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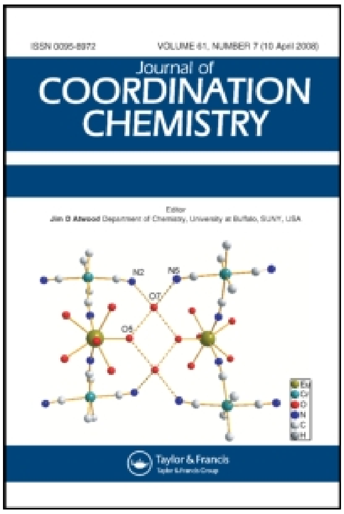

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STRUCTURAL FEATURES OF TRIMETHYLCHLOROSTANNANE IN APROTIC SOLUTIONS*

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The molecular structures of trimethylchlorostannane in various donor solvents have been investigated by far IR spectroscopy. The absorption frequency associated with the Sn–Cl stretching vibration is found to be linearly related to the solvent donor number. The Cl–Sn–C bond angle of the complex species in solution has been estimated from the ratio of the absorption intensities of the symmetrical and the antisymmetrical Sn–C stretching vibrations and is also found to be related to the solvent donor number. The experimental results are closely related to structural changes and charge distributions as calculated by means of the semi-empirical MNDO method. The results are compared to those involving ^{119}Sn and ^{1}H NMR-spectroscopy.

Keywords: Solute-solvent interactions; trimethylchlorostannane; infrared spectroscopy; bondlength–bond angle correlations; structural variations

INTRODUCTION

Trimethylchlorostannane is known to interact with Lewis bases,[1] whereby the molecules are converted from the tetrahedral into the trigonal bipyramidal form. Increasing donor strength of the base is expected to lead to increased lengthening of the Sn–Cl bond and to an increase in negative charge at the chlorine atom,[2,3] which, accordingly, may act as a donor towards the acceptor functions of the solvent. In aprotic solvents the latter are not well developed so that the bond lengthening may be regarded as mainly due to the donor effects by the incoming ligand. In order to learn more about the individual structural changes, we have applied spectroscopic methods as well as quantum-chemical calculations by means of the semi-empirical MNDO approach.

EXPERIMENTAL AND THEORETICAL METHODS

All solvents were purified according to standard methods. The water content was determined by Karl Fischer titration. 20–100 mg H_2O dm^{-3} were usually accepted. The spectra were recorded on a Nicolet 20F far IR Fourier transform spectrometer. The optical bench was held under reduced pressure (<0.3 torr) to avoid the IR absorption of water vapour within the spectrometer. Cells equipped with polyethylene windows and a path length of between 0.05 and 0.5 mm - depending on the IR absorption of the solvent - were used. A resolution of 4 cm^{-1} using 5376 data points (8192 Fourier-transformation points) and a mirror velocity of 1.4 mm/s was selected. 1000 scans where summed to achieve an acceptable signal-to-noise ratio.

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* Dedicated to Professor Edwin Hengge, Graz, on the occasion of his 60th birthday.

The spectra of trimethylchlorostannane in solution were obtained by subtracting the solvent spectra from the solution spectra. Peak intensities were measured by integration. Under these conditions the band position could be reproduced within an experimental error or 0.3 cm^{-1}. Concentrations of trimethylchlorostannane between 0.01 and 1 mol dm^{-3}, were used and no measurable concentration dependence of the spectra was found. The sensitivity of the spectra to the water content of the solvents was tested with DMSO and ethanol. No measurable changes were found in the range 30 to 500 mg H_2O dm^{-3}.

Quantum chemical calculations were performed within the usual MNDO–MO–SCF framework derived from single-determinant MNDO calculations without inclusion of configuration interactions.[4] The geometrical structures were optimized by the Davidson–Fletcher–Powell method.[5,6] Atomic charges correspond to the summation over the squares of the coefficients of the atomic orbitals of all occupied molecular orbitals as given in reference.[7] In the optimization of the geometries of the complexes the Sn–donor distance was fixed to values found in crystal structures of the investigated or similar substances.[8,9] The calculations were performed using the program AMPAC V 1.00[10] on an IBM 3090-400VF computer. X-ray structural data were taken from the Cambridge structural data file.

