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Aspects of Pentacoordinated Tin Compounds

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Aspects of Pentacoordinated Tin Compounds

INTRODUCTION

In the last 20 years structures with pentacoordinated central atoms have been the subject of increasing interest. This development was stimulated by both the progress of dynamic NMR spectroscopy and graph theory. Bond theoretical arguments show that only three of the five theoretically possible pentacoordinated structures having at least one symmetry element can be adopted, i.e., the trigonal bipyramid, the rectangular pyramid and the monocapped tetrahedron (Figure 1). These basic structures have been found in different compounds.[1–5]

Evidence has accumulated that the trigonal bipyramidal structure represents the most stable arrangement. However, the energies of the two other structures are only a few kJ/mol higher.[6] Pentacoordinated structures are characterized by three basic properties studied intensively on phosphorus compounds.[7] (i) The five ligands do not possess the same environment and are therefore nonequivalent, even in the case of five equal ligands. For instance, the bond distances of the apical fluorine atoms within the trigonal bipyramidal arrangement of PF_5 are 157 pm, those of the equatorial ones are only 153 pm.[8,9] (ii) The three actual existing pentacoordinated ligand arrangements are transmutable into each other due to the small differences in energy. This results in a high regular mobility of the pentacoordinated molecular framework. Thus, the ^{19}F and ^{31}P NMR spectra of PF_5 indicate the equivalence of all fluorine atoms even at $-100°C$. This behavior was explained by a fast regular permutation process (Berry pseudorotation) passing through the square pyramidal structure. (iii) In case of different ligands in a trigonal

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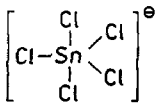
FIGURE 1 Ideal pentavalent structures having at least one symmetry element.

bipyramidal arrangement at phosphorus the ligands of higher electronegativity occupy the apical positions, whereas the less electronegative ligands prefer the equatorial ones. This principle, called the polarity rule,[8] has been confirmed by various data. This effect has been attributed to the different participation of *d* orbitals in the bonds to the ligands. For example, in the case of methyltetrafluorophosphorane the structure with the equatorial position of the methyl group is 163 kJ/mol more stable than that with an apical methyl group.[7]

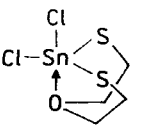
PENTACOORDINATED TIN COMPOUNDS

The increasing number of pentacoordinated tin compounds poses the question whether the general properties of pentacoordination are transferable to this class of compounds. Figure 2 shows some representative structures of pentacoordinated tin compounds. It can be seen that compounds without any tin–carbon bond as well as mono, di and triorganotin compounds can give rise to pentacoordination but most examples are known from the latter two. Recently Zuckerman and co-workers described the first example of a pentacoordinated tetraorganotin compound of type R_4SnX^-, but this compound has been characterized only by means of ^1H NMR spectroscopy.[23]

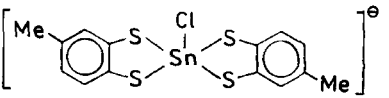
The observed pentacoordinated structures do not allow any conclusions about the theoretical conception of pentacoordination. No systematic studies have been carried out in regard to both the polarity rule and intramolecular mobility. The hitherto established structures allow the following conclusions. (i) The structure of the compounds is mainly trigonal bipyramidal, but perturbations of symmetry by different contact atoms and formation of ionic structures have been observed. In this regard a recent work of Holmes and co-workers[18] should be mentioned describing the first tin(IV)compound adopting a rectangular pyramidal



R.F. BRYAN[10]
1964



M. DRÄGER[16]
1975



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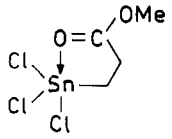
1981



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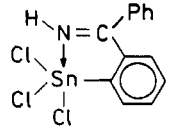

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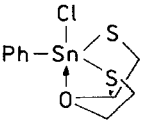

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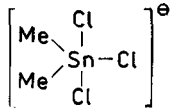
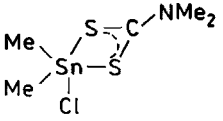


