rameters are given in Table SI.

Acknowledgment. We gratefully thank the Comisión Asesora de Investigación Científica y Técnica (ref 2001/83) and Italian Ministero della Pubblica Istruzione for financial support.

Registry No. 1, 12129-06-5; 2, 110825-75-7; 3, 110825-76-8; 4, 110850-66-3.

Supplementary Material Available: Table SI, thermal parameters (1 page); a listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

Sn–S and Sn–Se Bonding in Some Tin(IV) Compounds Studied by UV Photoelectron and NMR Spectroscopy and Pseudopotential ab Initio Calculations

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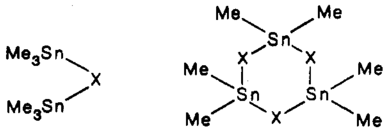
Received March 11, 1987

Tin–sulfur and tin–selenium bonding has been studied in the monomeric and trimeric units $(Me_3Sn)_2X$ and $(Me_2SnX)_3$ (X = S, Se) by means of ultraviolet photoelectron and NMR spectroscopy. The UPS results, supported by ab initio pseudopotential calculations, indicate that in $(Me_3Sn)_2X$ the HOMO is predominantly localized on the chalcogen p lone pair orbital, although a nonnegligible hyperconjugation with the orbitals of the CH_3 groups does occur. In $(Me_2SnX)_3$ the interactions between the three p lone pairs are not very strong. In contrast, both in the monomeric and in the trimeric molecules extensive delocalization of σ-electron density is suggested by the experimental and theoretical data. The NMR results show that the ^{119}Sn nuclei are remarkably deshielded in these molecules. This may be attributed not only to the presence of electronegative ligands but also to the high degree of delocalization of σ-electron density as indicated by the ultraviolet photoelectron spectra. The smaller electronegativity of selenium compared to sulfur results in a shift of the ionization energies to lower values and in an increase in ^{119}Sn nuclear shielding. The pseudopotential "ab initio" calculations confirmed their utility in the description of the electronic structure of molecules containing heavy atoms.

Introduction

In the framework of an extensive investigation on the electronic structure of organometallic compounds of group XIV (14[32]) elements containing M–S bonds (M = C, Si, Ge, Sn, and Pb),[1-3] we studied by gas-phase UV photoelectron spectroscopy (UPS) some Tin(IV) compounds, hexamethyldistannathiane, hexamethyldistannaselenane, hexamethylcyclotristannathiane, and hexamethylcyclotristannaselenane, whose schematic structures are shown below:



X = S, Se

The joint study of cyclic compounds and smaller open units, which can be considered in some way precursors of the former, provides an opportunity for verifying the changes in the tin–chalcogen bonding on passing from open to cyclic molecules, also in light of previous experience on some group XIV (14) thiospiranes.[3] In particular, we wanted to ascertain the importance of interactions between the various tin–chalcogen bonds, which in principle are allowed but not extremely favored by the geometry of the molecule, a twisted boat of C_2 symmetry in the solid state, as demonstrated by an X-ray structural analysis.[4-6] In the following discussion we will assume the same geometry also in gas phase, where the mass spectra[7,8] indicate retention of the trimeric structure. The availability of selenium-containing compounds allowed an evaluation of the influence of the substitution of chalcogen atoms on the electronic distribution. The present study is the first UPS investigation of tin–selenium containing compounds.

The UPS results were interpreted on the basis of experimental evidence (for example, He I/He II intensity variations), the comparison within the series and with parent molecules, and quantum mechanical calculations,

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(2) Andoni, E.; Cauletti, C.; Furlani, C. *Inorg. Chim. Acta* **1983**, *76*, L35.

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Table I. Ionization Energies of Some Tristannathianes and Tristannaselenanes[a]

	IE, eV					
compd	a	b	c	d	e	
$(Me_3Sn)_2S$	8.22	9.07	9.36	9.73	10.23	13.60
$(Me_3Sn)_2Se$	8.00	8.94	9.30	(9.70)	10.10	13.59
$(Me_2SnS)_3$	8.50	9.55	10.03	10.82		13.59
$(Me_2SnSe)_3$	8.31	(9.07), 9.36	9.97	10.62		13.58

[a] Shoulders in parentheses.