RESULTS AND DISCUSSION

The far IR spectrum of a solution of $(CH_3)_3SnCl$ in *n*-hexane is given in Fig. 1. The assignment of the bands was based on a normal coordinate analysis,[11] as well as on matrix isolation spectra showing isotope splitting due to ^{35}Cl and ^{37}Cl.[12] This splitting is reflected in a shoulder of the Sn–Cl band in *n*-hexane. By calculating the second derivative of the spectrum, this shoulder was resolved into two bands at 344 and 336 cm^{-1} (Fig. 2) in agreement with the two bands at 342 and 335 cm^{-1} found in a matrix of solid nitrogen.[12]

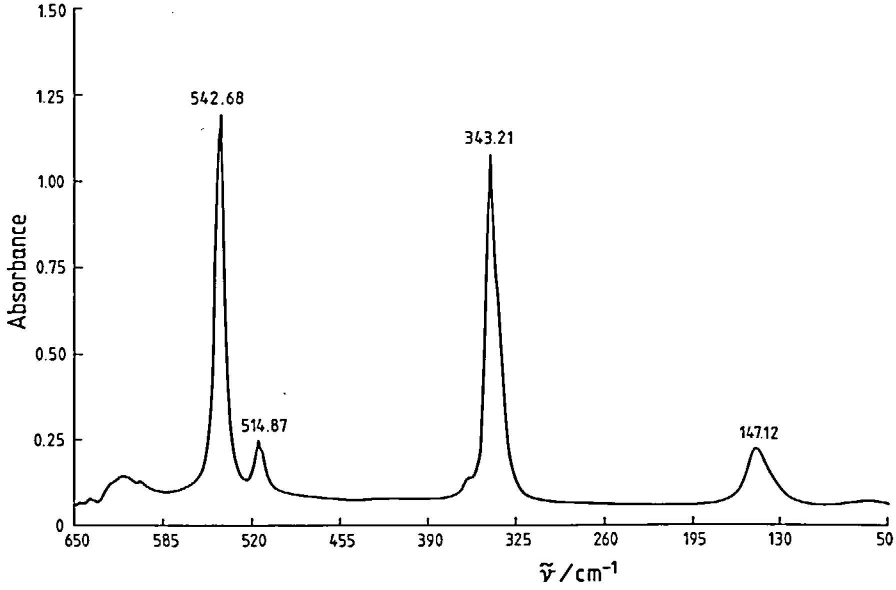

FIGURE 1 Far IR spectrum of a 0.1 M solution of $(CH_3)_3SnCl$ in *n*-hexane.

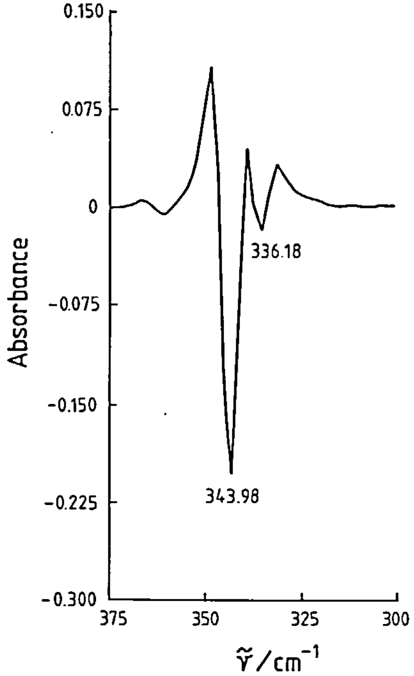

FIGURE 2 Splitting of the Sn–Cl stretching vibration due to ^{35}Cl and ^{37}Cl resolved by calculating the second derivative of the spectrum of a 0.1 M solution of $(CH_3)_3SnCl$ in *n*-hexane.