F.W.B. EINSTEIN[13]
1968



K. FURUE[14]
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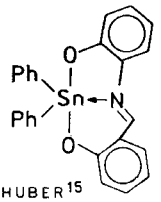

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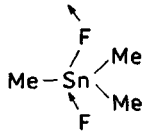
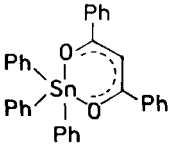
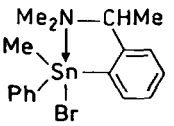


H.C. CLARK[19]
1964



M. BANCROFT[20]
1975



J.G. NOLTES[55]
1978

FIGURE 2 Representative structures of pentacoordinated tin compounds.

structure. (ii) Obviously, the polarity rule is valid. (iii) Molecular mobilities have been found in different examples, but until now no regular permutation isomerizations have been proven unambiguously. Apparently, these mobilities are motion processes based on fast dissociation–association equilibria.

Cyclic Pentacoordinated Structures

In recent years our research group has carried out systematic investigations of the problems of pentacoordinated tin structures. In order to exclude dissociation–association processes mono, di and tricyclic tin compounds have been studied (Figure 3). These compounds are also interesting for their biological properties. The compounds are denoted either as triptychstannolidines (A), diptychstannolidines (B) and stannolidines (C) or as mono, di and triorganostannatranes.*

The influence of the atoms or atom groups X and E, the organic groups R and the variation of the ring part on the behavior of these classes of compounds have been studied. The following investigation should yield information concerning three problems: (i) the dependence of the transannular interaction within cyclic pentacoordinated organotin compounds upon the various parameters; (ii) the validity and restrictions of the polarity rule applied to pentavalent tin compounds; (iii) mechanistic conceptions of the dynamic processes of the different types of compounds studied.

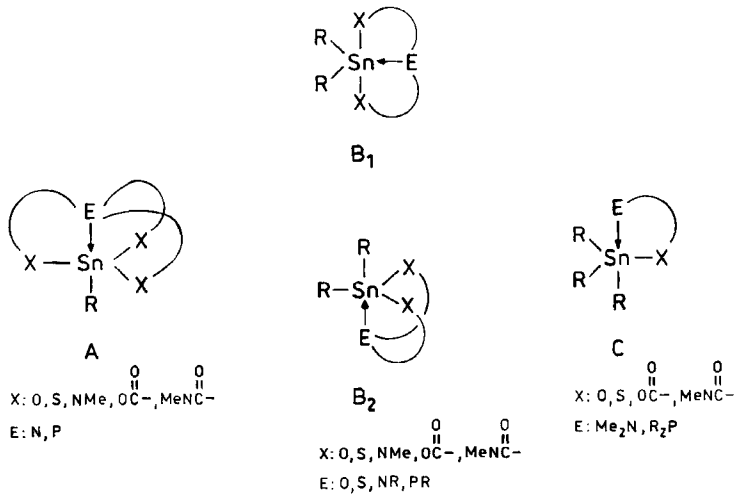


FIGURE 3 Cyclic pentacoordinated structures.

*Of course, the use of the rational nomenclature for organic compounds is also possible.[29]

Methods of Synthesis

The tin compounds shown in Figure 3 are prepared with yields of 50%–95% by cyclocondensation of stannonic acids, organotin oxides and alkoxides, respectively, with the corresponding α or β functional ligands according to Eqs. (1)–(6).[25–37]

$$1/n(RSnOOH)_n + N(CH_2CH_2XH)_3 \xrightarrow[-H_2O]{\text{xylene, KOH}} RSn(XCH_2CH_2)_3N \quad X = O,S \qquad (1)$$

$$1/n(RPhSnO)_n + N(CH_2CH_2XH)_3 \xrightarrow[-H_2O,\ -C_6H_6]{\text{xylene, KOH}} RSn(XCH_2CH_2)_3N \quad X = O,S \qquad (2)$$

$$RSn(OEt)_3 + N(CH_2CONMeH)_3 \xrightarrow[-3\ EtOH]{\text{toluene}} RSn(NMeCOCH_2)_3N \qquad (3)$$

$$RSn(NEt_2)_3 + N(CH_2CH_2NMeH) \xrightarrow[-3\ HNEt_2]{\text{toluene}} RSn(NMeCH_2CH_2)_3N \qquad (4)$$

$$R_2Sn(OMe)_2 + E(CH_2XH)_2 \xrightarrow[-2\ MeOH]{\text{toluene}} R_2Sn(XCH_2)_2E$$