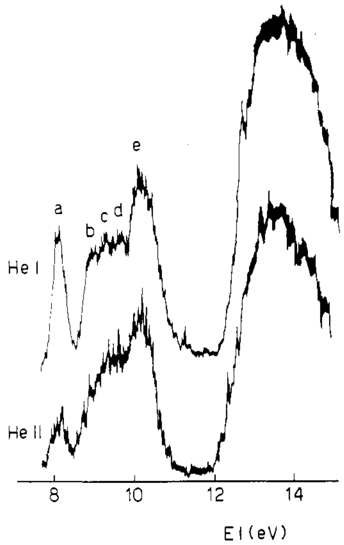

Figure 1. Gas-phase UV photoelectron spectra of $(Me_3Sn)_2S$.

namely, pseudopotential ab initio calculations performed for the sulfur-containing compounds. Such calculations already proved very reliable for organotin compounds.[9-11]

Experimental Section

The compounds were prepared by literature methods.[12,13] He I (21.22 eV) and He II (40.81 eV) spectra were recorded on a Perkin-Elmer PS 18 spectrometer equipped with a He I/He II lamp (Helectros Development) and calibrated by N_2 and He^+ as internal standards.

The ab initio LCAO-MO-SCF calculations were performed with the introduction of pseudopotentials to deal with all core electrons by using the formalism proposed by Durand and coworkers.[14,15] The pseudopotential for tin includes the major relativistic corrections[14,15] (mass and Darwin correction). The 3-1G split Gaussian basis sets[10,16,17] were optimized for each valence shell of C, S, and Sn by a pseudopotential version of the ATOM program,[18] whereas for H the standard Huzinaga Gaussian basis set[19] has been 3+1 contracted. All the molecular calculations were carried out by running the PSHONDO program[20] on a VAX 730

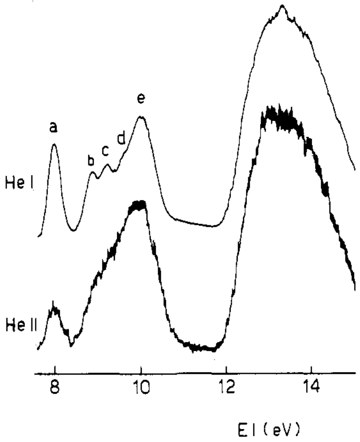

Figure 2. Gas-phase UV photoelectron spectra of $(Me_3Sn)_2Se$.

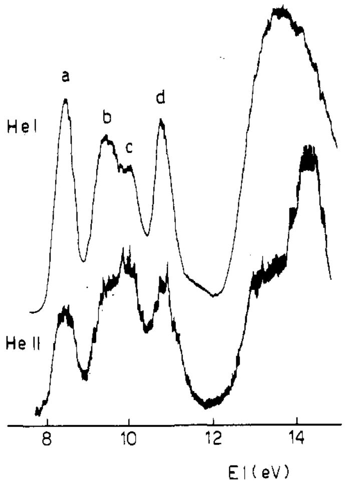

Figure 3. Gas-phase UV photoelectron spectra of $(Me_2SnS)_3$.

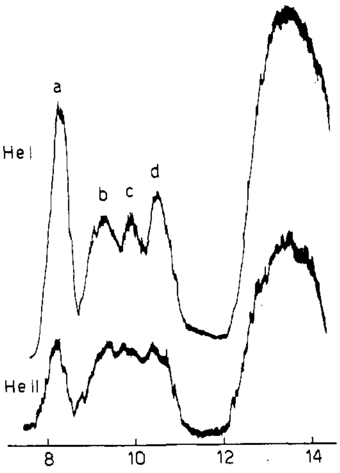

Figure 4. Gas-phase UV photoelectron spectra of $(Me_2SnSe)_3$.

