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Structural analysis of 2,6-[bis(alkyloxy)methyl]-phenyltin derivatives using electrospray ionization mass spectrometry

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Electrospray ionization (ESI) mass spectrometry was applied to the structural analysis of 23 2,6-[bis(alkyloxy)methyl]phenyltin(IV) derivatives. The mass spectra were measured in both polarity modes and multistage tandem mass spectrometric (MS^n) measurements were performed on the ion trap analyser for positively charged tin-containing ions. The sum of complementary ions observed in the positive-ion mode (i.e. $[M-R^3]^+$ ion) and in the negative-ion mode (i.e. $[R^3]^-$ ion) permits molecular mass determination in spite of the fact that the molecular adducts were often missing even in the first-order mass spectra. The subsequent fragmentation of $[M-R^3]^+$ ions studied by MS^n and the correlation of observed fragment ions with the expected structures of synthesized organotin(IV) compounds allowed us to understand the fragmentation behaviour and the mechanism of the ion formation for studied compounds. The typical neutral losses are alkenes, alcohols and aldehydes. The fragmentation pattern of one selected compound was supported by MS^n measurements of an isotopically labelled analogue to confirm unusual ion–molecule reactions of some fragment ions with water in the ion trap. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: electrospray ionization; organotin(IV); organometallic compounds; speciation; ion trap

INTRODUCTION

Organotin(IV) compounds exhibit interesting biological properties with important industrial and agricultural applications.[1] They are frequently used as biocides, for example as antifouling paints on ships or wood preservatives. Other typical applications are in agricultural herbicides, fungicides and insecticides and in industry as stabilizers for PVC or catalysts.[2] They are also studied because of potential antitumor activity.[1] However, their further study in the medical area is limited by their low aqueous solubility. This drawback could be improved by using new organotin compounds with ionic character, which should have better solubility in water.[3] The wide range of applications and the synthesis of new organotin compounds has led to a need for a reliable and, if possible, fast and cheap analytical method for their structural characterization.

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Nuclear magnetic resonance (NMR) spectroscopy is an established technique for the structural analysis of organotin compounds, where the values of $\delta(^{119}Sn)$ and $^nJ(^{119}Sn, ^{13}C)$ are especially important. Organotin compounds containing intramolecularly coordinating Y,C,Y-chelating ligands (Y = donor-containing substituent), which represents a group of so-called hypervalent or hypercoordinated organotin(IV) compounds,[4–10] have been extensively studied to understand the properties and stereochemistry, mainly using temperature-dependent NMR spectra parameters (^1H and ^{119}Sn). The synthesis, characterization and properties of phenyltin derivatives of 2,6-[bis(dimethylaminomethyl)phenyl](N,C,N-pincer) ligands[3,11,12] and some 2,6-[bis(alkyloxy)methyl]-phenyl-(O,C,O) ligands[13] were described in our previous papers with brief descriptions of their electrospray mass spectra.

Electrospray ionization (ESI) is one of the softest ionization techniques, which can be easily coupled to liquid-phase separation techniques, such as high-performance liquid chromatography (HPLC). The soft character of ESI allows the molecular mass (M) determination of many organometallic[14–16] and metal complex compounds.[17] Applications of ESI to the analysis of organotin compounds have been reported from the beginning of the electrospray

era.[18] Most studies were performed on simple organotin compounds.[18–22] The potential of coupling ESI to HPLC for the sensitive quantitation of organotin pollutants[18,22,23] has also been investigated, e.g. tributyltin in a sediment reference material[18] and tri- and diphenyltin and tri-, di- and monobutyltin in water.[22]

Before the advent of ESI, the conventional electron ionization (EI) was the ionization technique of choice in the analysis of more volatile organotin compounds. EI fragmentation patterns of simple organotin compounds with one to four aryl or alkyl substituents have been described.[24–27] The typical neutral losses are alkenes and the majority of fragment ions are even-electron ions except for the molecular radical-cation $M^{+\bullet}$ and diaryl- and dialkyltin radical ions, which are similar to those in soft ionization techniques. EI mass spectra yield many fragment ions, but this advantage may also be a limiting factor of EI owing to the extensive fragmentation and hence the lack of molecular mass information. This drawback can be overcome by ESI with an ion trap analyser, which combines the information about the M obtained from the first-order mass spectra and additional structural information based on multistage tandem mass spectrometric (MS^n) analyses, as shown recently in our study of metal complexes of azo dyes.[17] The application of such an approach for studying the fragmentation behaviour of more complex organotin compounds[28,29] is rare and many papers orientated mainly towards synthetic aspects only claim that the structures or molecular masses were confirmed by ESI-MS without further reasoning. Cluster ions with more tin atoms can be also analysed by ESI-MS,[30,31] but the isotopic patterns are very complex, and therefore the use of a high-resolution mass spectrometer, such as ion-cyclotron resonance mass spectrometer with Fourier transformation, is advantageous.[32,33]

In the present work, the possibilities of ESI-MS for the structural analysis of a series of 23 2,6-[bis(alkyloxy)methyl]-phenyltin derivatives were studied using first-order and MS^n spectra in both positive and negative-ion modes. The basic mechanisms of ion formation are suggested. Some unusual adduct formations are discussed and confirmed with isotopically labelled standards.

EXPERIMENTAL

Organotin(IV) compounds

All organotin(IV) compounds studied (Table 1) were synthesized in our laboratory according to published methods.[3,8,9] The structures were confirmed by ^1H, ^{13}C and ^{119}Sn NMR spectra and x-ray diffraction measurements in the solid state. Prior to the mass spectrometric analysis, the individual organotin compounds were extracted into hexane, filtered and evaporated to dryness to remove inorganic material.

