by a least-squares fit from three line pairs for **2** and **3**, and from two pairs for **4**. As an example, two van't Hoff plots are presented in Figure 4.

Table 5 summarises the ΔH values together with the relevant band pairs and the statistical error. In these experiments, severe interference from overlapping with overtones or combination bands occur quite often. Fermi resonances between overtones and fundamentals are also encountered quite frequently. It is also a prerequisite of the method that the bands of the two conformers both have reasonably high intensity and are sitting on a flat baseline. These difficulties have been reviewed recently by Klaboe.^[18]

The discrepancies between the experimental ΔH values obtained from the different band pairs can easily be explained on that basis. Average ΔH values of -0.57 ± 0.37 , 0.21 ± 0.07 and 0.56 ± 0.50 were obtained for **2**, **3** and **4**, respectively, by neglecting the statistical uncertainties resulting from the least-squares fits. Due to the uncertainties mentioned above, the standard deviations are quite large.

Opposite to the gaseous state, the *anti* rotamer of CH₂ClSiHCl₂ is slightly more stable in the liquid. This can

Table 3. Comparison of observed and calculated wavenumbers (cm^{-1}) for the fundamental vibrations of *anti* and *gauche* dibromo(chloromethyl)silane

Fundamental	Ra(l)	Obsd.	anti		gauche	
		Ir(l)	ab initio	scaled	ab initio	scaled
CH ₂ antisymmetric stretch	2974 ms	2980 m	3302.4	3038	3320.9	3055
CH ₂ symmetric stretch	2930 vs	2940 vs	3232.1	2974	3246.6	2987
SiH stretch	2216 vs	2220 s	2382.1	2192	2408.9	2216
CH ₂ deformation	1377 w	1386 s	1532.4	1410	1534.0	1411
CH ₂ wag	1171 vw	1177 ms	1322.5	1217	1320.2	1215
		1125 w				
CH ₂ twist	1091 vw	1100 mw	1217.0	1120	1214.3	1117
SiH bend	826 w	823 vs	878.6	808	904.8	832
SiH bend		795 vs	875.2	805	837.8	771
CCl stretch	773 w,b	763 vs,b	863.3	794	851.4	783
CH ₂ rock	666 m	667 vs	759.8	699	727.8	670
SiC stretch	649 sh				705.9	649
SiC stretch	606 w		641.5	590		
	587 w					
SiBr ₂ antisymmetric stretch	466 w	463 vs			489.4	450
SiBr ₂ antisymmetric stretch	435 w		483.9	445		
SiBr ₂ symmetric stretch	397 vs	395 vs			419.4	386
SiBr ₂ symmetric stretch	385 sh	380 sh	403.3	371		
SiBr ₂ wag	309 w	307 mw	336.9	310		
ClSiC bend	234 w				222.7	205
	216 w					
SiBr ₂ wag	197 vs				205.6	189
SiBr ₂ twist	162 w		174.9	161		
SiBr ₂ deformation	130 sh		132.5	122		
SiBr ₂ deformation	119 s				120.8	111
SiBr ₂ twist			96.3	89	106.2	98
torsion			52.4	48	60.2	55

Table 4. Comparison of observed and calculated wavenumbers (cm^{-1}) for the fundamental vibrations of *anti* and *gauche* (chloromethyl)diiodosilane

Fundamental	Ra(l)	Obsd.	anti		gauche	
		Ir(l)	ab initio	scaled	ab initio	scaled
CH ₂ antisymmetric stretch	2975 ms	2983 m	3302.6	3039	3322.5	3057
CH ₂ symmetric stretch	2928 vs	2942 ms	3231.3	2973	3246.6	2987
SiH stretch	2198 vs	2200 s	2371.6	2182	2397.3	2206
CH ₂ deformation	1388 w	1390 s	1532.0	1409	1533.9	1412
CH ₂ wag	1175 vw	1180 m	1319.5	1214	1318.9	1213
CH ₂ twist	1090 vw	1180 m	1216.4	1119	1216.7	1119
CCl stretch	812 w	820 vs	870.2	801	845.9	778
SiH bend	789 w	795 vs	853.7	785	896.4	825
SiH bend	766 w		851.1	783		
SiH bend	724 w				810.1	745
CH ₂ rock	687 vw		753.5	693		
CH ₂ rock	653 m	660 vs			713.9	657
SiC stretch	636 sh				698.9	643
SiC stretch	596 w	590 w	632.0	581		
SiI ₂ antisymmetric stretch	403 mw	403 vs	416.9	384	427.0	393
SiI ₂ symmetric stretch	333 vs	333 ms	351.4	323	357.0	328
SiI ₂ wag	280 m		302.6	278		
ClSiC bend	203 m				210.0	193
ClSiC bend	170 vs		167.5	154		
SiI ₂ wag					177.2	163
SiI ₂ twist			102.0	94	99.3	91
SiI ₂ deformation			81.5	75	88.5	81
torsion			49.7	46	58.0	53

