

Experimental and theoretical study of the reaction of difluorostannylene with methyl chloride. The first direct IR spectroscopic detection of a complex between a carbene analog and an alkyl halide in low temperature inert matrix

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Complex between a carbene analog (SnF_2) and organo halide (CH_3Cl) was stabilized by a low-temperature (Ar, 12 K) matrix isolation technique and characterized by IR spectroscopy for the first time. The bands at 567 and 543 cm^{-1} were assigned to this complex. The potential energy surface of the system $\text{SnF}_2 + \text{CH}_3\text{Cl}$ was studied by *ab initio* MP2/3-21G(d)//HF/3-21G(d) and semiempirical PM3 methods. Calculations shown that the reaction between SnF_2 and CH_3Cl results in the formation of a donor-acceptor complex. The calculated energy of the complex formation is $14.2\text{ kcal mol}^{-1}$ (*ab initio*) and $15.7\text{ kcal mol}^{-1}$ (PM3). Quantum-chemical calculations were used to interpret the IR spectrum of the complex. Insertion of SnF_2 into the C—Cl bond with formation of $\text{CH}_3\text{SnF}_2\text{Cl}$ is an energetically favored process but it requires surpassing of a high energetic barrier and does not occur under the experimental conditions. A complex of CH_3Cl with H_2O codeposited in argon matrix was detected by IR spectroscopy for the first time.

Key words: difluorostannylene, methyl chloride, water, donor-acceptor complex; matrix IR spectra; quantum-chemical calculations, *ab initio*, semiempirical PM3 methods.

Insertion into σ -bonds, in particular, into C—Hal bond, is one of the characteristic reactions of carbenes¹ and their group IVB analogs (silylenes,² germynes,³ stannylenes^{3,4}). The mechanism of this reaction for carbene analogs is little understood despite copious experimental data. Two main mechanisms are considered nowadays for the insertion of carbene analogs into a C—Cl bond: the concerted and nonconcerted (radical or ion-radical)^{2–4} ones. The latter one involves an atom transfer^{5,6} (abstraction—recombination mechanism) or an electron transfer^{7,8} as the key step. It is not easy to make a choice between the mechanisms mentioned above. Therefore it is very important to establish the factors favoring one or another pathways of the insertion. One such important factor is the formation of complexes between carbene analogs and alkyl halides.

The ability of carbene analogs to form complexes with a strong Lewis bases is well known.^{9,10} Alkyl halides are weak Lewis bases and the possibility of their complexation with carbene analogs is not evident. The formation of donor-acceptor complexes of zwitterion type in reactions of silylenes^{11,12} and germynes¹³ with organohalides has been postulated. Complexation of SnF_2 with chlorotrifluoromethoxyalkanes was suggested¹⁴ to involve the C—Cl bond.

The blue shift of absorption maxima of germynes observed in hydrocarbon matrices in the presence of

cyclohexyl- or allyl chlorides was explained by the formation of the complexes.^{15,16} Strong experimental and theoretical evidence of a complex involvement in the reaction of dimethylsilylene with bromoform was reported recently.¹⁷ The results of semiempirical¹⁸ and *ab initio*¹⁹ calculations have shown the possibility of the existence of donor-acceptor complexes between carbene analogs and halogen-containing compounds. However there is no unequivocal spectral evidence for the existence of such complexes to date.

Dihalostannlenes, in particular SnF_2 , are widely used in various catalytic processes^{14,20–22} where coordination of divalent tin derivatives with various substrates (weak Lewis bases) takes place. Furthermore, the interaction of SnHal_2 with alkyl halides has recently drawn the attention of investigators as the first and an important step in introduction of various functional groups into the parent alkyl halide molecule.^{23–26} At the same time, SnF_2 is one of the few known sterically non-overloaded carbene analogs stable under normal conditions, having intense absorption bands in the middle IR range. It makes SnF_2 convenient for work and allows one to study its reactions by matrix IR spectroscopy.

Thus, the study of intermediate complexes and their structure and stability has a predominant role for understanding the mechanisms of interaction of carbene analogs with saturated substrates.

It has been shown previously that difluorostannylene forms complexes with such weak electron donors as alkenes²⁷ and alkynes.^{28,29} In this work we studied the interaction of difluorostannylene with methyl chloride in the search for an intermediate complex using matrix IR spectroscopy and quantum-chemical methods.

