

# Intramolecular Coordination in Organotin Chemistry<sup>1</sup>

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<sup>1</sup> This article is dedicated to the 80th birthday of Prof. Dr. G. J. M. van der Kerk in recognition of his fine and pioneering contribution to organotin chemistry and its applications.

## I

## INTRODUCTION

A. *Historical Perspective*

The field of organotin chemistry has a long history that started as early as 1849, when Frankland isolated a specimen of diethyltin diiodide (1,2). In 1852, Löwich independently reported on the reaction of alkyl halides with a tin-sodium alloy giving alkyltin compounds (3). This last publication is usually considered to represent the beginning of organotin chemistry.

By 1935, about 200 publications concerning organotin chemistry had appeared in the literature. Important names in the development of organotin chemistry at that time were Krause in Germany, Kraus in the United States, and Kozeshkov in Russia [for a review, see Ref. (4)]. The discovery of industrial applications of organotin compounds as stabilizers against loss of HCl in polyvinyl chloride (5-7), as agrochemicals (8-11), as wood preservatives (12-16), and biocides (17-19) produced a renaissance of organotin chemistry. Particularly van der Kerk and his group in the Netherlands played a dominant role in this development [see Refs. (20) and (21) and references cited therein].

It was not until the early sixties that it was recognized that the tin atom in organotin compounds is capable of extending its coordination number beyond four. Based on colligative studies, a polymeric structure was proposed for trimethylpyrazolytin in apolar solvents with pentacoordinate tin centers; see Fig. 1a (22). Similarly, on the basis of IR spectroscopic studies, oligomeric structures with pentacoordinate tin centers were proposed for trimethyltin fluoride (23) and trimethyltin carboxylates (24-26) in which a fluoride or carboxylate group bridge trimethyl tin units; see Fig. 1b. However, the trimethyltin chloride pyridine adduct, Fig. 1c, was the first authenticated five-coordinate triorganotin halide complex for which the structure was proven by an X-ray crystal structure determination (27).

Although divalent inorganic tin compounds have been known for a long time,<sup>2</sup> it was in 1956 that the first example of a divalent organotin compound, i.e., bis(cyclopentadienyl)tin(II), was reported (29).

B. *Tin: Its Bonds and Valency*

In the periodic table of the elements, tin is listed in group 14, together with the elements carbon, silicon, germanium, and lead. The four electrons

<sup>2</sup> The first scientist who experimentally demonstrated the existence of two oxidation states of tin seems to have been B. Pelletier in 1792 (28).

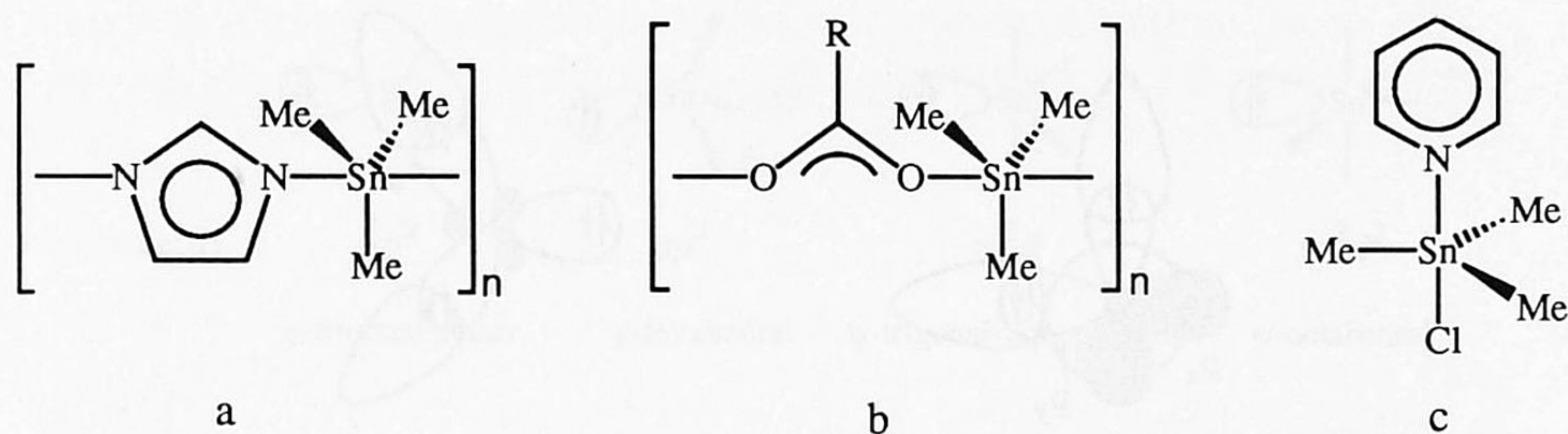


FIG. 1.

in the valence shell of the tin atom have the  $5s^25p^2$  electronic configuration. These valence electrons can undergo  $sp^3$  hybridization, and tetravalent tin atoms are therefore tetrahedral. The bonding of tin is almost entirely covalent, at least in crystalline solids, in nonpolar solvents and in the vapor phase. This is true even for tin—halogen bonds. The polarity that should follow from the difference in electronegativities is not observed, probably because of the large bond lengths.

Within group 14, the bond lengths to carbon increase considerably: C—C 1.54, C—Si 1.94, C—Ge 1.99, C—Sn 2.15, and C—Pb 2.29 Å. The increased bond length for tin is the cause of the increased reactivity and the related lower thermal stability of the tin alkyls compared with their C, Si, and Ge analogs. Long bonds naturally have low strength and also lessen the screening of the central atom by the ligands. Attacking reagents thus have easier access. This is particularly evident in organolead compounds (30).

Tin, like its congeners germanium and lead, can form compounds in the  $\text{II}^+$  formal oxidation state. Such compounds may be regarded as carbene analogs (31,32). Their main characteristics are that there are only six electrons in the valence shell and that one electron pair is nonbonding. This nonbonding electron pair may occupy one orbital with antiparallel spins (singlet,  $^1\sigma^2$ ) or two different orbitals with antiparallel (singlet,  $^1\sigma p$ ) or parallel spins (triplet,  $^3\sigma p$ ). In contrast to carbenes, the heavier analogs all have one property in common: The energetically most favorable electronic state is the singlet  $^1\sigma^2$  one (31). There are two ways to describe the structure of these singlet carbene analogs: (i) the nonbonding electron pair occupies an  $s$  orbital, the bonding electrons occupy  $p$  orbitals, and the third  $p$  orbital remains empty. The bond angles should then be strictly  $90^\circ$  (Fig. 2A), and (ii) both nonbonding and bonding electron pairs occupy  $sp^2$ -hybrid orbitals while again a  $p$  orbital is unoccupied. In this case, the bonding angle should be  $120^\circ$  (Fig. 2B).