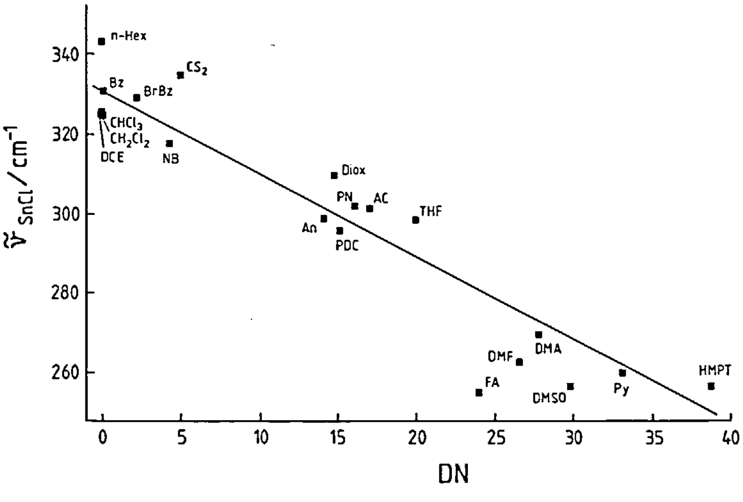

FIGURE 3 Frequency of the Sn–Cl stretching vibration in various solvents *versus* their Donor number.

TABLE I

Positions of maxima of observed far IR absorption bands, ratio of intensities of the symmetric and the antisymmetric Sn–C vibrations, the Cl–Sn–C angle calculated from this ratio and the Donor number of the solvent.

Solvent	$\nu SnC_{asm}/cm^{-1}$	$\nu SnC_{sym}/cm^{-1}$	$\nu SnCl/cm^{-1}$	$\nu SnC_3/cm^{-1}$	Isym/Iasym	$\alpha Cl–Sn–C/°$	DN
n-hexane	542.9	514.9	343.7	145.9	0.106	108.0	0.0
trichlormethane	544.7	514.8	325.7	149.8	0.100	107.6	0.0
1,2-dichlorethane	545.5	514.9	324.6		0.088	106.5	0.0
benzene	544.1	514.9	330.6	147.5	0.093	107.0	0.1
methylenchloride	545.1	514.9	324.9	149.2	0.097	107.3	0.0
brombenzene	544.0	514.8	328.9	145.8	0.116	108.8	2.2
nitrobenzene	545.8	515.9	317.5	148.5	0.086	106.3	4.4
CS_2	542.7	515.8	334.8		0.111	108.4	5.0
acetonitrile	548.5	515.5	298.8		0.067	104.5	14.1
1,4-dioxane	546.4	514.3	309.5	150.6			14.8
propandiol-1,2-carbonate	548.8	515.6	295.4	150.7	0.065	104.3	15.1
propionitrile	547.8	516.5	302.0	150.3	0.061	103.8	16.1
acetone	547.7	515.2	301.2	150.8			17.0
tetrahydrofuran	546.4	513.3	298.2	148.9	0.055	103.2	20.0
formamide			255.0				24.0
dimethylformamide	546.6	511.2	262.6	148.7	0.049	102.4	26.6
dimethylacetamide	548.1	515.0	269.3	154.5	0.064	104.2	27.8
dimethylsulfoxide	547.9		256.5	155.3	0.025	99.0	29.8
pyridine	545.6		259.9	151.4	0.013	96.5	33.1
hexamethyl-phosphamide	546.4		256.5	147.9	0.006	94.3	38.8

Four different vibrational modes have been found in the IR region 650 to 50 cm^{-1}, namely the antisymmetrical and the symmetrical Sn–C stretching vibrations (543 and 515 cm^{-1}), the Sn–Cl stretching vibration (343 cm^{-1}) and three degenerate SnC_3 deformation and rocking modes (145 cm^{-1}). The band positions and the ratio of the absorption intensities of the symmetric to the asymmetric Sn–C vibrations are given in Table I. The frequency of the Sn–Cl stretching band is shifted to lower values as the donor strength of the solvent is increased. A fairly linear relationship is found between the band position and the donor number (DN) of the solvent (Fig. 3).