Experimental

A sample of SnF_2 (Aldrich, 99 % purity) was evaporated from a graphite Knudsen cell with orifice diameter 1 mm positioned inside a quartz pyrolyzer, coupled to a vacuum optical helium cryostat. A flow of argon was passed through the pyrolyzer in order to reduce the contact of SnF_2 vapors with the walls. Heating was done by an electrical coil wound around the pyrolyzer above the asbestos isolation coat. The temperature was measured with a chromel-alumel thermocouple positioned on the external wall of the pyrolyzer under the insulating coat. The evaporation temperature was varied in a range 550–700 °C.

The mixtures of argon with CH_3Cl were prepared ~24 h before the beginning of experiment in a glass vessel; the dilution of CH_3Cl in argon was measured by a mercury gauge. Mixtures of CH_3Cl with water and argon were prepared in the same way. The mixtures were brought into the cryostat *via* an unheated pipeline, bypassing the pyrolyzer.

The products of SnF_2 evaporation together with the mixtures of CH_3Cl –Ar were deposited on a surface of a mirror copper plate cooled to 12 K, located inside the cryostat 80 mm from the orifice of the Knudsen cell and at a distance of 50 mm from an outlet of the mixture introduction pipeline. The plate was cooled by a Displex-CSW-208R closed-cycle refrigerator. The working pressure in the cryostat was $\sim 10^{-5}$ Torr.

The total flow of argon was checked by mercury gauges and was around 17 mmol h⁻¹. The time of deposition varied from 0.5 to 1.5 h. The amount of frozen SnF_2 was estimated from the weight loss of the Knudsen cell after the experiment, taking into account the geometrical factor of pyrolyzer equal to 0.5. The final dilution of reagents with argon in the matrix estimated from this data was in the range from 1 : 30 to 1 : 500 for CH_3Cl , and from 1 : 150 to 1 : 1000 for SnF_2 . The lowest dilution used in the experiments on the deposition of water with CH_3Cl was 1 : 200.

IR spectra were recorded in the range of 4000–400 cm^{-1} on an IKS-24-LOMO spectrophotometer using the reflection scheme.

Methods of Calculations

Quantum-chemical calculations were done with the full geometry optimization. Semiempirical PM3^{30,31} calculations were carried out with MOPAC³² program. *Ab initio* SCF calculations were done with GAUSSIAN 92W³³ and GAMESS³⁴ programs. We used the 3-21G(d)^{35,36} basis set that includes polarization d-functions on C, F, and Sn atoms. The nature of the calculated stationary points, *e.g.*, minima or transition states (TS) were characterized by calculations of the eigenvalues of matrix of second derivatives of energy. Energies of stationary points optimized at the HF/3-21G(d) level were corrected by second-order Møller–Plesset MP2/3-21G(d)/HF/3-21G(d)³⁷ single point calculations. All calculations were done with 486DX2-66 computers.

Results and Discussion

Matrix IR spectra. The spectra of individual starting reagents isolated in an argon matrix were recorded before

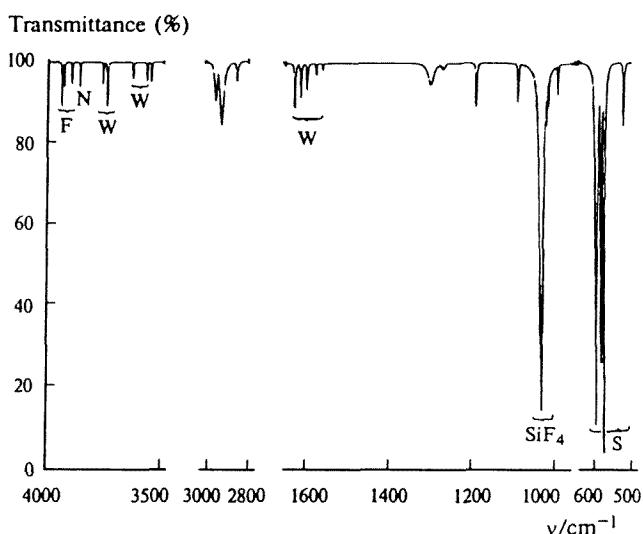


Fig. 1. The IR spectrum at 12 K of the products of SnF_2 vaporization (at 615 °C) in Ar matrix (14 mmol); Ar : $\text{SnF}_2 \approx 100 : 1$; S — the bands of $(\text{SnF}_2)_n$ ($n > 1$); F — the bands of HF; N — the band of $\text{N}_2 \cdot \text{HF}$; W — the bands of $(\text{H}_2\text{O})_n$ ($n > 1$); unmarked bands are those of products of vacuum oil pyrolysis.

the experiments on codeposition of SnF_2 with CH_3Cl .