$X = CH_2O, CH_2S, CONMe, CH_2COO, S, O$

$E = NR, PR, S, O \qquad (5)$

$$R_2SnCl_2 + E(CH_2CH_2XNa)_2 \xrightarrow[-2\ NaCl]{\text{thf or ethanol}} R_2Sn(XCH_2CH_2)_2E$$

$X = O,S$

$E = NR, PR, O, S \qquad (6)$

The high yields of some of these reactions are remarkable for large ring synthesis and indicate the existence of an intermediate containing a transannular tin–element interaction (Figure 4). The importance of this transannular interaction for the formation of the cyclic compound is

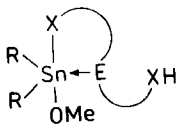


FIGURE 4 Intermediate with transannular tin–element interaction.

substantiated by the decrease of the yield in dependence on E: NR > O > S ~ PR (X = S). Obviously this sequence represents qualitatively the difference of the donor strength of E towards tin. Note the synthesis of the stannatranes $RSn(XCH_2CH_2)_3N$ (X = O,S) and $RSn(OC_6H_4)_3N$ from alkylphenyltin derivatives by splitting of the tin bonded phenyl group according to Eq.(2).

Attempts to prepare the corresponding phosphorus containing derivatives $RSn(SCH_2CH_2)_3P$ and $RSn(OC_6H_4)_3P$ by this method failed, presumably due to the weaker Sn–P interaction of the cyclic intermediate. Suitable starting materials for pentacoordinated tin compounds are also tin(II)-containing eight-membered ring compounds that are readily transformed into the corresponding atranelike derivatives according to Eq.(7).[38,39]

$$Sn(XCH_2CH_2)_2E + Y\text{–}Y \rightarrow Y_2Sn(XCH_2CH_2)_2E$$

$$X = O,S,\ E = NR, PR, O, S$$

$$Y = Cl, Br, I, SPh, OCOPh \qquad (7)$$

Most of the compounds obtained are monomeric in solution as well as in the gas phase and show a low tendency towards adduct formation even with strong donors like HMPA, DMSO or pyridine, indicating a prevailing valence saturation of the tin atom by intramolecular coordination of the donor atom E.

EVIDENCE FOR THE TRANSANNULAR INTERACTION

Evidence for the transannular Sn–E interaction has been obtained from NMR spectroscopy, especially from the coupling constants $^1J(^{119}Sn\text{–}E)$ E = ^{15}N, ^{31}P) and $^3J(^{119}Sn\text{–}E\text{–}C\text{–}^1H)$ (Table I). The high field shift of these compounds in the ^{119}Sn NMR spectra compared with compounds of coordination number four with similar substituents at tin as well as the change of the $^1J(^{119}Sn\text{–}^{13}C)$ and $^2J(^{119}Sn\text{–}C\text{–}^1H)$ coupling constants are in agreement with pentacoordination. In this regard it is noteworthy that the relationship between the increasing coupling constants and the increase of the coordination number of the tin atom is found to be valid only for the equatorially bonded organo groups in a trigonal bipyramidal arrangement. These aspects will be discussed in more detail in connection with the description of individual types of compounds.