Instrumentation

ESI mass spectra were measured on an Esquire 3000 ion trap analyser (Bruker Daltonics, Bremen, Germany). The samples were dissolved in acetonitrile (Merck, Darmstadt, Germany) at concentrations of ~0.1–0.5 mmol l^{-1} and analysed by direct infusion at a flow-rate of 1–3 µl min^{-1}. Mass spectra were recorded in the range m/z 15–1000 both in the negative- and positive-ion modes. The ion trap analyser was tuned to give an optimum response for m/z 400–600 according to the expected m/z values, i.e. the tuning parameter 'target mass' was set to m/z 400–600. The ion source temperature was 300 °C and the flow-rate and pressure of nitrogen were 4 l min^{-1} and 10 psi, respectively. The isolation width for MS^n experiments was set to $m/z = 8$ and the collision amplitude was selected depending on the stability of particular fragment ions in the range 0.6–1 V (exact values are given in Table 2). The negative-ion ESI mass spectra of small inorganic anions with $m/z < 100$ (chlorides) were measured on a Platform quadrupole analyser (Micromass, UK) with the following settings: mass range m/z 35–400, ion source temperature 100 °C, cone voltage 30 V and flow-rate 10 µl min^{-1}.

ESI mass spectra

Positive-ion ESI mass spectra

The ions observed in the first-order ESI mass spectra, MS/MS of $[Cat]^+$ as a precursor ion and some other fragment ions observed in MS^n measurements are summarized in Table 2. The relative abundances of $[M + Na]^+$ and $[M + K]^+$ depend on the salt content in individual samples and may differ from the listed values for these ions.

Negative-ion ESI mass spectra

The following ions were observed in the first-order negative-ion ESI mass spectra. The theoretical relative abundances are given in parentheses.

$[Cl]^-$ (compounds **2**–**4**, **6**, **7**, **9**–**11**, **13**, **14**): m/z 35, 100% (theoretical 100%); m/z 37, 33% (32%).

$[CF_3COO]^-$ (**15**): m/z 113, 100%, $[CF_3COO]^-$; m/z 249, 70%, $[(CF_3COO)_2Na]^-$; m/z 385, 34%, $[(CF_3COO)_3Na_2]^-$; m/z 521, 77%, $[(CF_3COO)_4Na_3]^-$; m/z 665, 16%, $[M + CF_3COO]^-$.

$[CF_3COO]^-$ (**20**): m/z 113, 20%, $[CF_3COO]^-$; m/z 249, 73%, $[(CF_3COO)_2Na]^-$; m/z 385, 37%, $[(CF_3COO)_3Na_2]^-$; m/z 521, 77%, $[(CF_3COO)_4Na_3]^-$; m/z 749, 100%, $[M + CF_3COO]^-$.

$[CF_3SO_3]^-$ (**18**, **23**): m/z 149, 100% (100%); m/z 150, 1% (2%); m/z 151, 5% (5%); m/z 321, 17%, $[(CF_3SO_3)_2Na]^-$.

$[HgI_3]^-$ (**19**): m/z 579, 22% (34%); m/z 580, 39% (57%); m/z 581, 74% (78%); m/z 582, 40% (45%); m/z 583, 100% (100%); m/z 585, 20% (23%); m/z 127, 25%, I^-.

$[PF_6]^-$ (**17**, **22**): m/z 145, 100% (100%).

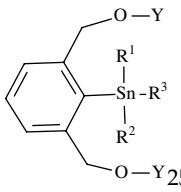
$[I]^-$ (**16**, **21**): m/z 127, 100% (100%); m/z 381, 8%, I_3^-.

RESULTS AND DISCUSSION

Analytical approach

Twenty-three 2,6-[bis(alkyloxy)methyl]phenyltin derivatives were analysed using both positive- and negative-ion ESI-MS together with MS^n. The structures of the compounds studied are shown in Table 1 with different substituents R^1, R^2 and R^3 and four different ligands containing methyl (Me), ethyl (Et), isopropyl (Pr) and *tert*-butyl (Bu). The substituents R can be the combinations of phenyl and Cl for compounds

Table 1. Organotin compounds studied with their molecular masses (*M*) and *m/z* values of cationic (Cat) and anionic (An) parts of molecules: $[Cat]^+$ is the base peak in positive-ion ESI mass spectra and corresponds to $[M-R^3]^+$; $[An]^-$ is the base peak in negative-ion ESI mass spectra and corresponds to $[R^3]^-$