According to matrix IR spectroscopy (Fig. 1) the products of SnF_2 evaporation contain, besides monomer SnF_2 and its dimer,^{27,38} trace quantities of water,^{39–41} desorbed from cryostat walls, HF (the product of SnF_2 reaction with desorbed water), HF dimer, and a complex of HF with dinitrogen (dinitrogen also appears in matrix as a result of desorption from cryostat walls), as well as SiF_4 ⁴³ (the product of interaction of SnF_2 vapors with

Table 1. Assignment of bands observed in matrix IR spectra

Compound	ν/cm^{-1}
HF	3963, 3953, 3918
$\text{N}_2 \cdot \text{HF}$	3881
$(\text{HF})_2$	3823
$\text{H}_2\text{O} \cdot \text{HF}$	3554
H_2O	3775, 3754, 3636, 1624, 1610, 1594, 1573, 1557
$(\text{H}_2\text{O})_n$ ($n > 1$)	3573, 3519
$\text{CH}_3\text{Cl} \cdot \text{HF}$	3724, 434
$\text{CH}_3\text{Cl} \cdot \text{H}_2\text{O}$	3715, 3609, 1594, 714, 707
CH_3Cl	3040, 2966, 2867, 1448, 1353, 1019, 725, 719
$(\text{CH}_3\text{Cl})_2$	3033
SiF_4	1027, 1014, 1010
$\text{SiF}_4 \cdot \text{H}_2\text{O}$	989
SnF_2	593, 571
$(\text{SnF}_2)_2$	580
$(\text{SnF}_2)_n$ ($n > 2$)	520
$\text{CH}_3\text{Cl} \cdot \text{SnF}_2$	567, 543
The products of vacuum oil pyrolysis	2960, 2929, 2860, 1295, 1265, 1185, 1084