When the experimentally determined bond angles of carbene analogs are compared, e.g., in  $\text{MX}_2$  ( $\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$ , and  $\text{X} = \text{F}$  or  $\text{Cl}$ ), the values

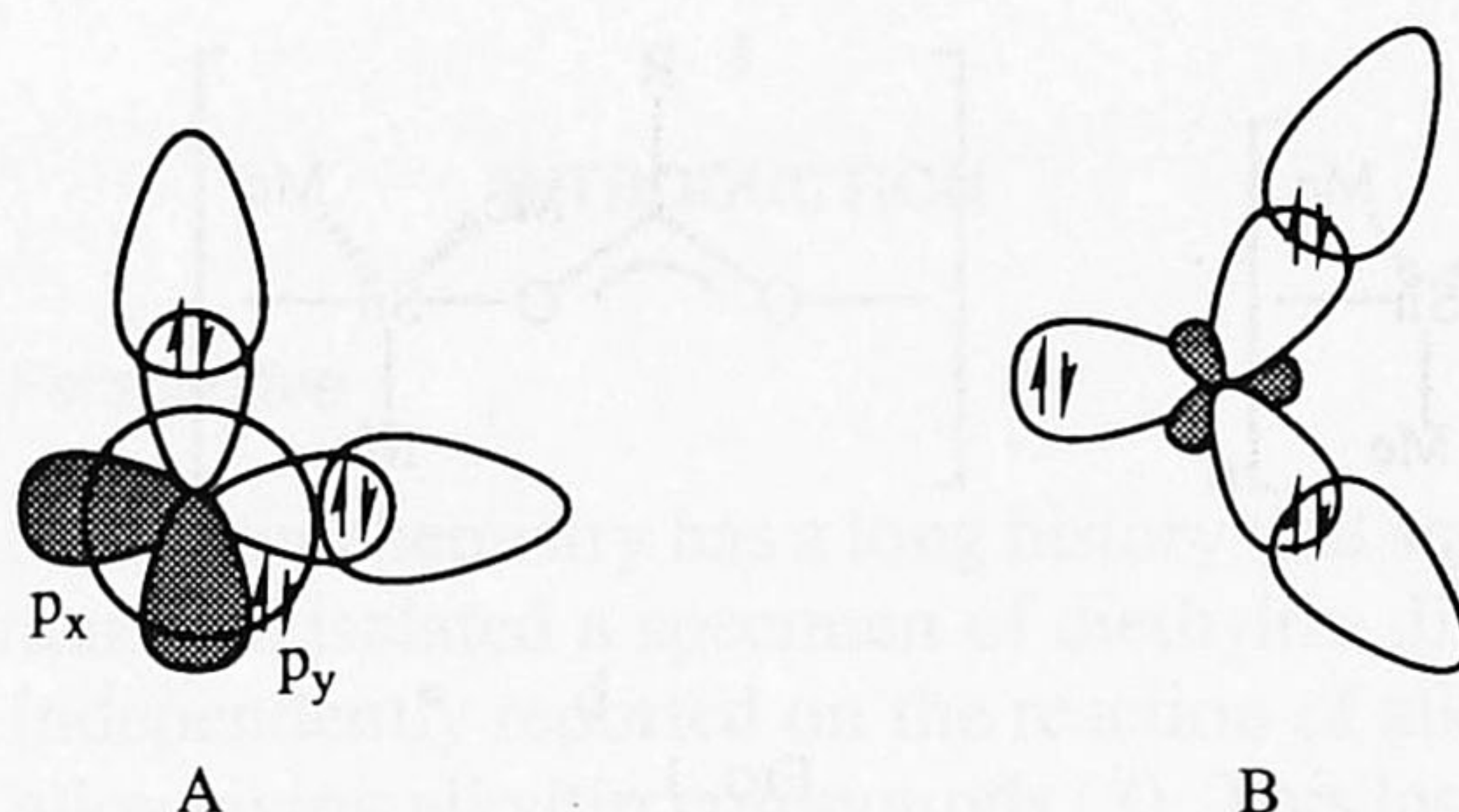


FIG. 2. The two possibilities to describe the structure of singlet carbene analogs.

are found to be between these two possibilities (31). With increasing atomic number of the central atom, the angles seem to approach  $90^\circ$ . The deviation from the angles predicted by the models A and B is accounted for by repulsion forces between the ligands (model A) or repulsion between the lone pair and the ligands in model B (valence-shell electron-pair repulsion theory) (33–35). For heavy elements, model A seems to be more important, and it is expected that divalent tin compounds have this geometry. For all inorganic divalent tin compounds known, so far this is the case (36). It should be noted that the nonbonding electron pair at the tin atom is not stereochemically active because it is located in a radially distributed  $s$  orbital. However, structures of solid tin(II) compounds often show the contrary (36). It is therefore assumed that the  $s$  orbital is mixed with energetically favorable orbitals, allowing a deviation from a spherical shape (37,38).

### C. Principal Coordination Geometries at the Tin Center in Organotin Compounds

Since empty  $5d$  orbitals of suitable energy also may be involved in the hybridization in divalent as well as in tetravalent tin, higher coordination numbers at tin are possible. In Fig. 3, the principal coordination geometries for both divalent and tetravalent tin are given, while it is assumed that in the case of divalent tin, the lone pair is also involved in the hybridization.

Some general trends for organotin coordination compounds [see Ref. (39) and references cited therein] have been well established. Based on the decreasing Lewis acidity with increasing number of organic groups present at tin, tetraorganotin compounds were regarded until recently as being unable to extend their coordination number due to the poor acceptor properties of the tin atom in these compounds. However, various examples showing that this assumption needs correction are now known.