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Table II. Pseudopotential ab Initio Results for $(Me_3Sn)_2S$

				% pop.				
	IE				2Sn			
MO	calcd	exptl	band label	S	s	p	6CH$_3$	dominant character
6b$_2$ (HOMO)	8.29	8.22	a	76		1	23	S lone pair
9a$_1$	8.85	9.07	b	60		10	30	Sn–S bonding MO
8b$_1$	9.41	9.36	c	20		18	62	Sn–C bonding MO
5a$_2$	9.75	9.73	d			20	80	
7b$_1$	10.10	10.23	e	36		20	44	Sn–S bonding MO
8a$_1$	10.27			15		24	61	Sn–C bonding MO
5b$_2$	10.34			18		20	62	
4a$_2$	12.87	13.60					100	CH$_3$-based MOs
6b$_1$	13.10					3	97	
3a$_2$	13.48						100	
7a$_1$	13.52				1		99	
4b$_2$	13.53						100	
5b$_1$	13.57						100	
2a$_2$	13.69					3	98	
3b$_2$	13.73			1		2	97	
4b$_1$	13.81					5	95	
6a$_1$	13.82			2	2	1	95	
5a$_1$	14.36			9	30	4	57	Sn(5s)–C bonding MO
2b$_2$	14.47						100	CH$_3$-based MOs
4a$_1$	14.72				5	3	92	
3b$_1$	15.06			12	47	1	40	Sn(5s)
3a$_1$	22.14			74	3	5	18	S(3s)
1a$_2$	22.67					2	98	CH$_3$-based MOs
2b$_1$	22.69					2	98	
2a$_1$	22.80			1		2	97	
1b$_2$	23.03					2	98	
1b$_1$	23.22				9		91	
1a$_1$	23.65			10	13		87	

(DEC) computer. Sulfur 3d and Sn(5d) polarization functions were added in a preliminary calculation on $(Me_3Sn)_2S$ to test their importance in the calculations. However, negligible occupancies were computed, which prompted us to exclude such time-consuming basis functions from the definitive calculations. The geometrical parameters for the cyclic compound were taken from the solid-state structure reported in ref 5. For the open analogue we assumed the same bond distances and Sn–S–Sn bond angle as in the cyclic structure. ^{77}Se (38.2 MHz) and ^{119}Sn (74.6 MHz) NMR spectra were measured on a Bruker WP 200 spectrometer, equipped with a multinuclear unit.

Results and Discussion

The ultraviolet photoelectron spectra are reproduced in Figures 1–4, and the corresponding ionization energies (IEs) are reported in Table I. Ab initio results for tin–sulfur (open and cyclic) compounds are reported in Tables II and III, where only those MOs detected by He I radiation (21.22 eV) are shown. The calculated IEs are obtained adopting Koopman's theorem[21] and rescaling by nine tenths the computed eigenvalues. Such a procedure gives rise to some excellent matching with the experimental figures, as found in previously studied cases.[9–11]

$(Me_3Sn)_2X$ (X = S, Se). The He I spectrum of the sulfur-containing compound has already been measured and interpreted by Distefano et al.[22] Our results, extended to the He II induced spectrum, are in numerical agreement with the previous ones, while the interpretation, supported by new experimental and theoretical data, is at variance in some points.

The spectra of hexamethyldistannathiane and hexamethyldistannaselenane (see Figures 1 and 2), quite similar with each other, show a first band, around 8 eV, strongly decreasing in intensity on passing from He I to He II spectra, followed by a series of four partly resolved bands between 9.0 and 10.5 eV and by an envelope of unresolved bands that peak around 13.0 eV. A detailed assignment of this envelope is prevented by the extended band overlapping.

The first band clearly arises from the ionization of a chalcogen-based MO. Its decrease in relative intensity on passing from He I to He II spectra in both compounds shows that the photoionization cross section of selenium 4p orbitals is smaller in He II, as expected on the basis of theoretical calculations ($\sigma_{HeI/HeII} = 17$),[23] and is analogous to the widely proven behavior of the 3p sulfur orbitals. The shift of this band by 0.22 eV to a lower IE on passing from the sulfur to the selenium derivative is consistent with the lower electronegativity of selenium.

In these molecules, therefore, the HOMO can be considered as an orbital with largely predominant chalcogen lone pair character. However, an hyperconjugative interaction of the lone pair with the σ orbitals of the rest of the molecule is in principle allowed by the molecular symmetry (C_{2v} point group) and is not in contrast with the fwhms (0.36 and 0.34 eV in the sulfur and the selenium compounds, respectively) of the first band.