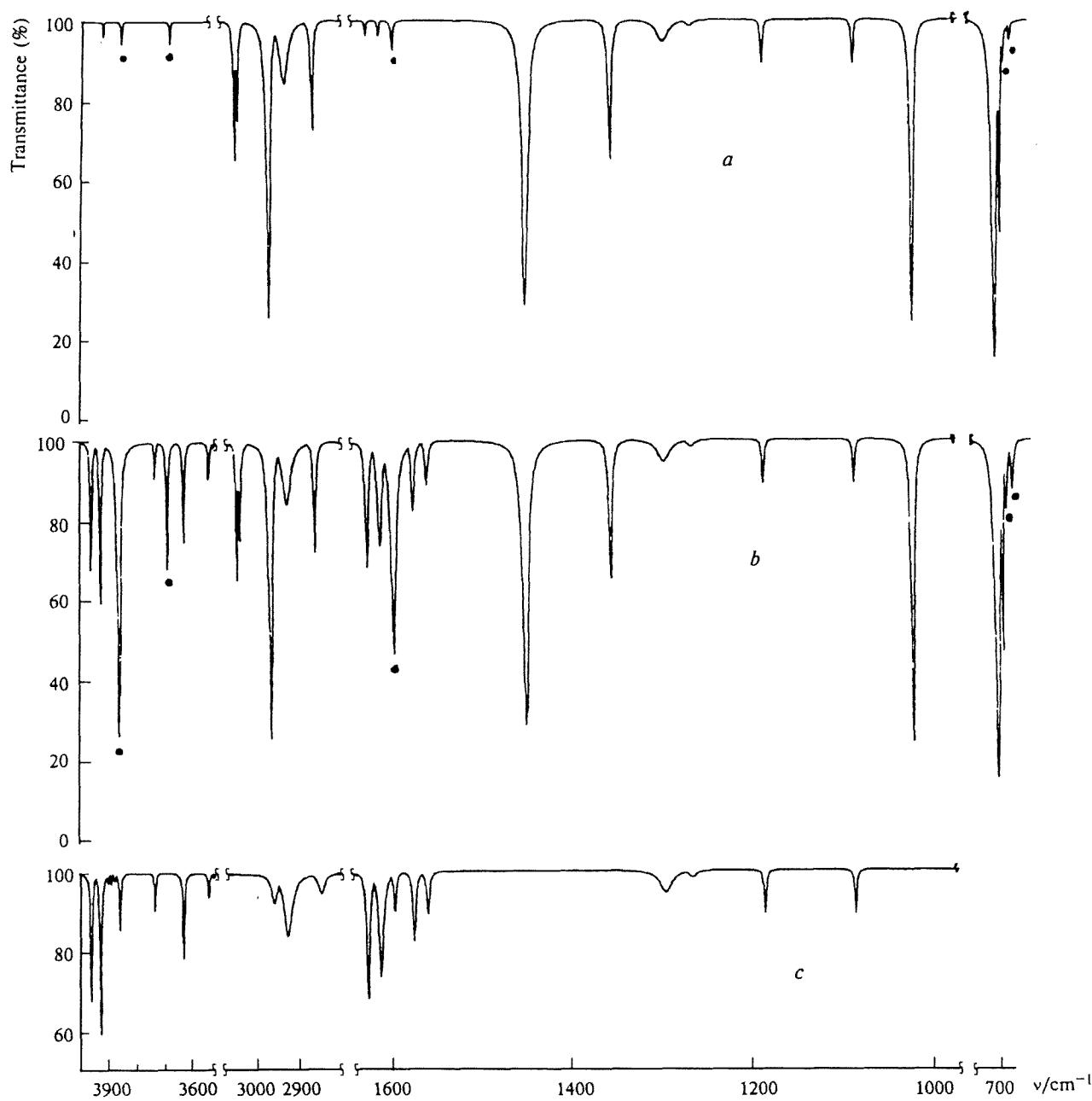


Fig. 2. a. The IR spectrum of CH_3Cl in Ar matrix (20 mmol) at 12 K; $\text{Ar} : \text{CH}_3\text{Cl} \approx 200 : 1$. Points mark the bands of the complex $\text{CH}_3\text{Cl} \cdot \text{H}_2\text{O}$. b. The IR spectrum of the products of codeposition of CH_3Cl with H_2O in Ar matrix (10 mmol) at 12 K; $\text{Ar} : \text{CH}_3\text{Cl} \approx 100 : 1$, $\text{Ar} : \text{H}_2\text{O} \approx 200 : 1$. c. The IR spectrum of H_2O in Ar matrix (10 mmol) at 12 K, $\text{Ar} : \text{H}_2\text{O} \approx 200 : 1$.

pyrolyzer walls). The bands of the compounds mentioned above were identified based on the matrix IR spectra reported earlier and are collected in Table 1. All these bands were also observed in SnF_2 and CH_3Cl codeposition runs; moreover, its intensities varied from one experiment to another.

Besides the bands belonging to methyl chloride monomer and dimer⁴⁴ (Fig. 2, see Table 1), the matrix IR spectrum of CH_3Cl shows bands of water, which is present in trace quantities. Moreover, five bands were found in

the spectra; their intensities grew simultaneously with the increase in water concentration in CH_3Cl —water codeposition experiments. The bands observed were close to that of the monomer water fundamental frequencies and the frequency of methyl chloride C—Cl bond stretching vibrations, split because of the presence of two chlorine isotopes (Table 2). Thus these two bands were assigned to the complex of water with CH_3Cl . As far as we know the matrix IR spectrum of this complex has not yet been reported.

Table 2. Assignment of bands of $\text{CH}_3\text{Cl} \cdot \text{H}_2\text{O}$ complex

Complex	ν/cm^{-1}	Assignment
Starting reagent		
3715	3736	$\nu_3 (\text{H}_2\text{O})$
3609	3639	$\nu_1 (\text{H}_2\text{O})$
1594	1591	$\nu_2 (\text{H}_2\text{O})$
714	725	$\nu_3 (\text{CH}_3^{35}\text{Cl})$
707	719	$\nu_3 (\text{CH}_3^{37}\text{Cl})$