The changes in absorption frequencies of the asymmetric and the symmetric Sn–C stretching vibrations, and of the SnC_3 deformation vibrations are much less pronounced. The asymmetric Sn–C stretching vibration frequency (exhibiting the strongest IR absorption of all investigated vibrations) increases with decreasing Sn–Cl stretching frequency and hence the C–Sn bonds are slightly shortened. In order to learn about the changes in Cl–Sn–C bond anlges, we applied the method of Beck *et al.*[13] for calculating bond angles of metal carbonyls from IR spectra. For the estimation of the Cl–Sn–C bond angles, α, from the intensities of the symmetrical Sn–C stretching band (I_{sym}) and the antisymmetric Sn–C stretching band (I_{asym}) the following equation was used:

$$\alpha = 180 - \operatorname{arccotan} \sqrt{\frac{I_{sym}}{I_{asym}}}$$

The results obtained in different donor solvents are presented in Table I. For the poorly coordinating solvents *n*-hexane and carbon disulfide, α is found to be 108°, as found for $(CH_3)_3SnCl$ by gas-phase electron diffraction.[14] The value of α is decreased as the solvent DN is increased. For HMPT, the strongest donor investigated, an angle of 94.3° is found, close to that of 95.7° reported for solid $(CH_3)_3SnCl{\cdot}HMPT$ from X-ray diffraction data. There is good agreement between the α values obtained in solution and in the solid state with the exception of the pyridine complex, where X-ray diffraction yields an angle of nearly 90°,[8] whereas we obtained 94.3° in pyridine solution. This difference may be due to structural differences between solid state and solution or to unreliable interpretation of the X-ray data where only the positions of the tin and the chlorine atoms but not those of the carbon atoms were refined thus yielding a poor crystallographic *R* factor of 0.186. A clear relationship is found between $\alpha_{C-Sn-Cl}$ and the solvent DN (Fig. 4), showing that the bipyramidal configuration is more closely approached as the donor strength of the ligand (solvent) is increased.

The plot of $\alpha_{C-Sn-Cl}$ with the absorption frequency of the Sn–Cl stretching band depicted in Fig. 5 illustrates more clearly that coordination by weakly donating solvent molecules is hardly developed, whereas in solvents of donor numbers of more than 25 the geometric changes become increasingly pronounced.

This is also expressed by the relation between the length of the Sn–Cl bond and the Cl–Sn–C angle (Fig. 6) in different compounds of the type R_3SnCl obtained from X-ray diffraction data taken from the Cambridge structural data file (Fig. 6). Exceptions are chloro(trimethyl)pyridinetin[8] and 1-aza-5-stanna-5-chlorotricyclo(3.3.3.$0^{1,5}$)undecane.[15] In the former the positions of the carbon atoms are not precisely known whereas in the latter the tin atom is part of a tricyclic system and hence the motion of the carbon atoms is restricted and a Cl–Sn–C angle greater than expected from the length of the Sn–Cl bond is found.