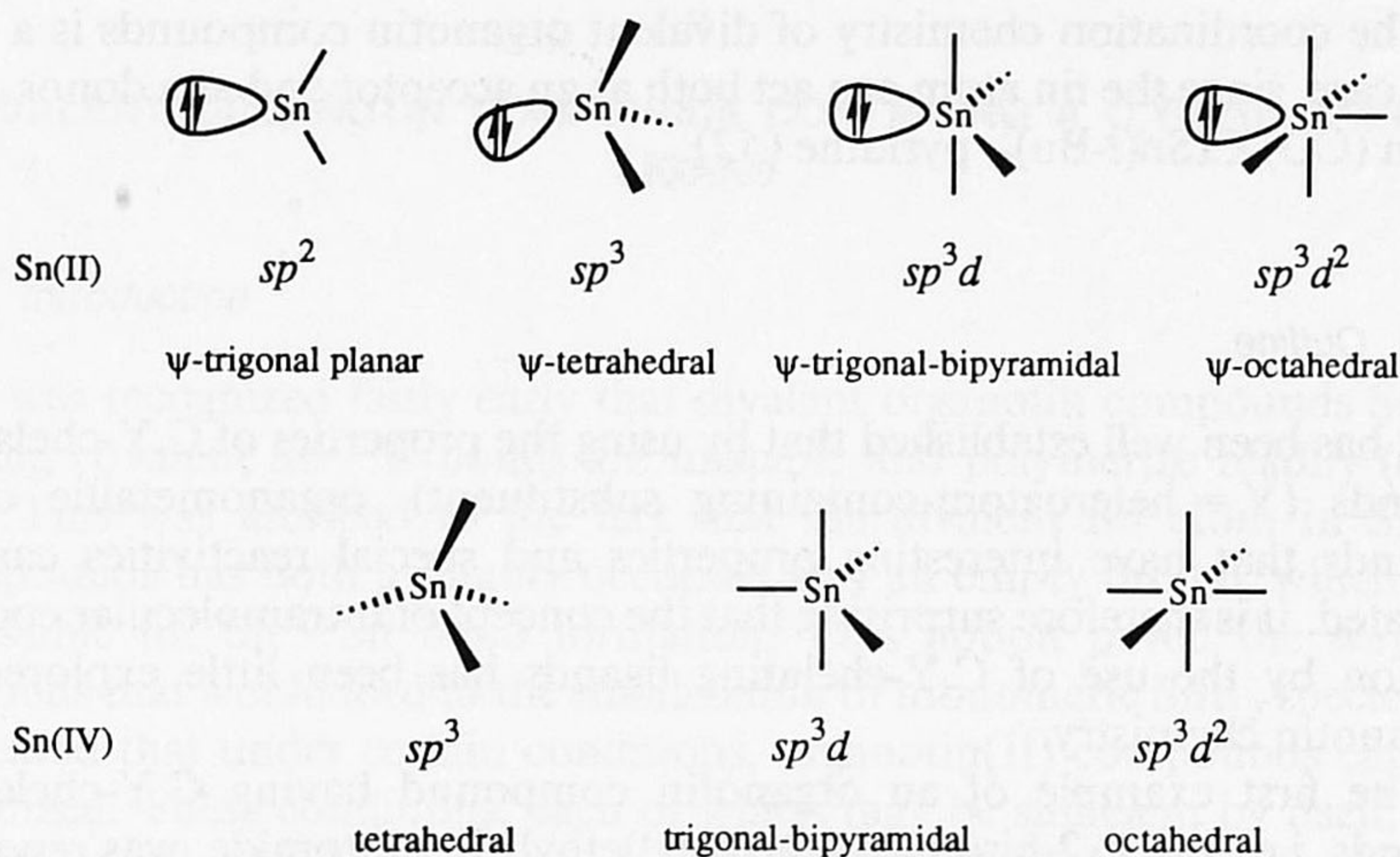
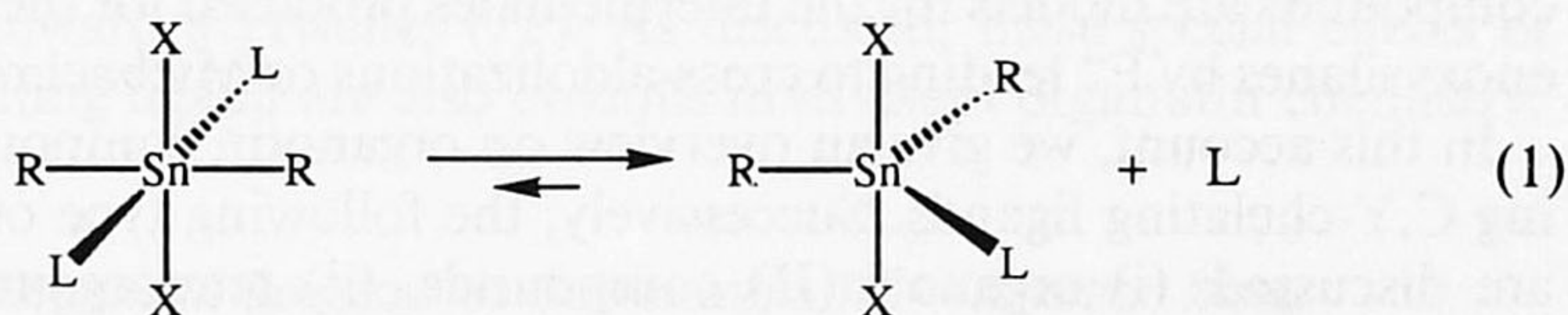


FIG. 3. The principal coordination geometries of divalent and tetravalent tin.

The preferred coordination geometry of the tin atom in triorganotin halides is trigonal bipyramidal with the carbon ligands at the equatorial sites and the more electronegative halide and donor atom at the axial positions (39).

Both trigonal bipyramidal and octahedral coordination geometries have been found for the tin atom in adducts of diorganotin dihalides with Lewis bases. The solid-state structures of complexes,  $\text{SnX}_2\text{R}_2 \cdot 2\text{L}$  (L = monobasic ligand), have generally two *trans*-oriented carbon ligands (R), whereas the two halide and the two donor molecules can adopt either mutual *trans*- or *cis*-configurations, depending upon the nature of the substituent (40–48). In solution, these complexes exist as an equilibrium of a hexacoordinate and a pentacoordinate species, with the latter as the predominant one (49),



Little has been reported yet on the coordination chemistry of monoorganotin compounds. Coordination numbers of five to eight for the tin atom have been reported in such compounds (39,50,51). It has been suggested, however, that in solution a trigonal bipyramidal arrangement at tin is the most favorable one (49).

The coordination chemistry of divalent organotin compounds is a special case, since the tin atom can act both as an acceptor and as a donor, e.g., as in  $(\text{CO})_5\text{CrSn}(t\text{-Bu})_2 \cdot \text{pyridine}$  (52).