TABLE I
^{119}Sn–^{15}N, ^{119}Sn–^{31}P and ^{119}Sn–^{1}H coupling constants in the ^{15}N, ^{31}P and ^{1}H NMR spectra of atranelike organotin derivatives

Constant	Derivative	Hz
$J(^{119}Sn–^{15}N)$	t-$BuSn(OCH_2CH_2)_3{}^{15}N$	64.9
	t-$Bu_2Sn(OCH_2CH_2)_2{}^{15}NH$	37.1
$J(^{119}Sn–^{31}P)$	$Ph(Cl)Sn(SCH_2CH_2)_2PPH$	1185
	n-$BuSn(OC_6H_4)_3P$	874
	t-$Bu_2Sn(OC_6H_4)_2P$–t–Bu	488
$J(^{119}Sn–N–C–^{1}H_3)$	t-$Bu_2Sn(OCH_2CH_2)_2NMe$	14
	t-$Bu_2Sn(OCOCH_2)_2NMe$	14
	$Ph(Cl)Sn(SCH_2CH_2)_2NMe$	6

Triorganotin Compounds

Most of the triorganotin compounds R_3SnX (X = electronegative ligand) are pentacoordinated either by intermolecular tin–ligand bridge bonds or by intramolecular dative tin ligand interaction, representative examples being Me_3SnF[19] and $Me_3SnCl \cdot HMPA$.[22] Special cases of the latter type are such compounds containing an intramolecular donor as a built in ligand (Figure 5).[21,55] The three tin bonded carbon atoms occupy the equatorial positions in the trigonal bipyramidal arrangement. Other structures are less favorable and have never been found.[24] The situation of triorganotin compounds containing a chelate ligand is more complicated. Two different structures are possibly differentiated by an apical-equatorial or a diequatorial arrangement of the chelating ligand (Figure 6). For stereochemical reasons five-membered ring structures should be arranged unambiguously apical-equatorial whereas six-membered rings can occupy either diequatorial or apical-equatorial positions. But until now only structure C_1 has been confirmed for several compounds in the solid state by x-ray analysis, i.e., $Ph_3Sn(PhCO–CH–COPh)$[20] and $Ph_3Sn(ONPhCOPh)$[40]. Due to the unusual Mössbauer data several authors proposed a C_2 structure for $Me_3Sn(acac)$[24] and Me_3Sn

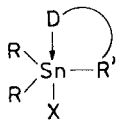
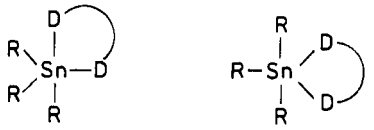


FIGURE 5 Triorganotin compound containing a built in ligand.



C_1 C_2

FIGURE 6 Structures of triorganotin chelates.

$[Ph_2(O)As]_2CH_2$.[41] In these structures two electropositive ligands occupy the apical positions of the trigonal bipyramid. This arrangement is opposite to the polarity rule and should therefore be less favored. In this connection we refer to structure investigations of tetrahedral tin compounds of low symmetry which showed small distortions of the angles to cause significant changes of the Mössbauer data.[42]

In both the C_1 and the C_2 structure the organo groups R are not equivalent since they occupy equatorial as well as apical positions. Contrary to the solid state, nonequivalence of these groups has never been found in solution by means of NMR spectroscopy.[20,40,41,44] Obviously, these compounds undergo rapid dynamic processes which can be either regular permutational isomerizations[7] or dissociation–association processes with tetracoordinated intermediates. Also in $Me_3SnOCH_2CH_2NMe_2$ and $Me_3SnOC_6H_4NMe_2$ the tin–methyl groups are equivalent down to $-130°C$ according to the ^1H and ^{13}C NMR spectra. The coupling constants are in agreement with a fast equilibrium between tetra and pentacoordinated structures. In the *N,N*-dimethyl glycine derivative $Me_3SnOCOCH_2NMe_2 \cdot H_2O$, however, two signals have been observed for the methyl groups at $-90°C$ (integral ratio 2:1) in the ^1H NMR spectrum. This is in agreement with the following structure given in Figure 7.

Diorganotin Compounds

Pentacoordinated diorganotin compounds are comparatively rare. Thus, studies on such compounds with tridentate ligands have opened up an

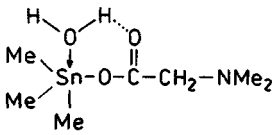
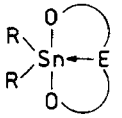


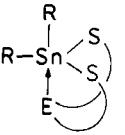
FIGURE 7 Proposed structure for $Me_3SnOCOCH_2NMe_2 \cdot H_2O$ in solution at low temperature.

interesting field.[15,25–27,30,31,45–48] From a theoretical point of view only two of the possible stereoisomers have a real probability due to stereochemical considerations.[49]

The B_1 structure is represented by compounds containing oxygen or nitrogen atoms directly bonded to tin. The electronegative atoms are expected to occupy the apical positions whereas the two organo groups and the donor atom occupy the equatorial ones.