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Compound	Y	R^1	R^2	R^3	M	$[Cat]^+$	$[An]^-$
1	CH_3	Phenyl	Phenyl	Phenyl	516	439	—
2	CH_3	Phenyl	Phenyl	Cl	474	439	35
3	CH_3	Phenyl	Cl	Cl	432	397	35
4	CH_3	Cl	Cl	Cl	390	485[a]	35
5	CH_2CH_3	Phenyl	Phenyl	Phenyl	544	567[b]	—
6	CH_2CH_3	Phenyl	Phenyl	Cl	502	467	35
7	CH_2CH_3	Phenyl	Cl	Cl	460	425	35
8	$(CH_3)_2CH$	Phenyl	Phenyl	Phenyl	572	495	—
9	$(CH_3)_2CH$	Phenyl	Phenyl	Cl	530	495	35
10	$(CH_3)_2CH$	Phenyl	Cl	Cl	488	453	35
11	$(CH_3)_2CH$	Cl	Cl	Cl	446	597[a]	35
12	$(CH_3)_3C$	Phenyl	Phenyl	Phenyl	600	623[b]	—
13	$(CH_3)_3C$	Phenyl	Phenyl	Cl	558	523	35
14	$(CH_3)_3C$	Phenyl	Cl	Cl	516	481	35
15	CH_3	Phenyl	Phenyl	CF_3COO	552	439	113
16	CH_3	Phenyl	Phenyl	I	566	439	127
17	CH_3	Phenyl	Phenyl	PF_6	584	439	145
18	CH_3	Phenyl	Phenyl	CF_3SO_3	588	439	149
19	CH_3	Phenyl	Phenyl	HgI_3	1022	439	583
20	$(CH_3)_3C$	Phenyl	Phenyl	CF_3COO	636	523	113
21	$(CH_3)_3C$	Phenyl	Phenyl	I	650	523	127
22	$(CH_3)_3C$	Phenyl	Phenyl	PF_6	668	523	145
23	$(CH_3)_3C$	Phenyl	Phenyl	CF_3SO_3	672	523	149

[a] Instead of $[Cat]^+$, we observed $[M^* - Cl]^+$, where $M^* = 2M - SnCl_4$.

[b] $[M + Na]^+$ is observed instead of $[Cat]^+$.

Table 2. Ions observed in the first-order positive-ion ESI mass spectra, tandem mass spectra (MS/MS) of the cationic part $[Cat]^+$ as a precursor ion and other fragment ions in MS^n spectra[a]

Compound	MS	MS/MS of $[Cat]^+$	Other fragment ions observed in MS^n
1	*m/z* 477, 9%, $[M + K - C_6H_6]^+$; *m/z* 461, 11%, $[M + Na - C_6H_6]^+$; *m/z* 439, 100%, $[M - C_6H_5]^+$	*m/z* 407, 10%, $[Cat - methanol]^+$; *m/z* 377, 95%, $[Cat - methanol - methanal]^+$; *m/z* 375, 100%, $[Cat - 2 \times methanol]^+$; *m/z* 347, 15%, $[Cat - 2 \times acetone]^+$; *m/z* 299, 4%, $[Cat - methanol - methanal - C_6H_6]^+$; *m/z* 255, 22%, $[Cat - 2 \times methanol - Sn]^+$; *m/z* 197, 7%, $[C_6H_5Sn]^+$; *m/z* 179, 6%, $[C_6H_3C_6H_4CH_2(CH_2)]^+$; *m/z* 165, 4%, $[C_6H_4C_6H_3CH_2]^+$	*m/z* 242, $[C_6H_5C_6H_3CH_2C_6H_4]^{+\bullet}$; *m/z* 229, $[C_6H_5C_6H_4C_6H_4]^+$; *m/z* 211, $[C_6H_5CH_2Sn]^+$
5	*m/z* 583, 56%, $[M + K]^+$; *m/z* 567, 100%, $[M + Na]^+$	No fragment ions[b]	
8	*m/z* 495, 100%, $[M - C_6H_5]^+$; *m/z* 453, 7%, $[M - C_6H_5 - propene]^+$	*m/z* 453, 100%, $[Cat - propene]^+$; *m/z* 411, 15%, $[Cat - 2 \times propene]^+$; *m/z* 393, 11%, $[Cat - 2 \times propene - H_2O]^+$; *m/z* 351, 23%, $[Cat - 2 \times propene - C_6H_6 + H_2O]^+$;	*m/z* 333, $Cat - 2 \times propene - C_6H_6]^+$; *m/z* 211, $[Cat - propene - propane - C_6H_6 - Sn]^+$; *m/z* 137, $[SnOH]^+$

(*continued overleaf*)

Table 2. (*Continued*)