#### D. Outline

It has been well established that by using the properties of C,Y-chelating ligands (Y = heteroatom-containing substituent), organometallic compounds that have interesting properties and special reactivities can be isolated. It is therefore surprising that the concept of intramolecular coordination by the use of C,Y-chelating ligands has been little explored in organotin chemistry.

The first example of an organotin compound having C,Y-chelating ligands, i.e., bis[1, 2-bis(ethoxycarbonyl)ethyl]tin dibromide, was reported in 1968 for which the structure in the solid state was unambiguously established by an X-ray crystal structure determination (53). However, from 1976 a more systematic study of the properties of organotin halides containing C,N-chelating ligands was started (54).

It was recognized at an early stage of this research that the presence of an intramolecular coordinating substituent considerably increases the configurational stability of chiral triorganotin halides (54). Moreover, modern NMR techniques allowed a detailed interpretation of the fluxional processes operative in solution of these compounds. Furthermore, the penta-coordinate tin center in triorganotin halides may be considered as a model for the transition state of the  $\text{S}_{\text{N}}2$  substitution reaction at tetrahedral carbon centers, by which the intramolecular coordinating heteroatom may be regarded as the incoming nucleophile and the halogen atom as the leaving group.

It should be noted here that Corriu and co-workers have reported on organosilicon compounds containing C,N-chelating ligands in which the silicon atom is penta- or hexacoordinate (55–58). Such organosilicon compounds are models for the intermediates proposed for the activation of enoxysilanes by  $\text{F}^-$  leading to cross-aldolizations or Michael reactions (59).

In this account, we give an overview on organotin compounds containing C,Y-chelating ligands. Successively, the following type of compounds are discussed: (i) organotin(II) compounds, (ii) tetraorganotin(IV), (iii) triorganotin(IV), and (iv) di- and monoorganotin(IV) compounds. Special attention is given to (i) structures in the solid state, (ii) fluxional behavior in solution, and (iii) stereochemical aspects. Also attention is given to the enhanced reactivity of tin—carbon bonds in tetraorganotin compounds as result of intramolecular coordination.

## II

## DIVALENT ORGANOTIN COMPOUNDS CONTAINING A C,Y-CHELATING LIGAND

## A. Introduction

It was recognized fairly early that divalent organotin compounds  $\text{SnR}_2$  having covalent Sn—C bonds are unstable and polymerize readily (60–65). This was ascribed to the fact that the divalent tin atom in  $\text{SnR}_2$  compounds has both a doubly occupied and an empty orbital, which are accessible for Sn—Sn bond formation. This notion paved the way to methods that would lead to the stabilization of monomeric  $\text{SnR}_2$  species. It appeared that under certain conditions, organotin(II) compounds can be stabilized. These conditions, each of which may be sufficient by itself, are (i) the use of bulky organic groups as, e.g., in  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  (66), (ii) the coordination of the lone pair at tin to a suitable transition metal acceptor as, e.g., in  $(\text{CO})_5\text{CrSn}(t\text{-Bu})_2 \cdot \text{pyridine}$  (52), and (iii), the completion of the tin coordination sphere by the introduction in the organo-groups of substituents that are capable of intramolecular coordination. Since the first two approaches are beyond the scope of our account, only divalent organotin compounds that met the last condition are discussed. In general, it is now known that by using the steric and electronic properties of C,Y-chelating ligands, organometallic compounds that have interesting properties and special reactivities can be isolated. Special features of some of these compounds are: (i) stabilization of organometallic compounds in which the metal has an unusual oxidation number, e.g., Fe(III) (67), Co(II) (68), and Ni(III) (69); (ii) the trapping of organometallic species that are supposed to be intermediates in reactions, e.g., organoplatinum compounds in which a diiodine molecule is coordinated end-on to platinum as a first step in oxidative-addition reactions (70); (iii) the use of a novel organonickel(II) compound as a catalyst in the selective Karasch addition of polyhaloalkanes to olefines (71); and (iv) the unexpected reactivity of organocopper compounds toward acetylenes (72). As discussed, these special effects of the C,Y-chelating ligand are also obvious in divalent organotin chemistry.

## B. Divalent Organotin Compounds Containing a Tin—Transition Metal Coordination Bond

The earliest isolated organotin species in which the tin atom is in the  $\text{II}^+$  formal oxidation state are compounds in which the tin atom acts as a Lewis base that coordinates to a suitable transition metal fragment,