be explained by considering the dipole moments of the two rotamers, as the conformer with the larger dipole moment is normally stabilized in a polar solvent. The predicted dipole

moments for *gauche* and *anti* CH₂ClSiHCl₂ are 1.53 and 3.22 D, respectively, and the latter is therefore stabilized in the liquid. *anti* CH₂ClSiHBr₂ and *anti* CH₂ClSiHI₂ are also

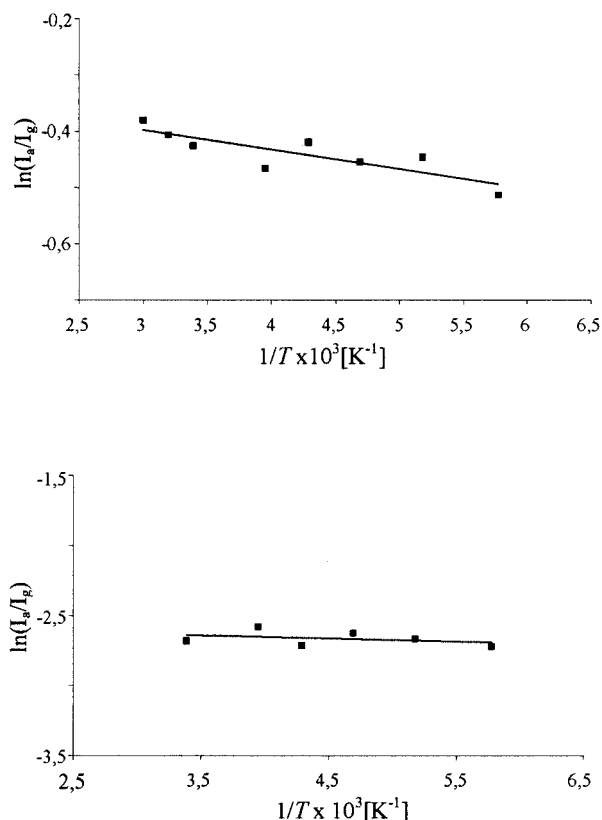


Figure 4. Van't Hoff plots for the line pairs 687/653 cm^{-1} of $\text{ClCH}_2\text{SiH}_2$ (left) and 435/466 cm^{-1} of $\text{ClCH}_2\text{SiHBr}_2$ (right)

Table 5. Line pairs (cm^{-1}) and experimental ΔH values (kJ/mol ; $\Delta H = H_{\text{anti}} - H_{\text{gauche}}$) obtained from least-square fits for **2**, **3** and **4**

$\text{CH}_2\text{ClSiHCl}_2$ line pair	ΔH	$\text{CH}_2\text{ClSiHBr}_2$ line pair	ΔH	$\text{CH}_2\text{ClSiH}_2$ line pair	ΔH
508/495	-0.18 ± 0.003	435/466	0.28 ± 0.007	687/653	0.20 ± 0.003
671/624	-0.92 ± 0.006	387/396	0.19 ± 0.005	596/636	0.91 ± 0.008
680/624	-0.61 ± 0.003	606/649	0.15 ± 0.003		

stabilized, but due to the smaller dipole moments and the larger *gauche-anti* energy differences (Table 2) the stabilizing effect is not able to reverse the sign of ΔH .

It is also of some note that the SiC valence force constants calculated from the Hessian matrices by use of symmetry coordinates increase with increasing electronegativity of the halogen substituents. The calculated values for *gauche* **5**, **2**, **3** and **4** [N/cm , scaled by $(0.92)^2$] are: 2.87, 2.77, 2.73 and 2.67, respectively; the force constants for the *anti* conformers are smaller by 0.03–0.04 N/cm .

Experimental Section

General Remarks: All compounds except (chloromethyl)diphenylsilane are sensitive towards moisture; some of them, such as (chloromethyl)diiodosilane, are also sensitive towards oxygen. All syntheses and manipulations were therefore carried out under an atmos-

phere of dry, oxygen-free nitrogen using Schlenk techniques. Solvents were dried over sodium or potassium and distilled under N_2 prior to use.