Actually, the ab initio calculation on the sulfur molecule suggests a nonnegligible contribution (~23%) of CH_3 orbitals to the HOMO, as reported in Table II. The inner sequence of four bands is expected to account for ionization of six orbitals, two of mainly Sn–S and four of mainly Sn–C bonding character. The remaining two Sn–C orbitals are more stable and give rise to a band lying under the envelope centered at 13.60 eV. This stabilization is mainly due to the contribution of Sn(5s) orbitals, as already observed in calculations for other tin-containing compounds.[9–11] Table II reports the MOs ordering and composition suggested by the ab initio calculation. The good agreement between the experimental IE values and the calculated eigenvalues leads us to follow the theoretical

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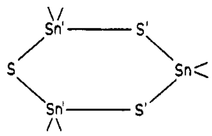
Table III. Pseudopotential ab Initio Results for $(Me_2SnS)_3$



	IE			% pop.		Sn		2Sn′		
MO	calcd	exptl	band label	S	2S′	s	p	p	$6CH_3$	dominant character
18b (HOMO)	8.32	8.50	a	47	21		1	1	10	S lone pairs
18a	8.51			30	30		1	1	38	
17b	8.63			21	50		1	3	25	
16b	9.03	9.55	b	22	31		5	7	38	Sn–S bonding
17a	9.22			21	33			10	36	
15b	9.63			20	14		1	20	34	Sn–S + Sn–C bonding MOs
16a	9.75			2	27		11	9	51	
15a	10.06	10.03	c	14	23		2	19	42	
14b	10.11			18	16		11	11	44	
13b	10.70	10.82	d	10	36		11	14	29	Sn–S bonding MO
14a	10.86			7	28		8	20	37	Sn–S + Sn–C bonding MOs
12b	10.91			10	17		11	18	54	
11b	12.98						1		99	CH_3-based MOs
13a	13.04			1	1		1	2	95	
12a	13.20			1			1		98	
11a	13.26						2		98	
10b	13.28			1			1		98	
9b	13.28							2	98	
10a	13.29						1		99	
9a	13.45			3	3		1	2	91	
8b	13.47							2	98	
7b	13.50			1	2		1	1	95	
8a	13.62			5	14		8(s)	19(s)	52	Sn(5s)–C bonding MO
6b	13.97								97	CH_3-based MOs
7a	14.01								98	
5b	14.78			11	10	2(s)	47		28	Sn(5s)–C + Sn(5d)–S bonding MOs
6a	14.81			3	19	32	16		29	

argument to assign these four bands. Accordingly, bands b, c, and d are to be assigned to single ionizations ($9a_1$, $8b_1$, and $5a_2$, respectively) while the more intense band e is attributed to three components, $7b_1$, $8a_1$, and $5b_2$. The $9a_1$ and $7b_1$ orbitals are predominantly Sn–S type, while the other ones are Sn–C type. However, an important and not unexpected result of the calculation is the significant mixing of all these orbitals, as described by the relatively high percent of sulfur and tin atoms in all outer orbitals. The He I/He II intensity ratio assignment criterion is in agreement with the proposed attribution.

Actually, taking bands c and d as a reference, we can observe that bands b and e suffer a nonnegligible relative intensity decrease due to a large chalcogen orbital contribution to the corresponding MOs. This assignment is also supported by the comparison with the data for the selenium analogue. In fact, the second band, assigned to ionization from a MO of main Sn–X character, decreases in IE on passing from the sulfur to the selenium derivative, in agreement with simple electronegativity arguments. The same shift is observed for band e, which has also a contribution from a Sn–X bonding orbital.

$(Me_2SnX)_3$ (X = S, Se). As already mentioned, these cyclic molecules possess a twisted boat conformation. The C_2 symmetry of the structure allows in principle through-space interactions between the chalcogen lone pairs and hyperconjugation of these localized functions with the rest of the molecular framework. A qualitative LCBO[24] treatment of the interactions between the chalcogen lone pairs indicates a splitting of the set of the three originally degenerate lone pairs into three levels, two of which, at higher energy, are accidentally degenerate. The value of the splitting is an indication of the importance of this through-space interaction. The ultraviolet photoelectron spectra, shown in Figures 3 and 4, suggest that this is actually quite weak, if at all. In fact, in the region between 8 and 9 eV, typical of the chalcogen lone pair ionizations, only one band is displayed, strongly decreasing in intensity on switching from He I to He II ionizing radiation, shifted by 0.19 eV upon replacing of sulfur with selenium. The expected splitting is therefore included in the width of this band (fwhm = 0.50 and 0.53 eV for sulfur and selenium derivatives, respectively). The ab initio calculation for $(Me_2SnS)_3$, whose results are reported in Table III, confirms this analysis, giving a splitting of 0.3 eV between the first, 18b, and the third, 17b, occupied MOs, all strongly localized on the sulfur atoms. It is interesting to observe that in the analogous molecule with the carbon atom, 1,3,5-trithiane, which, however, has a different geometry (chair conformation, C_{3v} symmetry), the interaction between the sulfur lone pairs is quite important, giving rise to a doublet of intensity ratio 1:2 in the photoelectron spectrum.[25]