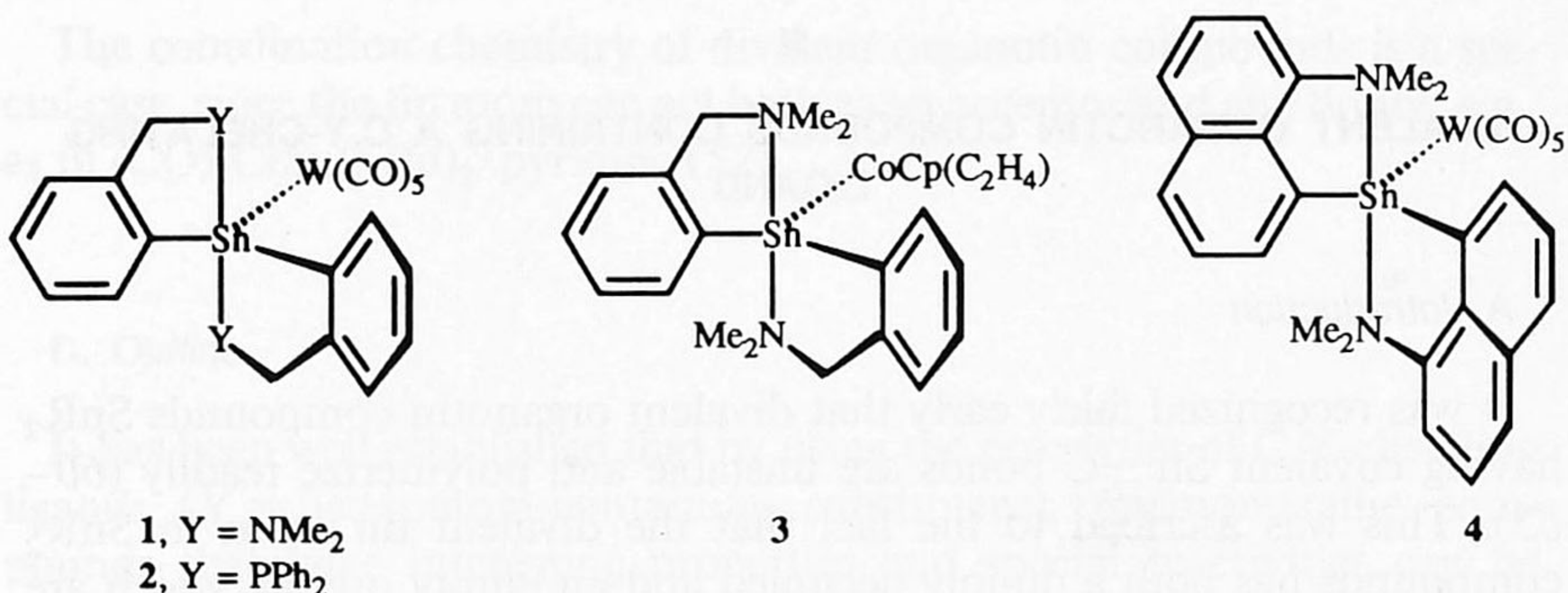
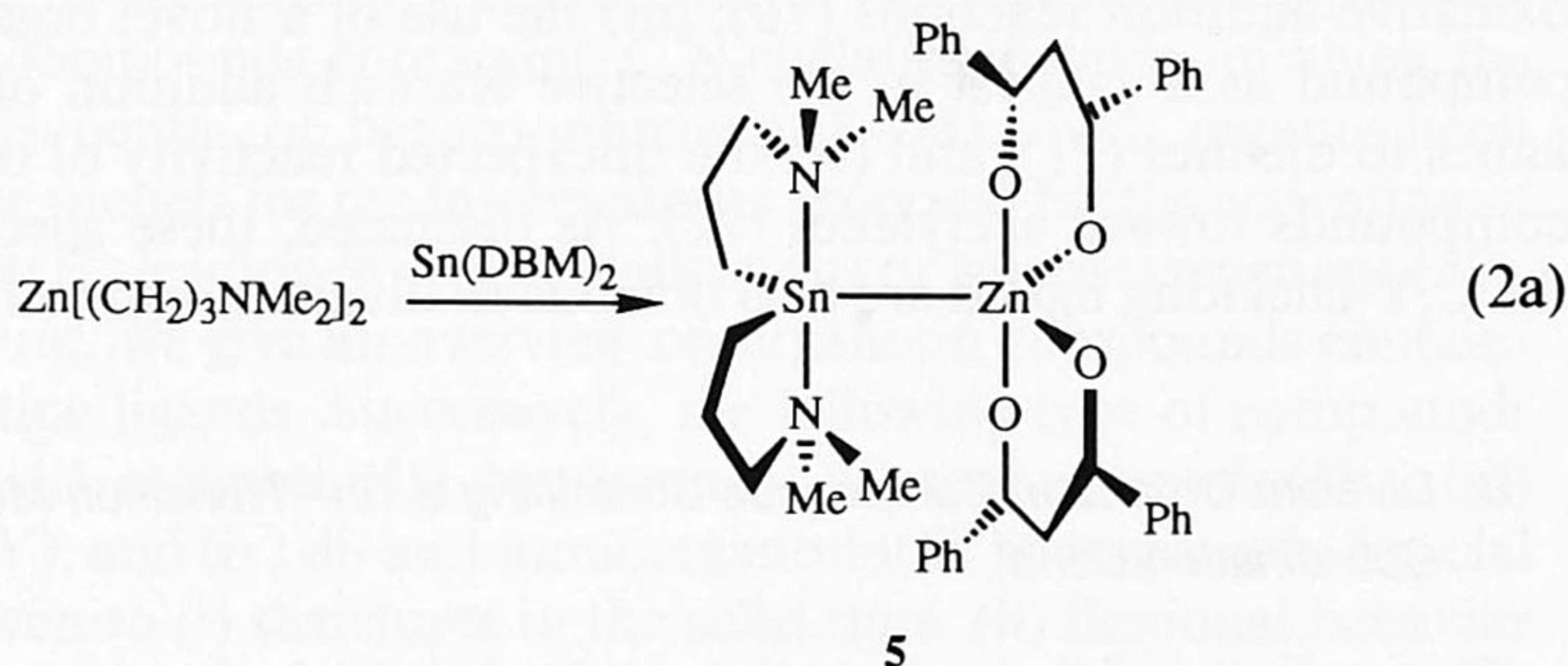


FIG. 4. Divalent organotin-transition metal compounds containing a C,Y-chelating ligand.

e.g., (CO)<sub>5</sub>CrSn(*t*-Bu)<sub>2</sub> · pyridine (52). It is therefore not surprising that the first reported divalent organotin compounds containing a C,Y-chelating ligand also contain a transition metal fragment, i.e., bis{2-[(dimethylamino)methyl]phenyl}tin tungsten pentacarbonyl, **1**; bis{2-[(diphenylphosphino)methyl]phenyl}tin tungsten pentacarbonyl, **2** (73); bis{2-[(dimethylamino)methyl]phenyl}tin cyclopentadienyl(ethylene)cobalt, **3** (74); and bis[8-(dimethylamino)-1-naphthyl]tin tungsten pentacarbonyl, **4** (75). It was found by X-ray crystallography that these compounds have closely related structures in which the tin centers have a trigonal bipyramidal coordination geometry, with the carbon ligands and the transition metal atom at the equatorial sites and both intramolecular coordinating heteroatoms at the axial positions; see Fig. 4.

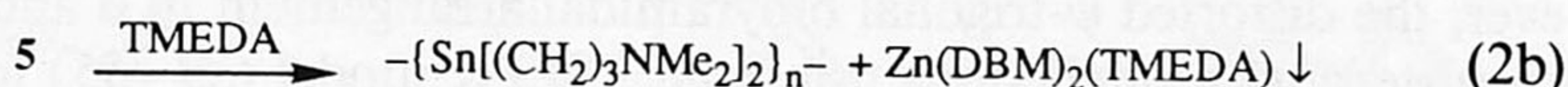
A novel example of this type of SnR<sub>2</sub> · Lewis acid compound is the product obtained from the transmetallation reaction of bis[3-(dimethylamino)propyl]zinc with bis(dibenzoylmethanato)tin(II).