Raman spectra were recorded with a Jobin–Yvon T64000 spectrometer equipped with a triple monochromator. A frequency-doubled Nd:YAG laser (20 mW) operating at 532 nm served as light source and a charge-coupled device (CCD) camera was used as detector. The samples were condensed into 1 mm capillary glass tubes that were sealed under nitrogen atmosphere. Variable-temperature Raman spectra were obtained by mounting the capillary on a copper block supplied with a heater and a thermocouple for temperature monitoring. Liquid nitrogen was used for cooling.

Infrared spectra in the range from 3000–250 cm^{-1} were measured with a Perkin–Elmer 883 spectrometer using a film of the pure liquid between CsBr plates

NMR spectra of **2–5** as solutions in CDCl_3 were obtained with a Bruker MSL 300 spectrometer.

(Chloromethyl)diphenylsilane (1): A solution of chlorodiphenylsilane (55.17 g, 250 mmol) and bromochloromethane (32.63 g, 250 mmol) in 500 mL of THF was cooled to -70°C , and 138 mL of a 2 M solution of BuLi in pentane was added dropwise over a period of 2 h, whilst maintaining the temperature. After completion of the addition the mixture was stirred at -70°C for another 2 h. It was then allowed to warm to room temperature and stirred overnight. After hydrolysis and extraction with n-hexane the organic layer was separated. Subsequently, the solvent is removed by evaporation in vacuo and the liquid residue was fractionated, giving 20.7 g (88.9 mmol, 35%) of **1** as a colourless liquid. $\text{B.p.}_{0.1} = 125^\circ\text{C}$. $\text{C}_{13}\text{H}_{13}\text{ClSi}$ (232.77): calcd. C 67.07, H 5.63; found C 66.98, H 5.6.

Dichloro(chloromethyl)silane (2): Triflic acid (6.46 g, 43.3 mmol) was added dropwise at a temperature of -30°C to a solution of **1** (5.01 g, 21.5 mmol) in 20 mL of toluene. After completion the mixture was allowed to warm to room temperature and stirred for 5 h. The benzene formed in the reaction and the toluene were completely removed in vacuo, this process was controlled by IR spectroscopy. Diethyl ether and 3 g of LiCl (100% excess) were added and the mixture was then stirred at room temperature for 2 d. After this time all volatile substances were condensed off. The diethyl ether was removed very carefully from the mixture by distillation. The liquid residue was fractionated under slightly reduced pressure giving 0.9 g (6 mmol) of **2** (28.1%) as colourless liquid. $\text{B.p.}_{200} = 42^\circ\text{C}$. $\text{CH}_3\text{Cl}_2\text{Si}$ (149.48).

Dibromo(chloromethyl)silane (3): Compound **3** was prepared using the same procedure as for **2**, except that LiBr was used instead of LiCl. The following amounts of starting materials were used: 5.67 g of **1** (24.36 mmol); 7.31 g of triflic acid and 5 g of LiBr. Fractionation in vacuo yielded **3** (1.4 g, 5.8 mmol; 24.1%) as a colourless liquid. $\text{B.p.}_{20} = 43\text{--}45^\circ\text{C}$. $\text{CH}_3\text{Br}_2\text{ClSi}$ (238.38): calcd. Br 64.04; found Br 64.18.

(Chloromethyl)diiodosilane (4): Compound **1** (4.37 g) and an excess of HI were placed in a sealed glass tube and stored for one week at room temperature. After removal of the excess HI and the benzene formed during the reaction, the liquid residue was fractionated in vacuo to give 3.7 g (mmol) of **4** (59.3%) as a colourless liquid. $\text{B.p.}_{0.1} = 33\text{--}35^\circ\text{C}$. $\text{CH}_3\text{ClI}_2\text{Si}$ (332.39): calcd. I 76.36; found I 76.15.

(Chloromethyl)difluorosilane (5): A solution of **4** (1.5 g, 4.5 mmol) in 15 mL of hexachlorobutadiene was added at a pressure of

30 Torr to a suspension of 5.7 g of zinc fluoride (excess) in 60 mL of hexachlorobutadiene. The volatile products were continuously condensed into a flask cooled with liquid nitrogen. After completion of the addition the mixture was stirred at 90 °C for 5 h. The volatile products contained just a small amount of the desired product, as deduced from the NMR spectra. No further attempts to isolate these small quantities of $\text{CH}_3\text{F}_2\text{ClSi}$ on a preparative scale were made.

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