In contrast, the ultraviolet photoelectron spectra of the silicon and germanium analogues $(Me_2MS)_3$ (M = Si, Ge), measured by Guimon et al.[26] but not discussed in detail, are quite similar to that of $(Me_2SnS)_3$, though showing an evident shoulder on the low-energy side of the first band.

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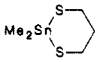
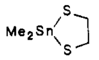
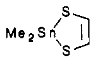
Table IV. $\delta(^{119}Sn)$ and $\delta(^{77}Se)$ Values[a] of Some Organotin–Sulfur and –Selenium Compounds

compd	$\delta(^{119}Sn)$	$\delta(^{77}Se)$	notes
$(Me_3Sn)_2S$	+87 [218.0]		*b*
$(Me_3Sn)_2Se$	+44.5 [234.7]	−547 (1060)	*b, c*
$(Me_2SnS)_3$	+128.6 [195.0]		*d, e*
$(Me_2SnSe)_3$	+42.0 [254.3]	−350 (1228)	*e, f*
$Me_3SnSeMe$	+45.6	−276.7 (1015)	*g*
$Me_2Sn(SeMe)_2$	+57.1	−237 (1190)	*g*
$Me_2Sn(SMe)_2$	+144		*h*
	+149		*i*
	+190		*i*
	+231		*k*

[a] δ Values relative to external Me_4Sn and Me_2Se, respectively; $^2J(^{119}Sn,^{119}Sn)$ values in square brackets and $^1J(^{119}Sn,^{77}Se)$ values in parentheses. [b] Kerschl, S.; Wrackmeyer, B.; Männig, D.; Nöth, H.; Staudigl, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1987**, *42B*, 387. [c] Kennedy, J. D.; McFarlane, W. *J. Organomet. Chem.* **1975**, *94*, 7. [d] Wrackmeyer, B. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 1464. [e] Blecher, A.; Mathiasch, B.; Mitchell, T. N. *J. Organomet. Chem.* **1980**, *184*, 175. [f] ^{77}Se NMR: this work in $CDCl_3$ (ca. 5%); 27–28 °C. [g] Reference 29. [h] van den Berghe, E. V.; van der Kelen, G. P. *J. Organomet. Chem.* **1971**, *26*, 207. [i] Kennedy, J. D.; McFarlane, W.; Pyne, G. S. *Bull. Soc. Chim. Belg.* **1975**, *84*, 289. [k] This work; in $CDCl_3$ (ca. 5%); 27–28 °C; $^1J(^{119}Sn,^{13}C)$ = 368.7 Hz.

This suggests a similar geometry for these molecules but a slightly greater interaction between the sulfur lone pairs in the Si and Ge derivatives.

Turning now to the Sn–S and Sn–C interactions, extended mixing is expected between the two sets of orbitals. This has already been found in the acyclic molecules and is likely to occur even to a larger extent in the cyclic molecules. The calculation for $(Me_2SnS)_3$ suggests a sequence of nine levels in the range 9–11 eV, grouped in three subsets (16b–16a, four orbitals; 15a–14b, two orbitals; 13b–12b, three orbitals), as shown in Table III. Some of these orbitals are more localized on Sn–S (16b, 17a, and 13b) or Sn–C bonds (16a), while the remaining ones are extensively delocalized along the whole molecular skeleton. Good agreement is found between the calculated and the experimental IEs. Actually, in this region the spectrum shows three partly resolved bands, whose assignment is given in Table III. He II spectrum analysis gives support to the above discussion, showing a marked decrease in the intensity of bands b and d, as compared to band c. This is in complete agreement with the population analysis reported in Table III. The spectrum of the selenium compound is very similar, the only difference being the appearance of a shoulder on the low-energy side of the band b and the shift of all the bands to lower ionization energy (see Table I).