An X-ray crystal structure determination showed this compound to be a unique complex, **5**, in which an intramolecularly coordinated dialkyl-



tin(II) compound is acting as an electron donor to a zinc- $\beta$ -diketonate acceptor (76). The importance of the coordination of the  $\text{Sn}[(\text{CH}_2)_3\text{NMe}_2]_2$  tin lone pair to the  $\text{Zn}(\text{DBM})_2$  moiety for the stability of **5** becomes evident when **5** is reacted with 1 equivalent of tetramethylethylenediamine (TMEDA)



This reaction results in the quantitative formation of insoluble  $\text{Zn}(\text{DBM})_2(\text{TMEDA})$  and a soluble organotin oligomer. It is clear that in this reaction  $\text{Sn}[(\text{CH}_2)_3\text{NMe}_2]_2$  is liberated by a ligand-substitution reaction and undergoes the fast oligomerization reaction that is common for simple dialkyl- and diaryl-tin(II) compounds (77).

### C. Divalent Organotin Compounds Stabilized by Intramolecular Coordination

Recently the first examples of divalent organotin compounds in which intramolecular coordination as such is sufficient for stabilization were reported. These compounds are bis[2-[(dimethylamino)methyl]phenyl]tin(II), **6** (74); bis[2-[1-(dimethylamino)ethyl]phenyl]tin(II), **7** (78); bis[8-(dimethylamino)-1-naphthyl]tin(II), **8** (75); bis[[2-(dimethylamino)phenyl](trimethylsilyl)methyl]tin(II), **9** (78); and bis[(2-pyridyl)bis(trimethylsilyl)methyl]tin(II), **10** (79) and are schematically shown in Fig. 5.

According to X-ray crystal structure determinations of **6** and **8**, the best description of the coordination geometry of the tin center in these compounds is a  $\psi$ -trigonal bipyramidal one, with the carbon ligands and the lone pair at the equatorial sites and both intramolecular coordinating nitrogen atoms at the apical positions (74,75). Compound **10** has a square-pyramidal structure, with the lone pair at the apex of the pyramid. Most

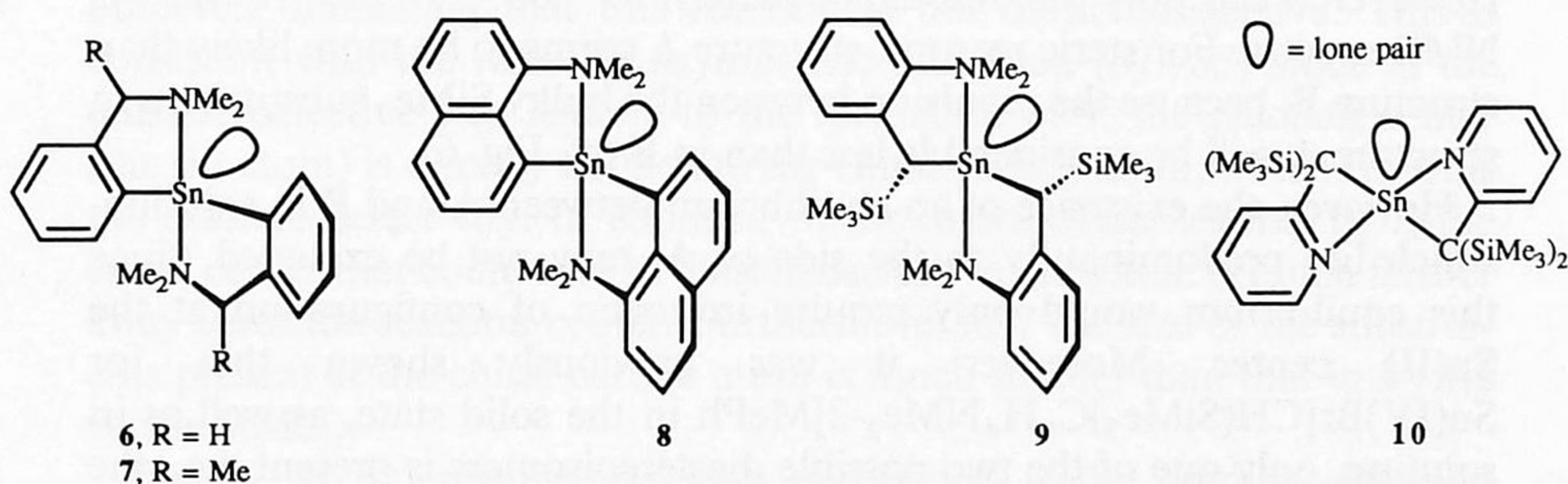


FIG. 5. Divalent organotin compounds stabilized by two C,N-chelating ligands.

likely, this latter geometry is the result of strain in the molecule due to the formation of two four-membered chelate rings (79).

The very acute C—Sn—C angles [100.5(1) and 93.8(5)° for **6** and **8**, respectively] seem to contrast with the values found for their corresponding W(CO)<sub>5</sub> adducts **1** and **4** [117.4(2) and 102.6(3)°, respectively]. However, the distorted  $\psi$ -trigonal bipyramidal arrangement in **6** and **8** is fully consistent with predictions using the VSEPR model (33–35) for discrete AX<sub>2</sub>Y<sub>2</sub>E species (A = central atom; E = lone pair; X, Y = ligands). In diorganotin N-donor complexes, repulsive forces between the Sn—C bonding electrons and the tin lone pair may be relieved either by a decrease in the C—Sn—C angle from 120° or by lengthening of the Sn—N bonds (35). In **6** and **8**, a reduction in the C—Sn—C angle is observed.

Based on the observed <sup>1</sup>H and <sup>13</sup>C NMR spectra of **7** and **9** at various temperatures, a  $\psi$ -trigonal bipyramidal coordination geometry at the tin center in these compounds was proposed also. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic studies of **6–10** showed that in solution, fluxional processes are operative. Although the coalescence of the diastereotopic NMe<sub>2</sub> resonances observed for **6** was explained in terms of a rapid “polytopal” rearrangement (74), studies on **7**, in which the chiral C<sub>6</sub>H<sub>4</sub>CH(Me)NMe<sub>2</sub>-2 ligand is present, showed unequivocal evidence for a process involving Sn—N dissociation/association (78).

As a consequence of the anticipated coordination geometry ( $\psi$ -trigonal bipyramidal) of the tin center in **9**, this atom becomes an additional chiral center. Since this compound is prepared starting from a racemic precursor, in principle three different diastereoisomers **A**, **B**, and **C** are expected (Fig. 6).