B_1



B_2

$R_2Sn(OCH_2CH_2)E$	E = NR′, O,S	$R_2Sn(SCH_2CH_2)_2E$
$R_2Sn(XCOCH_2)_2NMe$	X = O, NMe	E = NR′, PR′, O,S
$R_2Sn(OC_6H_4)_2E$	E = PR′, NR′	

This assumption is based upon the observation that the organo groups R bonded at tin are nonequivalent in regard to the groups NR and PR, respectively, or to the lone pair at sulfur or oxygen.

The ^{13}C and ^{1}H NMR spectra display two signals of equal intensity which have the same or nearly the same coupling constants $^{1}J(^{119}Sn–^{13}C)$, $^{2}J(^{119}Sn–C–^{1}H)$ or $^{3}J(^{119}Sn–C–C–^{1}H)$. The values of these couplings are higher in comparison with similar substituted tetracoordinated organotin compounds $R_2Sn(OR')_2$, reflecting the change of the *s* character in the tin–carbon bond going from sp^3 hybridization in tetravalent tin compounds to sp^2 hybridization in trigonal bipyramidal coordinated species. At higher temperatures coalescence phenomena are observed, accounted for by either a dissociation-inversion[49] or a dissociation-electron pair exchange mechanism (Figure 8). A Berry process or other regular isomerization process is not favored due to intermediates of high energy.[49]

Those compounds with sulfur as contact atoms show nonequivalence of the tin bonded organo groups in the NMR spectra but the two signals have very different coupling constants, indicating the B_2 structure. But due to the similar electronegativities of sulfur and carbon the B_1 structure

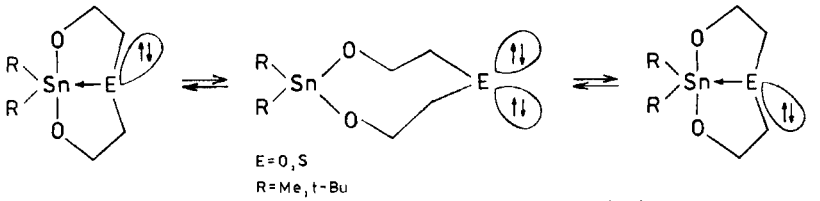


FIGURE 8 Dissociation electron pair exchange mechanism.

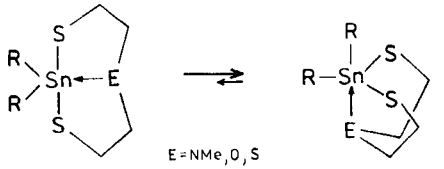
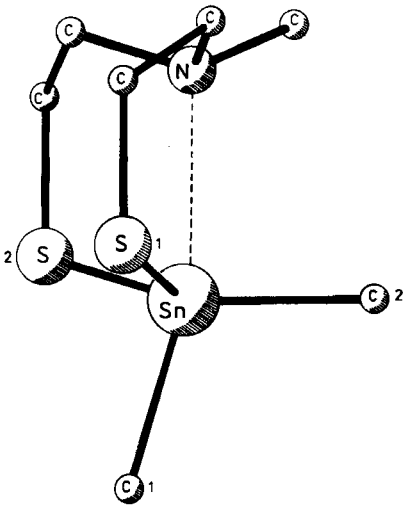


FIGURE 9 Equilibrium between the two different diptych structures.



Sn–N	: 256.6 pm	∢ C(1)–Sn–N	: 165.8°
Sn–C(1)	: 216.0 pm	∢ S(1)–Sn–S(2)	: 118.3°
Sn–C(2)	: 213.9 pm	∢ S(1)–Sn–N	: 78.2°

FIGURE 10 Molecular structure of *N*-methyl-5,5-dimethyldiptychthiaazastannolidine.