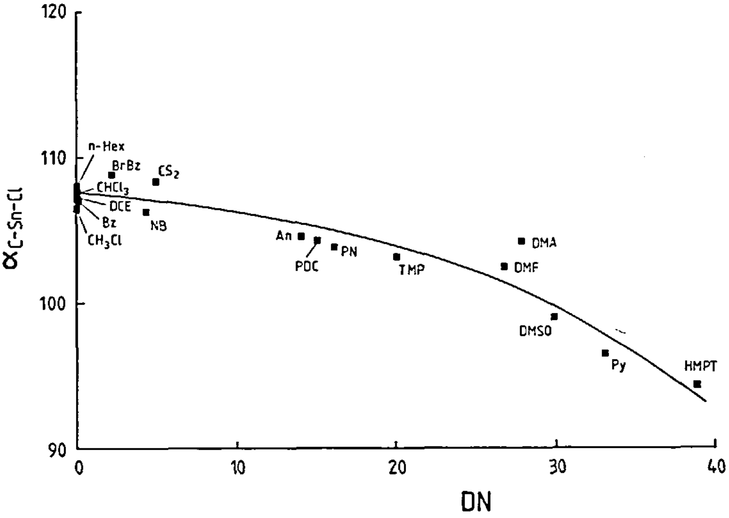

FIGURE 4 $\alpha_{C-Sn-Cl}$ calculated from the intensity ratio of symmetric and antisymmetric Sn-C vibrations *versus* DN.

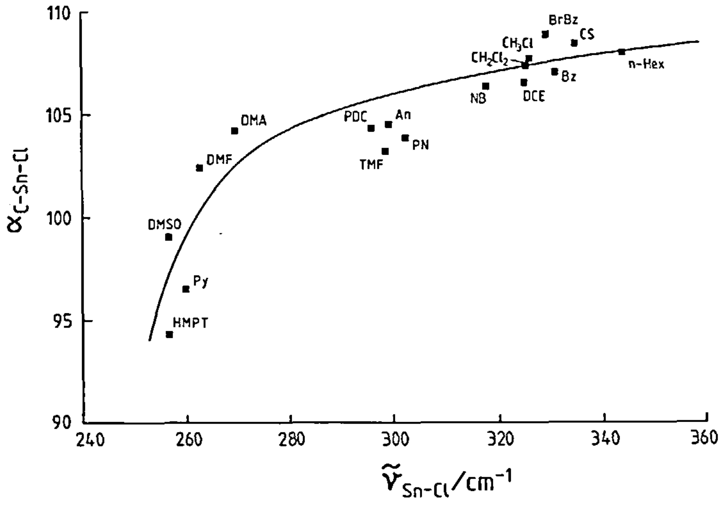

FIGURE 5 Relation of $\alpha_{C-Sn-Cl}$ to the Sn–Cl-stretching vibration.

Changes of bond lengths and angles are expected to be related to changes in partial charge.[2,3] For the molecules $(CH_3)_3SnCl$, $(CH_3)_3SnCl{\cdot}Cl^-$, $(CH_3)_3SnCl{\cdot}DMSO$, $(CH_3)_3SnCl{\cdot}Py$ and $(CH_3)_3SnCl{\cdot}HMPT$, charge distribution has been calculated by means of the MNDO method. The geometries of the first two molecules were optimized to minimize the total energy without implying geometrical restrictions. The results are in good agreement with those from electron diffraction[14] and from X-ray diffraction.[41] The geometries of the last three molecules were based on given

Sn–O or Sn–N distances[8,9] (see Table II). The $\alpha_{C-Sn-Cl}$ angles resulting from the MNDO calculation, with the exception of pyridine (see above), agree well with the values resulting from the IR experiments given in Table I. The complex formation of $(CH_3)_3SnCl$ with Cl^- results in a strong polarization of the original Sn–Cl bond with a strongly positively charged Sn, a negative charge towards the Cl and a considerable lengthening of this bond. The C–Sn–Cl angle of almost 90° shows that the Cl^- is acting as a strong donor. These effects are in agreement with the spillover effect (Q_{Sn}) and the pile up effect (Q_{Cl}), and with the bond length variation rules.[3,42] The solvent adducts exhibit the same effects, increasing in general with increasing donor number of the solvent.