Structure **C**, in which the two chiral carbon atoms have opposite configurations, may be excluded on the basis of the low-temperature <sup>1</sup>H and <sup>13</sup>C NMR spectra. Here, the two organic groups are inequivalent and thus should give rise to two different resonance patterns, as was indeed observed for racemic bis{2-[1-(dimethylamino)ethyl]phenyl}tin(II) **7**, *vide infra*. However, **9** has only one resonance pattern to –80°C in the <sup>1</sup>H and <sup>13</sup>C NMR spectra. For steric reasons, structure **A** seems to be more likely than structure **B**, because the repulsion between the bulky SiMe<sub>3</sub> substituents in structure **A** will be considerable less than in **B** (cf. Fig. 6).

However, the existence of an equilibrium between **A** and **B** in solution, which lies predominantly to the side of **A**, may not be excluded, since this equilibrium would only require inversion of configuration at the Sn(II) center. Moreover, it was previously shown that for Sn(IV)Br[CH(SiMe<sub>3</sub>)C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-2]MePh in the solid state, as well as in solution, only one of the two possible diastereoisomers is present, i.e., the sterically most favorable one in which the SiMe<sub>3</sub> substituent and the phenyl group of tin lie at opposite sites of the molecule (80).

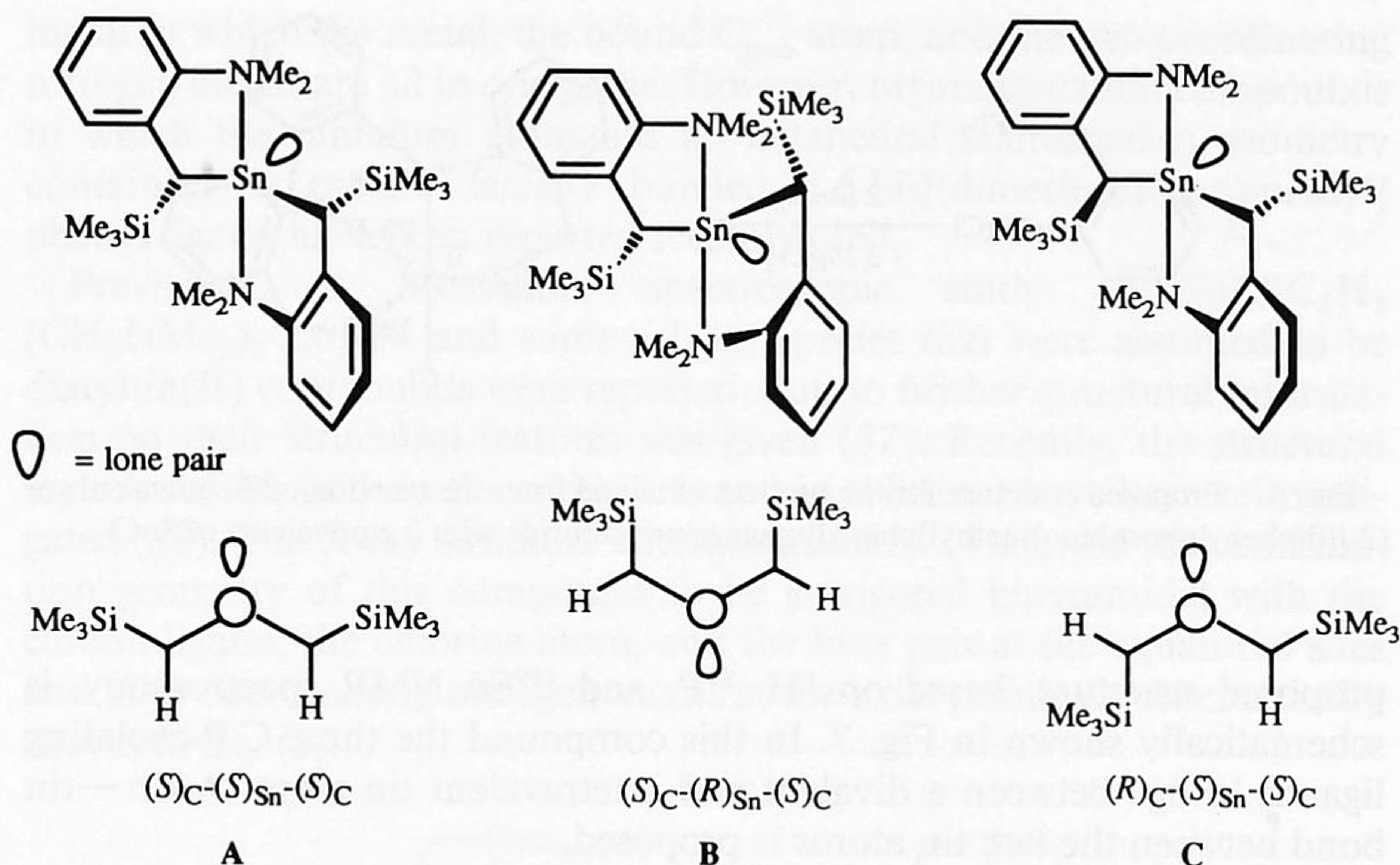


FIG. 6. Schematic representation of the three possible diastereoisomeric structures A, B, and C for **9**, together with a view along the axial vertex of the trigonal bipyramid, showing the relative positions of the bulky  $\text{Me}_3\text{Si}$  substituents.

The observation that only the diastereoisomer in which the two chiral carbon atoms have the same configuration is formed indicates that the reaction of racemic  $\text{Li}[\text{CH}(\text{SiMe}_3)(\text{C}_6\text{H}_4\text{NMe}_2-2)]$  with  $\text{SnCl}_2$  is diastereoselective. Most likely, the actual diastereoselection occurs in the second step of the reaction, i.e., during the reaction of the intermediate  $\text{SnCl}[\text{CH}(\text{SiMe}_3)(\text{C}_6\text{H}_4\text{NMe}_2-2)]$  with  $\text{Li}[\text{CH}(\text{SiMe}_3)(\text{C}_6\text{H}_4\text{NMe}_2-2)]$  to give **9**.

In contrast, the formation of two diastereoisomeric pairs of **7** in a 1:1 ratio from the reaction of racemic  $\text{Li}[\text{C}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2-2]$  with  $\text{SnCl}_2$  is observed, indicating that this reaction is not diastereoselective. This is consistent with the rules for asymmetric induction (81–83) since in the diastereoselective step leading to the formation of **9**, the reaction center (the tin atom) is directly bonded to the chiral carbon atom, which controls the diastereoselectivity. In contrast, in the intermediate leading to **7**, the chiral center that could lead to diastereoselective induction is much farther away from the reaction center. Furthermore, in **7** the size of the substituents present at the chiral carbon atom is much smaller than that in **9** (Me versus  $\text{SiMe}_3$ ).