Compound	MS	MS/MS of $[Cat]^+$	Other fragment ions observed in MS^n
		m/z 315, 45%, $[Cat - 2 \times propene - C_6H_6 - H_2O]^+$; m/z 285, 5%, $[Cat - 2 \times propene - C_6H_6 - H_2O - CH_2O]^+$; m/z 237, 6%, $[Cat - 2 \times propene - 2 \times C_6H_6 - H_2O]^+$; m/z 197, 4%, $[C_6H_5Sn]^+$; m/z 179, 39%, $[C_6H_3C_6H_3CH_3(CH_2)]^+$; m/z 165, 9%, $[C_6H_4C_6H_3CH_2]^+$	
12	m/z 639, 70%, $[M + K]^+$; m/z 623, 100%, $[M + Na]^+$	No fragment ions[b]	
2, **15**–**19**	m/z 513, 3%, $[M + K]^+$; m/z 497, 3%, $[M + Na]^+$; m/z 439, 100%, $[M - R^3]^+$	m/z 409, 7%, $[Cat - methanal]^+$; m/z 407, 7%, $[Cat - methanol]^+$; m/z 377, 97%, $[Cat - methanol - methanal]^+$; m/z 375, 100%, $[Cat - 2 \times methanol]^+$; m/z 299, 3%, $[Cat - methanol - methanal - C_6H_6]^+$; m/z 257, 8%, $[Cat - methanol - methanal - Sn]^+$; m/z 255, 19%, $[Cat - 2 \times methanol - Sn]^+$; m/z 197, 4%, $[C_6H_5Sn]^+$; m/z 179, 6%, $[C_6H_3C_6H_4CH_2(CH_2)]^+$; m/z 165, 2%, $[C_6H_4C_6H_3CH_2]^+$	m/z 242, $[C_6H_5C_6H_3CH_2C_6H_4]^{+\bullet}$; m/z 229, $[C_6H_5C_6H_4C_6H_4]^+$;
6	m/z 467, 100%, $[M - Cl]^+$	m/z 423, 7%, $[Cat - ethanal]^+$ m/z 421, 8%, $[Cat - ethanol]^+$; m/z 377, 100%, $[Cat - ethanol - ethanal]^+$; m/z 375, 91%, $[Cat - 2 \times ethanol]^+$; m/z 301, 14%, $[Cat - ethanol - ethanal - C_6H_4]^+$; m/z 299, 13%, $[Cat - ethanol - ethanal - C_6H_6]^+$; m/z 257, 12%, $[Cat - ethanol - ethanal - Sn]^+$; m/z 255, 14%, $[Cat - 2 \times ethanol - Sn]^+$; m/z 197, 10%, $[C_6H_5Sn]^+$; m/z 179, 10%, $[C_6H_3C_6H_4CH_2(CH_2)]^+$; m/z 165, 4%, $[C_6H_4C_6H_3CH_2]^+$	
9	m/z 495, 100%, $[M - Cl]^+$; m/z 453, 4%, $[M - Cl - propene]^+$	m/z 453, 100%, $[Cat - propene]^+$; m/z 411, 22%, $[Cat - 2 \times propene]^+$; m/z 393, 8%, $[Cat - propene - isopropanol]^+$; m/z 351, 18%, $[Cat - 2 \times propene - C_6H_6 + H_2O]^+$; m/z 333, 9%, $[Cat - 2 \times propene - C_6H_6]^+$; m/z 315, 53%, $[Cat - 2 \times propene - C_6H_6 - H_2O]^+$; m/z 285, 5%, $[Cat - 2 \times propene - C_6H_6 - H_2O - CH_2O]^+$; m/z 239, 8%, $[Cat - 2 \times propene - C_6H_6 - H_2O - C_6H_4]^+$; m/z 195, 3%, $[Cat - 2 \times propene - C_6H_6 - H_2O - Sn]^+$; m/z 179, 25%, $[C_6H_3C_6H_4CH_2(CH_2)]^+$; m/z 165, 6%, $[C_6H_4C_6H_3CH_2]^+$	
13, **20**–**23**	m/z 523, 100%, $[M - R^3]^+$; m/z 467, 61%, $[M - R^3 - isobutene]^+$; m/z 411, 58%, $[M - R^3 - 2 \times isobutene]^+$	m/z 467, 100%, $[Cat - isobutene]^+$; m/z 411, 92%, $[Cat - 2 \times isobutene]^+$; m/z 351, 5%, $[Cat - 2 \times isobutene - C_6H_6 + H_2O]^+$	m/z 333, $[Cat - 2 \times isobutene - C_6H_6]^+$; m/z 315, $[Cat - 2 \times isobutene - C_6H_6 - H_2O]^+$; m/z 285, $[C_6H_3C_6H_4(CH_2)Sn]^+$; m/z 179, $[C_6H_3C_6H_4CH_2(CH_2)]^+$; m/z 137, $[SnOH]^+$

(*continued overleaf*)

Table 2. (*Continued*)