Upon codeposition of CH_3Cl with SnF_2 (Fig. 3) four new bands were found that differ from those recorded in experiments on deposition of starting materials (SnF_2 or CH_3Cl). The intensity of two weak bands (3724 and 434 cm^{-1}) depended on the concentrations of CH_3Cl and HF only. Based on the published data⁴⁵ these bands were assigned to a complex between CH_3Cl and HF. Two other intense bands (543 and 567 cm^{-1}) repeating with a shift of several tens of inverse centimeters the frequencies of SnF_2 (571 and 593 cm^{-1}) vibrations were assigned to a complex of SnF_2 and CH_3Cl of $1 : 1$ stoichiometry based on the following considerations. The intensities of these bands did not depend on the quantities of the above-mentioned impurities. At the different ratios of starting compounds in the matrix the intensities of these bands varied synchronously. This indicates that these bands belong to the same species. In the experiments, when the concentration of one reagent (SnF_2 or CH_3Cl) was constant and the concentration of the other varied, the intensity of these bands changed simultaneously with the variations of the second reagent concentration, *i.e.*, it grows when the concentration increases and becomes lower when it decreases. This indicates that these bands arise from the product that results from SnF_2 interaction with CH_3Cl . Comparatively small frequency shifts of the bands mentioned above compared to those of SnF_2 imply that the interaction is weak and corresponds to formation of a complex. Note that shifts of similar magnitude were observed earlier upon complexation of SnF_2 with other reagents.^{27–29} The absence of other bands in the region of SnF_2 stretching frequencies upon a wide variation of reagent concentration allows one to suggest the simplest stoichiometry ($1 : 1$).

Upon annealing of the matrix up to 35 K for 10 – 30 min we observed the decay and finally complete disappearance of the bands corresponding to SnF_2 , $(\text{SnF}_2)_2$ and the complex, due to formation of oligomers transparent in this spectral region. The intensities of the bands of the complex decrease more slowly than those of SnF_2 . It shows a higher stability of the complex towards oligomerization compared to SnF_2 and its dimer.

Contrary to expectations, we failed to observe the bands corresponding to the complex $\text{SnF}_2 \cdot \text{CH}_3\text{Cl}$ in the stretching C–Cl bond vibrations region. In our opinion this is a result of their low intensities (see below).

To obtain the product of SnF_2 insertion into the C–Cl bond of methyl chloride, an experiment was car-