TABLE II
Mössbauer data for dialkyldiptychthiaazastannolidines (mm/s)

Compound	OS_{exp}	OS_{B1calc}	OS_{B2calc}	Proposed structure
$Me_2Sn(SCH_2CH_2)_2NMe$	1.31	1.86	1.33	B_2
t-$Bu_2Sn(SCH_2CH_2)_2NMe$	1.90	1.86	1.33	B_1

should also be possible. Therefore, we assume a fast equilibrium between these arrangements, which, however, has not yet been detected by NMR spectroscopy down to −150°C (Figure 9). The different structures found in solution have been confirmed by x-ray investigation of t-$Bu_2Sn(OCH_2CH_2)_2NMe$[50] and $Me_2Sn(SCH_2CH_2)_2NMe$ (Figure 10).[51] *N*-methyl-5,5-dimethyldiptychthiaazastannolidine is the first pentacoordinated diorganotin compound found to contain a methyl group in an apical position. The Mössbauer data suggest a B_1 structure for t-$Bu_2Sn(SCH_2CH_2)_2NMe$ (Table II).[52]

The influence of the different structure unities of the molecule upon the transannular tin–element interaction can be estimated from the calculated activation parameters ($\Delta G^{\ddagger}_c$) of the dynamic process.[49] These results as well as ^{119}Sn NMR measurements and systematic x-ray studies show that besides the decision between the B_1 or B_2 structure one should take into account the tetrahedral distortion of the trigonal bipyramid (Tables III and IV).

The data of Tables III and IV reflect very well the donor strength of the different elements attached to a tin atom of a given Lewis acidity. The influence of the organo groups R in $R_2Sn(SCH_2CH_2)_2E$ (E = O,S) on the Sn–E interaction has also been shown.[17]

TABLE III
Dependence of the ^{119}Sn NMR chemical shift, the Sn–E bond length and bond order of $Me_2Sn(SCH_2CH_2)_2E$ upon E

E	^{119}Sn (ppm)	Sn–E (pm)	Bond order[53]
NMe	34.2	256.6	0.6
O	95.5	278.5	0.24
S	120.4	351.3	0

The tetracoordinated dimethyltin dithiolate $Me_2Sn(SEt)_2$ has a ^{119}Sn NMR chemical shift of 127.0 ppm.

TABLE IV
Dependence of the ^{119}Sn NMR chemical shift of t-$Bu_2Sn(SCH_2CH_2)_2E$ upon E

E	^{119}Sn (ppm)
NMe	59.5
O	67.3
PPh	103.5
S	120.2

Finally, variation of the ring size leads to a change of the tin–element interaction. In ten-membered rings of types $R_2Sn(OCH_2CH_2CH_2)_2NMe$ and $R_2Sn(OCOCH_2CH_2)_2NMe$ no tin–nitrogen interaction has been observed. These compounds reach pentacoordination through autoassociation via oxygen bridges.[35] The same behavior has been found in the six-membered ring t-$Bu_2Sn(OCH_2)_2PPh$.[33]

Monoorganotin Compounds

Because of the higher Lewis acidity monoorganotin compounds are usually hexa or heptacoordinated.[24] Suitable ligands to stabilize pentacoordinated structures are β functional trialkyl or triaryl amines and phosphines, respectively. These compounds adopt trigonal bipyramidal arrangements with the organo group in an apical position. This is in contrast to the polarity rule (Figure 11). In solution these structures have been deduced from the decreased $^2J(^{119}Sn–C–^1H)$ coupling constants in comparison to similar tetracoordinated compounds (e.g., $MeSn(NMeCH_2CH_2)_3N$: $^2J(^{119}Sn–C–^1H)$, 61.0 Hz; $MeSn(NEt_2)_3$, 68.7 Hz; $MeSn(SCH_2CH_2)_3N$, 60.0 Hz; $MeSn(SEt)_3$, 65.2 Hz).[25,29] The pro-