Compound	MS	MS/MS of $[Cat]^+$	Other fragment ions observed in MS^n
3	m/z 471, 12%, $[M + K]^+$; m/z 455, 20%, $[M + Na]^+$; m/z 397, 100%, $[M - Cl]^+$	m/z 367, 21%, $[Cat - methanal]^+$; m/z 353, 25%, $[Cat - ethanal]^+$; m/z 335, 100%, $[Cat - methanol - methanal]^+$; m/z 299, 14%, $[Cat - methanol - methanal - HCl]^+$; m/z 179, 7%, $[C_6H_3C_6H_4CH_2(CH_2)]^+$; m/z 155, 18%, $[SnCl]^+$	m/z 197, $[C_6H_5Sn]^+$; m/z 165, $[C_6H_4C_6H_3CH_2]^+$
7	m/z 483, 3%, $[M + Na]^+$; m/z 425, 100%, $[M - Cl]^+$	m/z 397, 26%, $[Cat - ethene]^+$; m/z 379, 33%, $[Cat - ethanol]^+$; m/z 337, 64%, $[Cat - 2 \times ethanal]^+$; m/z 335, 100%, $[Cat - ethanol - ethanal]^+$; m/z 315, 49%, $[Cat - 2 \times ethanol - HCl + H_2O]^+$; m/z 301, 28%, $[Cat - 2 \times ethanal - HCl]^+$; m/z 299, 35%, $[Cat - ethanol - ethanal - HCl]^+$; m/z 237, 5%, $[Cat - 2 \times ethanol - HCl - C_6H_6 + H_2O]^+$; m/z 197, 5%, $[C_6H_5Sn]^+$; m/z 179, 42%, $[C_6H_3C_6H_4CH_2(CH_2)]^+$; m/z 165, 7%, $[C_6H_4C_6H_3CH_2]^+$; m/z 155, 9%, $[SnCl]^+$;	
10	m/z 527, 23%, $[M + K]^+$; m/z 511, 6%, $[M + Na]^+$; m/z 453, 100%, $[M - Cl]^+$; m/z 411, 3%, $[M - Cl - propene]^+$	m/z 411, 100%, $[Cat - propene]^+$; m/z 393, 5%, $[Cat - isopropanol]^+$; m/z 369, 68%, $[Cat - 2 \times propene]^+$; m/z 351, 22%, $[Cat - propene - isopropanol]^+$; m/z 315, 2%, $[Cat - propene - isopropanol - HCl]^+$; m/z 179, 10%, $[C_6H_3C_6H_4CH_2(CH_2)]^+$	
14	m/z 555, 15%, $[M + K]^+$; m/z 539, 32%, $[M + Na]^+$; m/z 519, 7%, $[M + K - HCl]^+$; m/z 503, 6%, $[M + Na - HCl]^+$; m/z 481, 100%, $[M - Cl]^+$; m/z 425, 54%, $[M - Cl - isobutene]^+$; m/z 369, 58%, $[M - 2 \times isobutene]^+$	m/z 425, 90%, $[Cat - isobutene]^+$; m/z 369, 100%, $[Cat - 2 \times isobutene]^+$	m/z 351, $[Cat - 2 \times isobutene - C_6H_6 + H_2O]^+$; m/z 315, $[Cat - 2 \times isobutene - C_6H_6 - H_2O]^+$; m/z 285, $[C_6H_3C_6H_4(CH_2)Sn]^+$; m/z 179, $[C_6H_3C_6H_4CH_2(CH_2)]^+$
4	m/z 485, 100%, $[M^* - Cl]^+$; m/z 455, 8%, $[M^* - Cl - CH_2O]^+$; m/z 355, 3%, $[M - Cl]^+$	m/z 455, 94%, $[M^* - Cl - methanal]^+$; m/z 425, 33%, $[M^* - Cl - 2 \times methanal]^+$; m/z 395, 8%, $[M^* - Cl - 3 \times methanal]^+$; m/z 365, 8%, $[M^* - Cl - 4 \times methanal]^+$; m/z 349, 8%, $[M^* - Cl - 3 \times methanal - acetone]^+$; m/z 285, 19%, $[C_6H_3(CH_2OCH_3)_2Sn]^+$; m/z 255, 7%, $[285 - methanal]^+$; m/z 223, 8%, $[285 - methanal - methanol]^+$; m/z 205, 100%, $[CH_3SnCl_2]^+$; m/z 192, 85%, $[H_2SnCl_2]^+$	m/z 363, $[M^* - Cl - 3 \times methanal - methanol]^+$; m/z 225, $[285 - 2 \times methanal]^+$
11	m/z 655, 3%, $[M^* + Na]^+$; m/z 597, 100%, $[M^* - Cl]^+$; m/z 519, 10%, $[M^* - Cl - HCl - propene]^+$; m/z 477, 1%, $[M^* - Cl - HCl - 2 \times propene]^+$	m/z 519, 100%, $[M^* - Cl - HCl - propene]^+$; m/z 477, 50%, $[M^* - Cl - HCl - 2 \times propene]^+$; m/z 435, 32%, $[M^* - Cl - HCl - 3 \times propene]^+$; m/z 393, 20%, $[M^* - Cl - HCl - 4 \times propene]^+$; m/z 375, 7%, $[M^* - Cl - HCl - 4 \times propene - H_2O]^+$	m/z 357, $[M^* - Cl - HCl - 4 \times propene - 2 \times H_2O]^+$

[a] $[Cat]^+$ corresponds to $[M-R^3]^+$. The fragmentation amplitude is 1 V for **1**, **2**, **4**–**6**, **8** and **14**–**19**, 0.9 V for **3** and **7**, 0.8 V for **9**, **12**, **20**–**24**, 0.7 V for **13** and 0.6 V for **10**. Organotin compounds were synthesized with four different ligands (L), which are methyl (Me), ethyl (Et), iso-propyl (Pr) and *tert*-butyl (Bu). The relative abundances are based on the ^{120}Sn ions.

[b] $[M + Na]^+$ is observed instead of $[Cat]^+$.

1–**14** or two phenyls with one other anionic species R^3 for **15**–**23** (see Table 1). The most labile (i.e. the most polar) bond is cleaved first, yielding the base peaks in the positive-ion ESI mass spectra, $[Cat]^+$, and in negative-ion ESI mass spectra, $[An]^-$. The symbol $[Cat]^+$ is used for $[M-R^3]^+$ ions through the text, where R^3 is the most polar substituent bonded to the central tin atom. The counterpart $[R^3]^-$ is written schematically as $[An]^-$. Unlike the ESI mass spectra of common organic molecules, the peaks of protonated molecules $[M + H]^+$ are absent in all cases, and the molecular adducts such as $[M + Na]^+$ and $[M + K]^+$ are often missing or with low relative abundances in the case of organotin or, in general, organometallic compounds.[14–16] For this reason, the ESI mass spectra in both polarity modes were recorded, and the masses of the complementary parts $[Cat]^+$ and $[An]^-$ were summed. In this way, the molecular masses can be calculated regardless of the absence of characteristic molecular adducts.

The fragmentation proceeds so easily that abundant fragment ions can be observed in the first-order positive-ion ESI mass spectra. From this reason, the value of the tuning parameter 'compound stability' can be reduced from the standard setting of 100% to, for example, 20% to avoid this unwanted fragmentation in the ion source. This approach is demonstrated in Fig. 1. The spectrum in Fig. 1(B) was measured under standard conditions (i.e. with the compound stability parameter set to 100%) and shows abundant neutral losses of one or two isobutene molecules in addition to $[M - Cl^+]$ ion. When the compound stability parameter is reduced from 100 to 20%, then all fragment ions disappear and $[M - Cl]^+$ is the only ion in the spectrum (see Fig. 1(C)), which simplifies the correct determination of $[Cat]^+$.