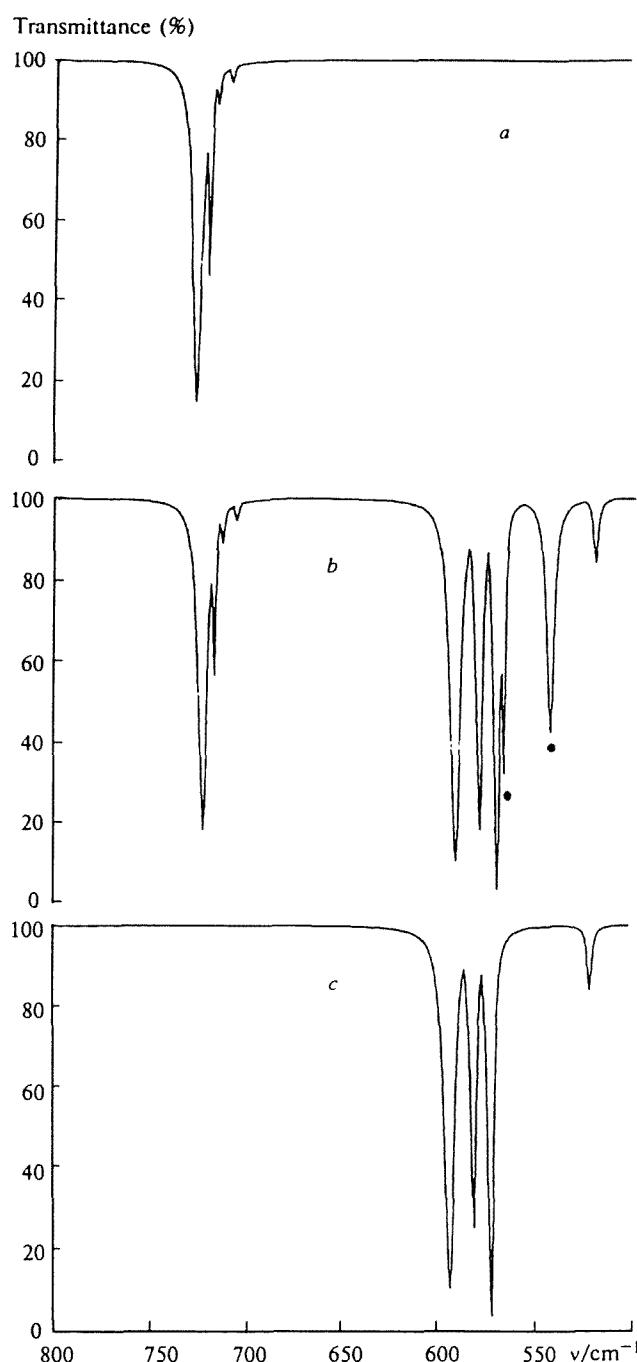


Fig. 3. *a*. The fragment of IR spectrum of CH_3Cl in Ar matrix (20 mmol) at 12 K ; Ar : $\text{CH}_3\text{Cl} \approx 200 : 1$. *b*. The fragment of IR spectrum of the products of codeposition of CH_3Cl with SnF_2 in Ar matrix (17 mmol) at 12 K , Ar : $\text{CH}_3\text{Cl} \approx 200 : 1$, Ar : $\text{SnF}_2 \approx 100 : 1$. Points mark the bands of the complex $\text{CH}_3\text{Cl} \cdot \text{SnF}_2$. *c*. The fragment of IR spectrum of SnF_2 in Ar matrix (16 mmol) at 12 K ; Ar : $\text{SnF}_2 \approx 100 : 1$.

ried out where CH_3Cl was passed through pyrolyzer (863 K) instead of argon. However even in this case we did not observe the bands of the insertion product in the IR spectrum of the resulting matrix. Estimates based on an

ab initio calculated activation energy (see below) show that the degree of conversion of starting materials into the product should be extremely small under the conditions of the experiment. Unfortunately, the experimental setup does not allow us to change these conditions significantly.

Quantum-chemical calculations on $\text{SnF}_2 + \text{CH}_3\text{Cl}$ system. Semiempirical and *ab initio* calculations show that the potential energy surface (PES) of $\text{SnF}_2 + \text{CH}_3\text{Cl}$ system has a local minimum of C_s symmetry corresponding to the complex **1** (Fig. 4).

Both methods of calculation give similar structures of **1**, but the semiempirical method produces a more compact complex than it follows from the *ab initio* calculations. The complex formation bring only small changes in the geometry of the reagents. One should note a small lengthening of C—Cl [0.014 Å (*ab initio*) and 0.034 Å (PM3)] and Sn—F [0.009 Å (*ab initio*) and 0.017 Å (PM3)] bonds.

The molecules of the reagents have large dipole moments (Table 3). Therefore one can expect that the interaction of the dipoles should determine the configuration of the complex to a great extent. Analysis of structure **1** shows that the symmetry axes of SnF_2 and CH_3Cl are quite parallel. According to *ab initio* (PM3) calculations the angle between them is 13° (16°). The dipole moment vectors of SnF_2 and CH_3Cl are oriented in opposite directions and to a significant degree counterbalance one another. The dipole moment of complex **1** with a high degree of accuracy is equal to the difference between SnF_2 and CH_3Cl dipole moments (see Table 3).

An analysis of electron density distribution suggests that structure **1** is stabilized by dipole-dipole interaction and a charge transfer in complex **1** occurs from CH_3Cl to SnF_2 .

The energies of isolated molecules and the complex are presented in Table 3. A shorter Sn...Cl distance in complex **1** calculated by the PM3 method corresponds to a higher complexation energy (15.7 kcal mol⁻¹) compared to that calculated by the *ab initio* RHF method (10.8 kcal mol⁻¹). Corrections due to electron correlation at the MP2 level, zero point energy (ZPE), and basis superposition errors completely compensate each other,

and the best estimate of complexation energy is equal to 10.8 kcal mol⁻¹.

Ab initio calculations correctly reproduce CH_3Cl frequencies but to a large extent overestimate (≥ 150 cm⁻¹) the frequencies of SnF_2 stretching vibrations. Semiempirical AM¹⁵ and PM3 methods overestimate the frequencies of SnF_2 stretching vibrations either.

The lengthening of C—Cl and Sn—F bonds should result in lowering of stretching vibration frequencies of these bonds. However experimentally we observed only the shifts of Sn—F stretching vibrations bands, but not of C—Cl stretching vibration. A possible explanation of this apparent contradiction follows from a detailed analysis of *ab initio* calculated shifts of frequencies and changes of the intensities upon the complexation.