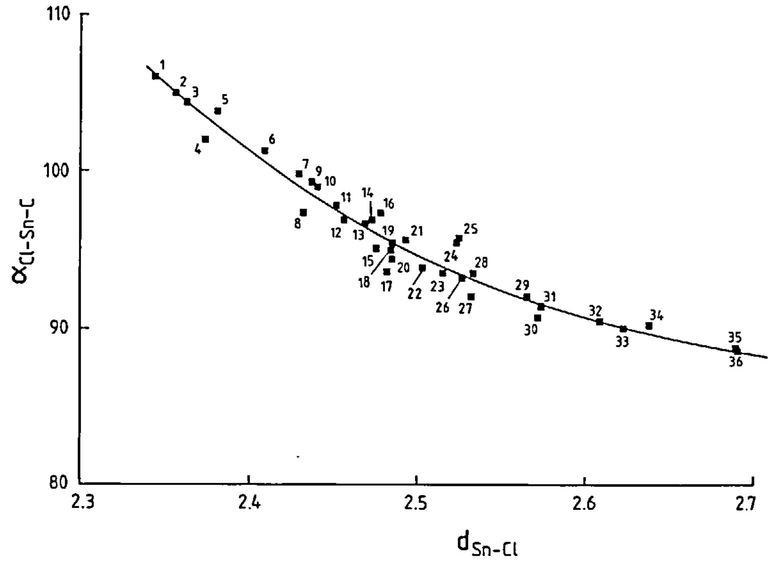

FIGURE 6 Sn-Cl distances *versus* Cl-Sn-C angles as found from X-ray diffraction: 1 = Chlorotris(tricarbonyl-η^5-cyclopentadienyl)manganese)-tin;[16] 2,3 = Chlorotriphenyltin;[17] 4,10 = bis(Chlorodiphenylstannyl)methane;[18] 5 = tris(bis(trimethylsilyl)methyl)chlorotin;[19] 6 = Chlorotricyclohexyltin;[20] 7 = Chlorotrimethyltin;[21] 8,32 = (μ_2-Methylene)(chlorodiphenyltin)(chlorodiphenylhexamethylphosphoramide-O)tin;[22] 9,24 = (μ_2-Pyrazine-*N,N'*)bis((μ_2-methylene)dichlorotetramethylditin);[23] 11 = Chlorodimethyl(2-(diphenylphosphinoyl)phenyl)tin;[24] 12,14 = (μ_2-Methylene)(μ_2-pyridazine-*N,N'*)dichlorotetramethylditin;[23] 13,35 = (μ_2-Methylene)dichlorotetramethyl-2-pyridylditin;[23] 15 = *m*-bis(diphenylphosphinyl)ethane-2-bis(chlorotriphenyltin);[2] 16,30 = 3,3-bis(Chlorodimethyltin)propylethylsulfoxide;[26] 17 = Chloro-(1-((4'-methylphenylimino)methyl)-2-naphthol)triphenyltin-1-((4'-methylphenyl)imino)methyl-2-naphthol;[27] 18 = μ_2-(*rac*-1,2-bis(*n*-Propylsulfinyl-ethylene)-2-(O,O')bis(chloro-*cis*-triphenyltin);[28] 19 = (ε-caprolactam-O)chlorotriphenyltin;[29] 20 = Chlorotetramethylureatriphenyltin;[30] 21 = (3-(*t*-Butyl(phenyl)phosphino)propyl)chlorodimethyltin;[31] 22 = 3-(1,10-Phenanthrolyl))-5,6-diphenyl-1,2,4-triazinechloroaquatriphenyltin;[32] 23 = Chlorotriphenyl(pyridinium-2-carboxylato)tin;[33] 25 = Chlorotrimethyl(hexamethylphosphamide)tin;[34] 26 = Chlorotriphenyl(quinolinium-2-carboxylato-O)tin monohydrate;[35] 27 = (μ_2-1,2-bis(diphenylarsonyl)ethane-O,O')bis(chlorotriphenyltin);[36] 28 = Chloro(2,6-dimethylpyridine-*N*-oxide)trimethyltin;[37] 29 = Chlorotrimethyl(triphenylphosphoranylideneacetone)tin;[38] 31 = Benzyltriphenylphosphoniumdichlorotributyltin;[39] 33,34 = bis(μ_3-sulfido)-bis-(bis(triphenylphosphine)gold)gold(I)dichlorotrimethyltin;[40] 36 = Benzyltriphenylphosphoniumdichlorotributyltin.[39]