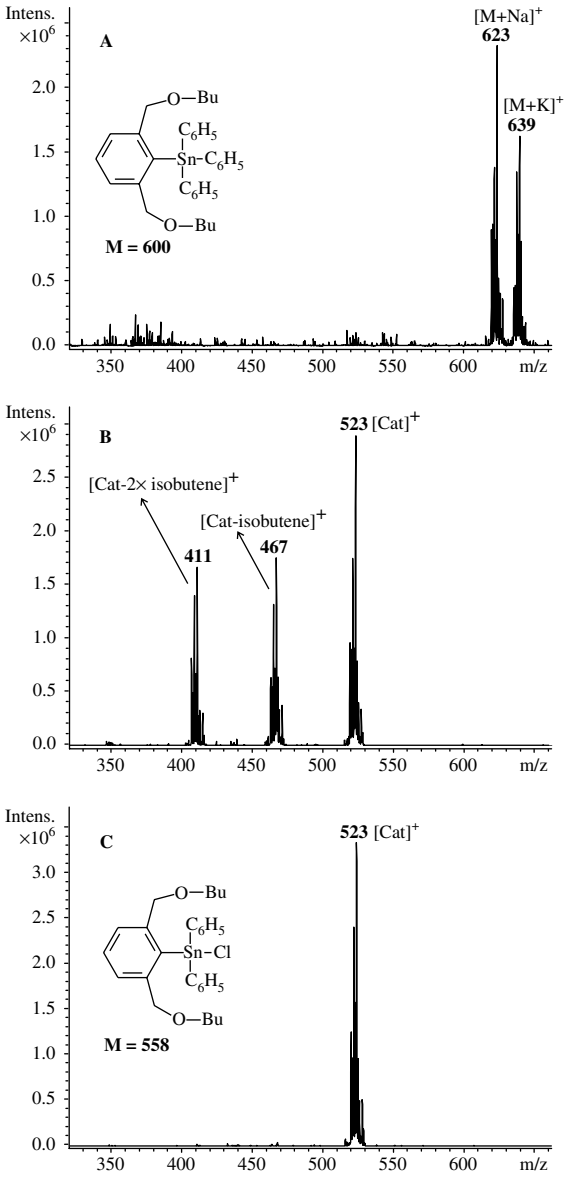

Figure 1. Positive-ion ESI mass spectra of: (A) compound **12** without a tin–halogen bond, (B) compound **13** and (C) compound **13** measured with a compound stability parameter reduced from 100 to 20%.

Mechanisms of ion formation of organotin(IV) compounds

The peaks of protonated molecules $[M + H]^+$ were totally absent in all measured spectra. Based on the analyses of bis(alkyloxy)methylphenyltin derivatives, three basic mechanisms were found to be involved in the ionization process of these organotin compounds under ESI conditions. The ionization mechanisms are listed here in order of decreasing importance.

Mechanism $M \rightarrow [M-R^3]^+ + [R^3]^-$

The basic process of ion formation is the cleavage of the most labile bond, i.e. the bond between tin and the most polar substituent bonded to the tin central atom yielding two complementary ions, $[Cat]^+$ and $[An]^-$, which are the base peaks in positive- or negative-ion ESI mass spectra for most compounds except for the positive-ion mass spectra of **4**, **5**, **11** and **12** and the negative-ion spectrum of **20**. Mostly, the polar substituent R^3 is chlorine (**2**–**4**, **6**, **7**, **9**–**11**, **13**, **14**) or other halogen- and oxygen-containing anionic species (see Table 1). The formation of base peaks in the spectra of **4**, **5**, **11** and **12** is explained below. A signal-to-noise ratio of 10 was measured for a 1×10^{-6} mol l^{-1} solution of **13** in acetonitrile, which is a typical value for this process of ion formation and also for the mechanism described in the section mechanism $M + M \rightarrow M^* + SnCl_4$ below.

Mechanism $M + Na^+ (or K^+) \rightarrow [M + Na]^+$ *(or* $[M + K]^+$*)*

When the labile tin–halogen or tin–oxygen bond is missing (**1**, **5**, **8** and **12**), then the formation of molecular adducts with alkali metal ions can be an important process of ion formation, as for **5** and **12**. Unlike common organic compounds, the ions of alkali metal adducts, $[M + Na]^+$ and $[M + K]^+$, are not accompanied by $[M + H]^+$ ions. For organotin compounds, the formation of $[M + Na]^+$ competes with the previous mechanism $M \rightarrow [M-R^3]^+ + R^3$. This competition between the two mechanisms depends on the salt content in the samples and solvents. It has been reported[21,22] that the appearance of first-order mass spectra of organotin compounds may depend on the tuning conditions, instrumentation and solvents. Fortunately, the strong dependence of the relative abundances on the precise

setting of the experimental conditions is observed only for the first-order spectra and not in MS^n experiments. The $[M + Na]^+$ ions are the base peaks in mass spectra of **5** and **12** together with abundant $[M + K]^+$ ions (Fig. 1(A)), but these are not observed at all for **1** and **8**, where the base peaks are $[M - C_6H_5]^+$ ions together with adducts $[M + Na - C_6H_6]^+$ and $[M + K - C_6H_6]^+$ in the case of **1**. Typically, the sensitivity is at least one order of magnitude worse for triphenyl-substituted derivatives than compounds containing at least one tin–chlorine bond. The addition of a small amount of formic or acetic acid (~0.1%) to the sample solution in acetonitrile may improve the signal-to-noise ratio of $[M + Na]^+$ and $[M + K]^+$ ions, but $[M + H]^+$ is again absent.