A comparison of calculated frequencies of SnF_2 , CH_3Cl and the complex **1** (Table 4) shows nine vibrations with frequencies higher than 400 cm⁻¹ that have significant (more than 10 cm⁻¹) shifts upon complexation. Of these bands only two vibrations, at 694 and 721 cm⁻¹, have significant intensities. A detailed analysis of these vibration shapes reveals that they are represent a superposition of certain modes of SnF_2 и CH_3Cl vibrations. The vibration at 694 cm⁻¹ is a superposition of antisymmetric stretching vibration of SnF_2 and the symmetric vibration of C—H bonds. Its intensity is close to that of the corresponding vibration in SnF_2 . The vibration at 721 cm⁻¹ represents a superposition of symmetric stretching vibration of SnF_2 and the stretching vibration of the C—Cl bond in CH_3Cl . In this mode the dipoles of both vibrations change in-phase, which results in an increase in its intensity compared to isolated SnF_2 and CH_3Cl . The opposite situation takes place for the vibration at 709 cm⁻¹, which is also a superposition of symmetric stretching SnF_2 vibration and stretching vibration of the C—Cl bond. However in this mode the changes of the dipole moments of both vibrations take place out of phase and its intensity is significantly lower than in isolated SnF_2 and CH_3Cl . That is why this band of the complex **1** has not been detected in our experiments. Thus instead of three expected characteristic bands of the complex we can observe only two.

Table 3. *Ab initio* and PM3 calculated energies and dipole moments (DM) of $\text{SnF}_2 + \text{CH}_3\text{Cl}$ system

Structure	<i>ab initio</i> 3-21G(d)					PM3			
	$-E(\text{RHF})^a$	ΔE^b	$-E(\text{MP2//RHF})^a$	$\Delta E(\text{MP2})^b$	$\Delta E(\text{MP2} +$ $+ \text{ZPE})^b$	DM ^c	$-\Delta_f H^b$	$\Delta\Delta_f H^b$	DM ^c
SnF_2	6194.75221		6195.18141			2.4	111.4		4.2
CH_3Cl	496.83208		497.09496			2.2 ^d	14.7		1.4
$\text{SnF}_2 +$ $+ \text{CH}_3\text{Cl}$	6691.58429	0.0	6692.27638	0.0	0.0	126.1	0.0		
1	6691.60157	-10.8	6692.29898	-14.2	-10.8 ^e	0.3	141.8	-15.7	2.7
TS	6691.50198	51.6	6692.19981	48.0	47.0	8.4	91.5	34.6	6.2
$\text{CH}_3\text{SnF}_2\text{Cl}$	6691.65424	-43.9	6692.35177	-47.3	-47.4	3.7	142.0	-15.8	4.1

^a In au. ^b In kcal mol⁻¹. ^c In Debye. ^d Experimental value 1.9 D.⁴⁶ ^e Taking into account basis superposition error 2.2 kcal mol⁻¹.