TABLE II
Sn–Cl distances, C–Sn–Cl angle and charges on Sn and Cl, calculated by means of the MNDO-calculation for $(CH_3)_3SnCl$ and its adducts with several donor molecules.

	Q_{Sn}	Q_{Cl}	d_{Sn-Cl}	$\alpha_{C-Sn-Cl}$
$(CH_3)_3SnCl$	0.322	−0.349	2.32	105.0
$(CH_3)_3SnCl \cdot Cl^-$	0.466	−0.677	2.50	89.2
$(CH_3)_3SnCl \cdot$DMSO	0.438	−0.471	2.37	98.0
$(CH_3)_3SnCl \cdot$Pyridine	0.413	−0.560	2.42	90.0
$(CH_3)_3SnCl \cdot$HMPT	0.478	−0.534	2.41	93.5

All structural changes, like changes in charge distribution and at the C–Sn–Cl angle are found to be sensitive to changes of distance between the tin atom and the donor. As an example, the distance between Cl^- acting as donor towards the Sn, *i.e.*, $d_{Cl^- \to Sn}$, has been varied to calculate the changes in atomic charges, $\alpha_{C-Sn-Cl}$ and the total energies for the adduct $(CH_3)_3SnCl \cdot Cl^-$ (see Table III). It can be seen that with decreasing $d_{Cl^- \to Sn}$ the positive charge at the tin atom is increased and the charge at the originally bound chlorine atom is shifted to more negative values, again indicating the spillover effect at the acceptor atom as well as the pile up at the Cl atom.[3,42] The total energy is decreased until it reaches its minimum at equal $d_{Cl^- \to Sn}$ and d_{Sn-Cl} distances.

TABLE III
MNDO-results for decreasing distance of Cl^- acting as a donor towards the Sn–atom in $(CH_3)_3SnCl$.

$d_{Cl^- \to Sn}$, Å α	d_{Sn-Cl}, Å	Q_{Sn}	Q_{Cl^-}[a]	Q_{Cl}	$\alpha_{C-Sn-Cl}$	E/kJ mol^{-1}
4.00	2.36	0.400	−0.994	−0.452	103.2	−107.9
3.80	2.36	0.411	−0.987	−0.465	102.5	−108.3
3.60	2.37	0.424	−0.974	−0.483	101.4	−108.8
3.40	2.38	0.439	−0.952	−0.506	99.9	−109.8
3.20	2.40	0.452	−0.914	−0.537	98.0	−111.6
3.00	2.41	0.458	−0.860	−0.565	97.0	−115.0
2.90	2.43	0.462	−0.828	−0.585	95.8	−117.0
2.80	2.44	0.465	−0.793	−0.605	94.6	−119.3
2.70	2.46	0.467	−0.755	−0.625	93.3	−121.3
2.60	2.48	0.468	−0.709	−0.656	90.6	−122.8
2.50	2.50	0.467	−0.669	−0.676	89.2	−123.6

[a] Cl^- represents the Cl-atom acting as a donor towards $(CH_3)_3SnCl$.

To see the mutual internal interactions of the structural changes, *i.e.* the bond angle, the Sn–Cl distance and the atomic charge of free $(CH_3)_3SnCl$ without the additional influence of a donor molecule have been calculated using increasing $\alpha_{Cl-Sn-C}$ as constraint, whereas the rest of the geometry was optimized to minimize the total molecular energy. The calculated dependence of d_{Sn-Cl} is similar to the distances experimentally found in the crystalline state (Table IV) and is the same as found at $(CH_3)_3SnCl \cdot Cl^-$. By analogy the charges on Sn and on Cl increase with decreasing $\alpha_{Cl-Sn-C}$ and decreasing d_{Sn-Cl}. This shows that the structural changes due to the attack of a donor can hardly be separated in terms of its electron-donating ability and changes of acceptor geometry due to steric interactions.