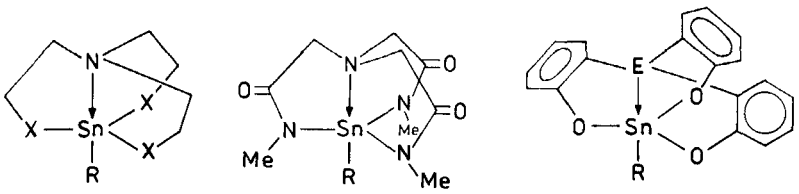
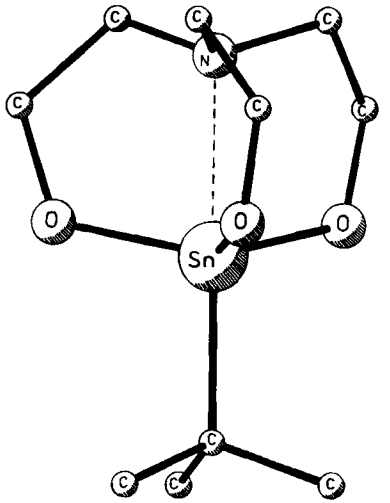


FIGURE 11 Different atranelike compounds.



Sn–N : 232 pm

Sn–C : 213 pm

Sn–O : 201 pm

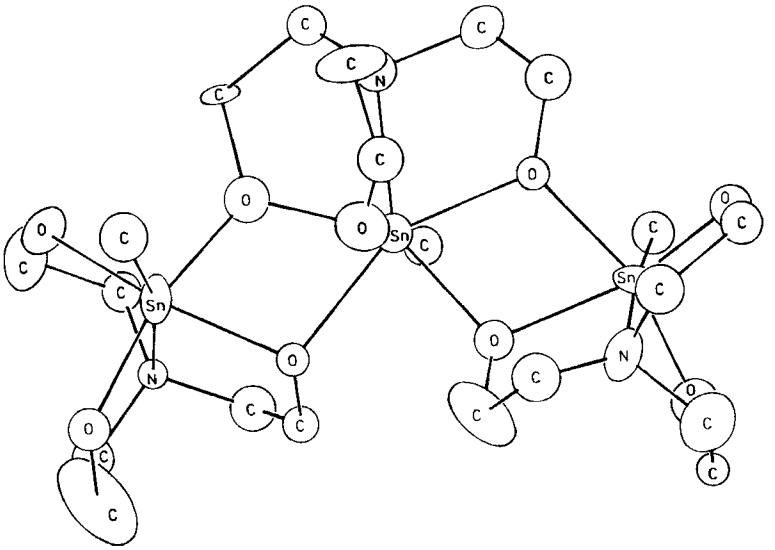


FIGURE 12 Comparison between the molecular structure of (a) 5-*t*-butyl and (b) 5-methyl-triptychoxazastannolidine.

posed structures of the 5-methyl-triptychthiaazastannolidine[49] and the 5-*t*-butyltriptychoxazastannolidine (Figure 12) have been confirmed by x-ray analysis. It is remarkable that contrary to the very low apicophilicity of the *t*-butyl group (studied on phosphorus compounds)[54] the structure shows no distortion from the ideal trigonal bipyramidal arrangement. Furthermore, the tin–carbon bond is remarkably short compared with that of *t*-$Bu_2Sn(OCH_2CH_2)_2NMe$ (219 pm).[50] The structure of $RSn(OC_2H_4)_3P$ with the two fewer electronegative ligands in apical positions would therefore be highly interesting. Unfortunately, so far no single crystals suitable for x-ray investigation have been obtained. 5-methyl-triptychoxazastannolidine adopts a more complicated structure which has been shown to be trimeric in solution[28,29] as well as in the solid state (Figure 12).

CONCLUSIONS

Systematic investigation of diptych structures proves the validity of the polarity rule. However, equilibria between different structures are possible due to the small differences in energy. Steric factors such as bulky organo groups or chelate rings can stabilize unusual structures against the polarity rule and are therefore interesting for further theoretical investigation. The stability of the pentacoordination depends on the electronegativity of the heteroatoms or atom groups attached to the tin atom and therefore on the Lewis acidity of the tin. In some cases one has to consider tetrahedral or octahedral distortions due to the electronic situation at the tin center.

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