Mechanism $M + M \rightarrow M^* + SnCl_4$

Unexpected behaviour was observed for all monoorganotin derivatives containing three chlorine atoms as R^1, R^2 and R^3 substituents (**4**, **11** and our previous studies). They react in the gas phase according to the equation $M + M \rightarrow M^* + SnCl_4$, where M^* corresponds to the dimeric molecule 2M—$SnCl_4$ (for structure, see inset in Fig. 2(A)). All identified ions in the spectra come from these condensed molecules except for the $[M - Cl]^+$ ion in the case of **4** (relative abundance 3%). We analysed identical samples dissolved in deuterated acetonitrile using NMR spectroscopy to confirm that **4** and **11** are stable in the acetonitrile solution. It was found that these compounds are really stable under the measurement conditions and their structures do not change in the acetonitrile solution. This means that the reaction $M + M \rightarrow M^* + SnCl_4$ takes place in the gas phase during the mass spectrometric experiment. Figure 2(A) illustrates the first-order mass spectrum of **11**. The identification of this unexpected compound is supported by identified fragment ions in the MS/MS of $[M^* - Cl]^+$ at m/z 597 (Fig. 2(B)), clearly showing the presence of four propyl groups, one chlorine, one tin and molecular mass of $M^* = 632$. The number of chlorine atoms in particular fragment ions of organotin compounds studied can be determined on the basis of the isotopic $(A + 2)/A$ ratio, where A is the mass of the most abundant ion (100%) in tin clusters containing the ^{120}Sn isotope. This ratio is in the range 14–19% for fragment ions without chlorine, 37–41% for one chlorine atom and 56–60% for two chlorine atoms.

Fragmentation behaviour in positive-ion mode

The fragmentation behaviour of positively charged tin-containing ions was studied using MS^n analysis. The isolation width used for MS^n experiments was set to $\Delta m/z = 8$, which makes possible the determination of the presence of tin in individual fragment ions based on ^{118}Sn and ^{120}Sn isotopes. For the complete isotopic pattern of tin, an isolation width $\Delta m/z = 12$ would be needed, but it was not used in our experiments to reduce the risk of isolation of co-ions. The comparison of theoretical and experimental isotopic patterns was sufficient for the determination of the number of chlorine atoms in addition to tin.

All fragment ions observed in MS/MS and MS^n are listed in Table 2 with the suggested interpretation. For each compound, many MS^n experiments were carried out to ensure that the fragmentation paths correspond to our proposals. The typical neutral losses (NL) observed in MS^n and also in some first-order mass spectra are alkenes, alcohols, aldehydes, Sn, C_6H_6, C_6H_4, etc. Some alkyls prefer the NL of alkenes (*tert*-butyl and isopropyl), whereas others favour the loss of alcohols and aldehydes (methyl and ethyl). Concerning the oxidation state of tin, it is changes between Sn(IV) and Sn(II) in agreement with previous studies performed with either ESI[21,28] or EI.[24–27] Almost all observed ions are even-electron ions with rare exceptions, e.g. $[H_2SnCl_2]^{+\bullet}$ found in the MS/MS of **4**.

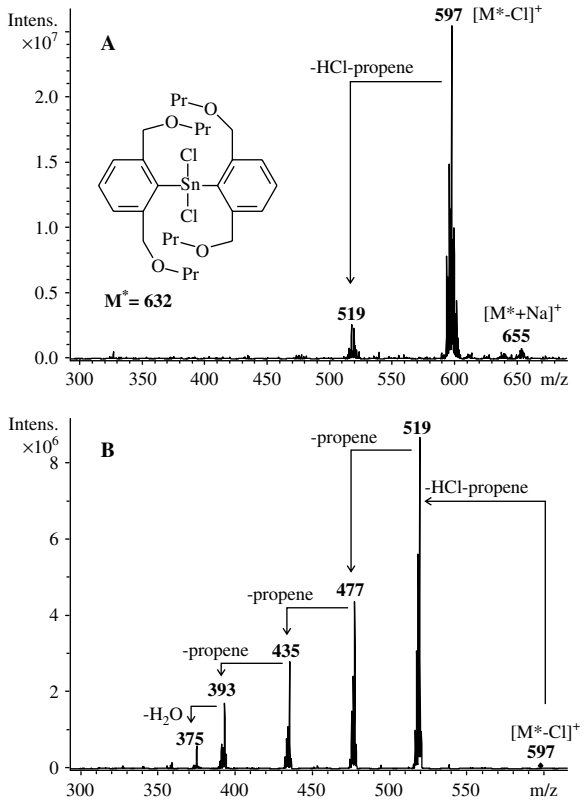

Figure 2. Positive-ion ESI mass spectra of compound **11**, which is condensed according to the reaction $M + M \rightarrow M^* + SnCl_4$. (A) First-order mass spectrum; (B) tandem mass spectrum (MS/MS) of $[M^* - Cl]^+$ at *m/z* 597. The structure of M^* is shown in (A).