NMR Spectra. In the compounds studied the ab initio calculations together with the UPS data should aid the interpretation of ^{119}Sn and ^{77}Se chemical shifts [$\delta(^{119}Sn)$, $\delta(^{77}Se)$, see Table IV]. For both nuclei changes in the magnetic shielding should be determined by the paramagnetic term σ^P of the screening constant σ.[27] In the absence of marked heavy-atom effects (e.g., substituents such as iodine) major contributions to σ^P arise from changes in the radial expansion term $\langle r_{np}^{-3}\rangle$ and from B_0-induced circulation of the electronic charge.[28] The former effect describes the increase of $|\sigma^P|$ due to electronegative ligands, whereas magnetically active transitions ($\sigma \rightarrow d$, $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, etc.; excitation from σ-orbitals into low-lying nonbonding or antibonding orbitals is of importance for the ^{119}Sn nuclear shielding of tetracoordinate tin compounds[29]) of low energy are taken into account with the latter contribution. If the overall effect of electronegative substituents at the tin atom reduces the energy gap between σ and appropriate nonbonding (d) or antibonding states (σ*), a deshielding of the tin atom is expected. This situation applies to the $\delta(^{119}Sn)$ values of tin–sulfur compounds (Table IV and ref 29).

Since both ab initio calculations and ultraviolet photoelectron spectra are in support of extensive delocalization of σ-electron density in $(Me_3Sn)_2S$ and $(Me_2SnS)_3$, the same behavior can be predicted for the other tin–sulfur compounds in Table IV. Thus the evidence of the UP spectra indicates that the comparatively low shielding of the ^{119}Sn nuclei in tin–sulfur compounds is related to the high degree of delocalization of σ-electron density.

The smaller electronegativity of selenium is reflected both in the ultraviolet photoelectron spectra and in the $\delta(^{119}Sn)$ values. We ascribe the increase in ^{119}Sn nuclear shielding (with respect to the sulfur compounds) mainly to the combined influence of two effects: (i) the smaller electron-withdrawing effect of selenium (as compared to sulfur) and (ii) the concomitant destabilization of the Sn(5d) orbitals (both effects reduce the contribution to σ^P). In contrast to the almost identical $\sigma(^{119}Sn)$ values for $(Me_3Sn)_2Se$ and $(Me_2SnSe)_3$, there is a dramatic change in the $\delta(^{77}Se)$ values from −547 ppm for the former[30] to −350 ppm for the cyclic system. The magnitude of this effect [$\Delta(^{77}Se)$ about 200 ppm] can be appreciated when one compares the difference between $\delta(^{77}Se)$ values for $Me_3SnSeMe$ and $Me_2Sn(SeMe)_2$[31] [$\Delta(^{77}Se)$ about 40 ppm]. There is no additional information available from the ultraviolet photoelectron spectra with regard to the large $\Delta(^{77}Se)$ value. Therefore, it is suggested that the rigid structure of the cyclic system enforces a change in the chemical shift anisotropy [$\Delta\sigma = \sigma_{\alpha\alpha} - {}^1/_2(\sigma_{\beta\beta} + \sigma_{\gamma\gamma})$] of the ^{77}Se nuclei, bearing in mind that the nuclear shielding of two-coordinate heavy nuclei can be highly anisotropic. Since the $\delta(^{77}Se)$ values are directly related to the isotropic shielding constant σ, which is the mean value of the principal shielding tensors [$\sigma = {}^1/_3(\sigma_{\alpha\alpha} + \sigma_{\beta\beta} + \sigma_{\gamma\gamma})$], the ring structure may induce a significant change in one of the shielding tensors (with respect to the noncyclic system). This will be the subject of a separate study by solid-state ^{77}Se NMR.

Registry No. $(Me_3Sn)_2S$, 1070-91-3; $(Me_3Su)_2Se$, 7262-34-2; $(Me_2SnS)_3$, 16892-64-1; $(Me_2SnSe)_3$, 58258-49-4.

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(32) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13–18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)