TABLE IV

Effects of variation of the Cl–Sn–C angle in free $(CH_3)_3SnCl$.

$\alpha_{Cl\text{-}Sn\text{-}C}$	dSn–Cl	Q_{Sn}	Q_{Cl}
110.0	2.310	0.3239	−0.3122
107.5	2.317	0.3234	−0.3308
105.0	2.324	0.3214	−0.3496
102.5	2.332	0.3180	−0.3686
100.0	2.341	0.3134	−0.3878
97.5	2.352	0.3077	−0.4070
95.0	2.363	0.3010	−0.4260
92.5	2.376	0.2935	−0.4446
90.0	2.389	0.2854	−0.4626

TABLE V

^{119}Sn NMR-shifts, ^{119}Sn-^{1}H coupling constants and reaction enthalpies for $(CH_3)_3SnCl$–donor complex formation.

Solvent	δ^{119}Sn/ppm[b]	J(^{119}Sn^{1}H)/Hz[a]	ΔH°$(CH_3)_3$SnCl.EPD/kJ mol^{-1} [c]
dichloromethane	−168.9		
hexane	−153.5	58.0	
CS_2	−152.7		
benzene	−161.6	58.1	
chloroform		57.8	
nitrobenzene		60.5	
1,4 dioxane	−121.5	61.6	
acetone	−109.3	66.2	23.8
acetonitrile	−111.5	64.7	20.1
tetrahydrofurane		65.8	
dimethylacetamide		69.5	33.1
dimethylformamide		69.6	
pyridine		68.0	27.2
dimethylsulfoxide	−179.3	70.0	34.3
hexamethyl-phosphotriamide		71.6	42.3

[a] From Ref. [1,43,46]

[b] From Ref. [51]

[c] From Ref. [44,47]

The solvent of trimethylchlorostannane has also been investigated by ^{119}Sn NMR spectroscopy,[43] ^{1}H NMR spectroscopy,[44,45,46] Moessbauer spectroscopy[47] and reaction enthalpy measurements.[44,47,48] ^{119}Sn NMR shifts and the ^{119}Sn–^{1}H coupling constants are found to decrease almost linearly with the absorption frequency of the Sn–Cl stretching vibration in the IR spectrum for all investigated solvents, with the exception of DMSO. A linear relationship between the ^{119}Sn-^{1}H coupling constant, J, and the participation of the tin s orbital in the Sn–C bond has been proposed[49] as $J(^{119}Sn^{1}H) = 2.16\rho$, where ρ is the contribution of the tin s orbital to the tin–carbon bond. The constant 2.16 was evaluated from the coupling constant measured for $(CH_3)_4Sn$ and ρ assumed to be 25% for an ideal tetrahedral structure. For trimethylchlorostannane dissolved in hexane (DN = 0) ρ is found to be 26.9% and in HMPT (DN = 38.8) 33.1%, which is close to the volume 33.3% expected for the ideal trigonal bipyramidal structure. In solvents of a DN between those of hexane and HMPT the ρ values lie between these two values following the order given by the donor number.[44] The Sn–H coupling constant has also been related to changes in the partial charge at the tin atom.[50,51] This approach has been criticized by Bolles and Drago,[44] but the results are in agreement with the spillover effect of negative charge at the acceptor atom,[3,42] and this effect has been confirmed by the results of the MNDO calculations.

All these results show that a continuous set of molecular geometries exist between the tetrahedral and trigonal bipyramidal arrangements and that the bipyramidal form is approached more closely as the solvent DN is increased.

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