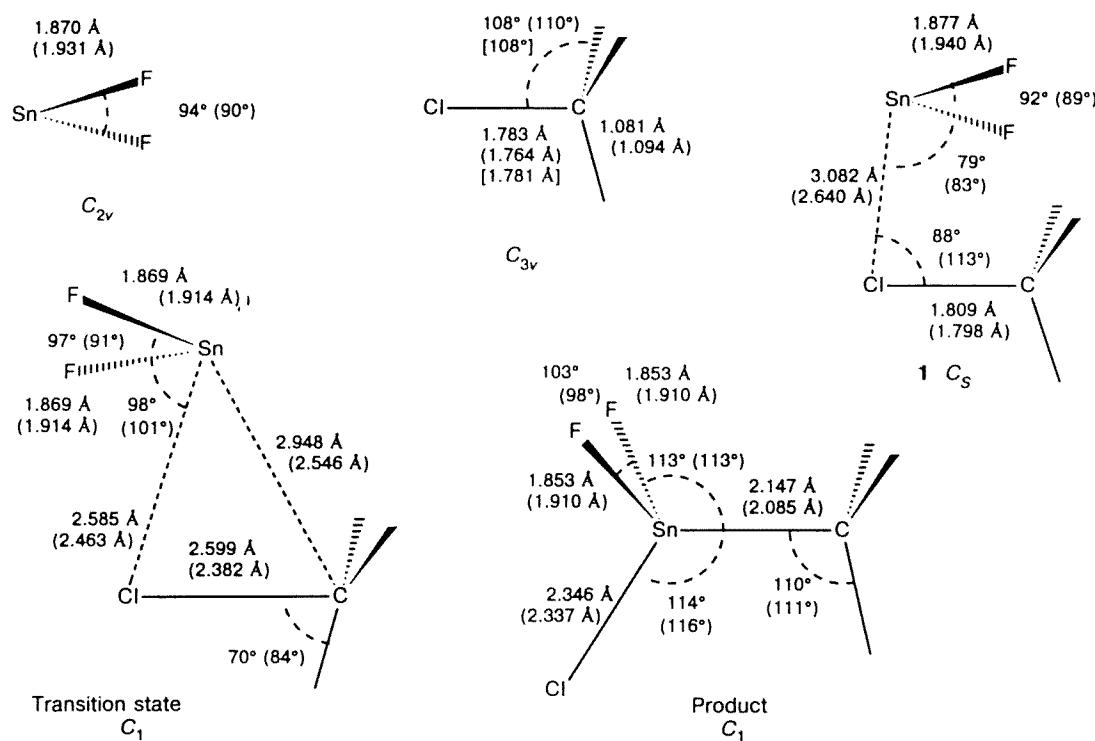


Fig. 4. Main geometric parameters of PES stationary points for $\text{SnF}_2 + \text{CH}_3\text{Cl}$ system calculated by HF/3-21G(d) and PM3 (in brackets) methods. The symmetry group is presented for every structure. Experimental values³¹ for CH_3Cl are given in parenthesis.

Quantum-chemical *ab initio* calculations on the energy of SnF_2 insertion into the C—Cl bond show that this reaction is extremely favorable from an energetic point of view ($\Delta E = -47.4 \text{ kcal mol}^{-1}$) and the resulting $\text{CH}_3\text{SnF}_2\text{Cl}$ should be rather stable. PM3 calculations markedly underestimate the exothermicity of insertion ($\Delta\Delta_f H = -15.8 \text{ kcal mol}^{-1}$).

The transition state of reaction $\text{SnF}_2 + \text{CH}_3\text{Cl} \rightarrow \text{CH}_3\text{SnF}_2\text{Cl}$ (see. Fig. 4) has energy 35—47 kcal mol^{-1}

higher than that of isolated reagents and, especially, complex 1. The PM3 method predicts more compact TS (see. Fig. 4) and a lower activation energy (34.6 kcal mol^{-1}) than *ab initio* calculation (47.0 kcal mol^{-1}).

We estimated the degree of conversion of SnF_2 into the product in the above mentioned experiment when methyl chloride was passed through the pyrolyzer at 863 K. We used the calculated value of activation energy (47 kcal mol^{-1}), the estimated values of partial pressures

Table 4. *Ab initio* calculated and experimentally observed frequencies (ν/cm^{-1}), the theoretical assignments and intensities ($I/\text{km mol}^{-1}$) in matrix IR spectra of SnF_2 , CH_3Cl , and their complex 1

$\text{SnF}_2 (C_{2v})$				$\text{CH}_3\text{Cl} (C_{3v})$				1 (C_s)				
Symmetry	ν_{calc}	I	ν_{exp}	Symmetry	ν_{calc}	I	ν_{exp}	Symmetry	ν_{calc}	I	$\Delta\nu_{\text{calc}}^*$	$\Delta\nu_{\text{exp}}^*$
A_1	251	21						A'	264	30		
B_2	730	93	571					A''	694	83	36	28
A_1	748	85	593	A_1	778	48	724	A'	721	144	29	26
				E	1135	3	1018	A'	709	7	69	
				E	1135	3	1018	A''	1151	8	-16	
				A_1	1531	24	1350	A'	1174	2	-39	
				E	1623	5	1444	A'	1527	10	4	
				E	1624	5	1444	A''	1607	9	16	
				A_1	3254	28	2965	A'	1625	21	-1	
				E	3353	8	3040	A'	3289	18	-35	
				E	3354	8	3040	A''	3404	1	-51	
									3418	1	-64	

*Frequency shifts upon complexation.

(p) of reagents at the pyrolyzer outlet ($p_{\text{SnF}_2} = 10^{-1}$ Torr, $p_{\text{CH}_3\text{Cl}} = 2 \cdot 10^{-2}$ Torr), and the effective volume (2.4 cm^3) where conversion takes place. The conversion was found to be less than 10^{-8} . At such a low degree of conversion detection of the insertion product by matrix IR spectroscopy is impossible.

Thus the results of this study show that interaction of SnF_2 with alkyl halides produces a donor-acceptor complex, a rearrangement of which into more stable product of the insertion into the C—Cl bond requires overcoming of a high activation barrier.

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