Tin-containing ions are known to form easily various adducts with water[21,22,28] and methanol[21,22] and also dimeric and polymeric species[21] can be identified. We performed measurements in acetonitrile, so the methanol adducts were avoided, but we observed adducts with water, such as $[(HOCH_2)_2C_6H_3Sn(OH)C_6H_5]^+$ at m/z 351 for **8**–**10**, **13** and **20**–**23**. The alternative explanation for the m/z 351 ion had to be considered, because the m/z 351 ion is a typical ion for triphenyltin compounds, $[(C_6H_5)_3Sn]^+$. We compared the MS/MS of m/z 351 in our samples with MS/MS of m/z 351 of $[(C_6H_5)_3Sn]^+$ from our other samples. In the former case, the only observed fragment ion is $[C_6H_5Sn]^+$ at m/z 197 with a characteristic tin isotopic pattern (similarly to Fig. 2 in Ref. 19), but in the latter case the m/z 179 ion without tin is the only peak in the spectrum. The second

proof supporting our explanation is shown in Fig. 3, for MS/MS of $[M - Cl]^+$ at m/z 533 and MS^3 of m/z 533–421 for deuterated analogue of **13** with 10 deuterium atoms on both phenyl rings (see structure in the inset in Fig. 3(A)). If the m/z 351 ion corresponds to $[(C_6H_5)_3Sn]^+$, then the mass shift of m/z 351 would be $+D_{10}$, but it is only $+D_5$ in practice (see m/z 356 in Fig. 3(A)). Some other adducts with water were found in the spectra, e.g. $[Cat - 2 \times ethanol - HCl + H_2O]^+$ at m/z 315 and $[Cat - 2 \times ethanol - HCl - C_6H_6 + H_2O]^+$ at m/z 237 for **7**.

Negative-ion ESI mass spectra

From the mass spectrometric point of view, the negative-ion mass spectra were trivial, but they provided important information about the complementary negatively charged species. When the ion formation follows the $M \rightarrow [M-R^3]^+ + [R^3]^-$ mechanism (see earlier), then the only ion observed in the spectrum should be $[R^3]^-$ (see columns R^3 and $[An]^-$ in Table 1). In some cases, the dimeric or polymeric ions, such as $[2 \times An + Na]^-$ and $[3 \times An + 2Na]^-$ may be observed in addition to $[An]^-$. The relative abundances of polymeric ions $[x \times An + (x-1) \times Na]^-$ increase with increase in concentration. The typical example is CF_3COO^- with a strong ion-pairing ability, so we can observe the mentioned polymeric ions and also the molecular adduct $[M + CF_3COO]^-$, which is the peak in the spectrum of **20**. When all R^1, R^2 and R^3 are phenyls, then no signal is obtained in the negative-ion mode. For anionic parts with more complex isotopic patterns, the experimental values can be compared with the theoretical isotopic distribution, as shown in the Experimental section under Negative-ion ESI mass spectra. For low-mass ions (chlorides), the quadrupole analyser had to be used instead of the ion trap.

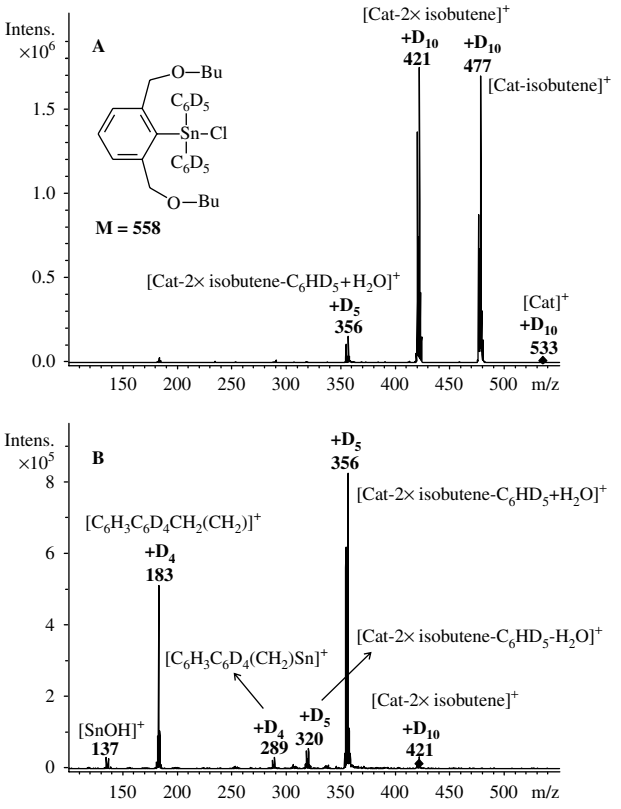

Figure 3. Positive-ion ESI mass spectra of the labelled analogue of compound **13** with 10 deuterium atoms on two phenyl rings (see inset): (A) tandem mass spectrum (MS/MS) of $[M - Cl]^+$ at *m/z* 533; (B) tandem mass spectrum (MS/MS/MS) of the fragmentation path *m/z* 533–421. The symbols $+ D_n$ show the number of deuterium atoms included in particular fragment ions.

CONCLUSIONS

ESI-MS^n not only is a powerful technique for simple organotin(IV) compounds, such as triphenyl- and tributyltin halides, but can also be successfully applied to the structural characterization of more complex organotin compounds and can be considered as a complementary analytical technique to the well-established NMR spectroscopy and x-ray diffraction. Parallel measurements in both polarity modes permit an unambiguous determination of molecular masses even in the case when the typical molecular adducts are missing. The primary formation of ions can be described by three basic mechanisms: $M \rightarrow [M-R^3]^+ + [R^3]^-$, $M + Na^+ \rightarrow [M + Na]^+$ and $M + M \rightarrow M^* + SnCl_4$, the first being the most widespread. MS^n analyses yielded many characteristic fragment ions for studying the fragmentation paths. Preference for some typical neutral losses were found. Only alkene losses are observed for *tert*-butyl and isopropyl substituents, whereas alcohol or aldehyde losses are preferred for methyl and ethyl substitution. Other neutral losses observed in MS^n spectra are Sn, C_6H_6, C_6H_4, etc. Some unusual ion–molecule reactions and adduct formation with water were recognized and confirmed with isotopically labelled standards.

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