Finally, an interesting organotin compound is the product obtained from the reaction of 3 equivalents of {2-[(diphenylphosphino)methyl]phenyl}magnesium chloride with 2 equivalents of  $\text{SnCl}_2$  (84). For **11**, the

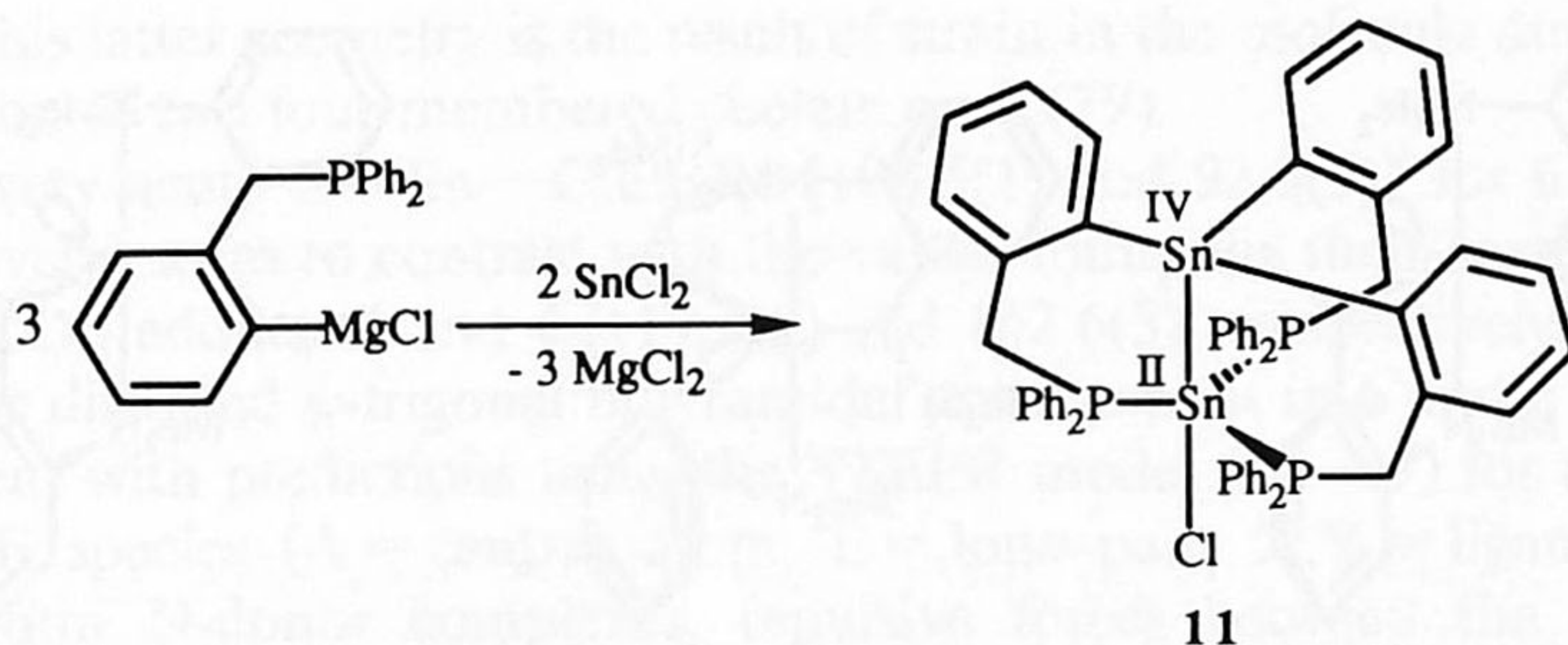
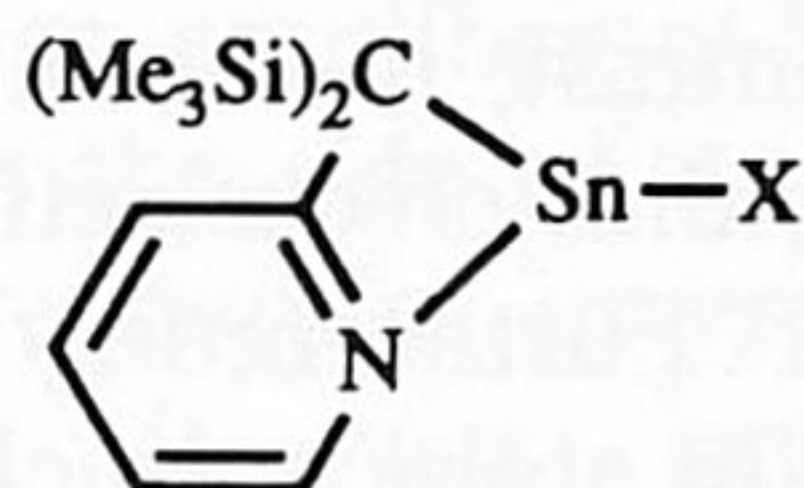


FIG. 7. Proposed structure for the product obtained from the reaction of 3 equivalents of 2-[(diphenylphosphino)methyl]phenylmagnesium chloride with 2 equivalents of  $\text{SnCl}_2$ .

proposed structure, based on  $^1\text{H}$ ,  $^{31}\text{P}$ , and  $^{119}\text{Sn}$  NMR spectroscopy, is schematically shown in Fig. 7. In this compound the three C,P-chelating ligands bridge between a divalent and a tetravalent tin atom: A tin—tin bond between the two tin atoms is proposed.

The first examples of heteroleptic divalent organotin compounds authenticated by X-ray crystal structure determinations are: [2-pyridylbis(trimethylsilyl)methyl]tin chloride **12** and [2-pyridylbis(trimethylsilyl)methyl]bis(trimethylsilyl)amidotin **13**, for which the structures are schematically shown in Fig. 8 (73). The distorted trigonal pyramidal coordination geometry of the tin center in these compounds may be a result of the formation of a four-membered chelate ring.

It has been well established that the monoanionic terdentate 2,6-bis[(dimethylamino)methyl]phenyl ligand stabilizes otherwise unstable or transient organometallic species to such an extent that they become isolable (85). Especially in late transition metal chemistry, the three hard donor atoms of this ligand have been shown to enhance the nucleophilic character of Ni(II) and Pt(II) centers and, moreover, stabilize organometallic species in which the metal has an unusual oxidation number, e.g., Fe(III), Co(II), and Ni(III) (67–69) for an organometallic compound. Previously it was thought that this ligand enforces a coordination geometry to the



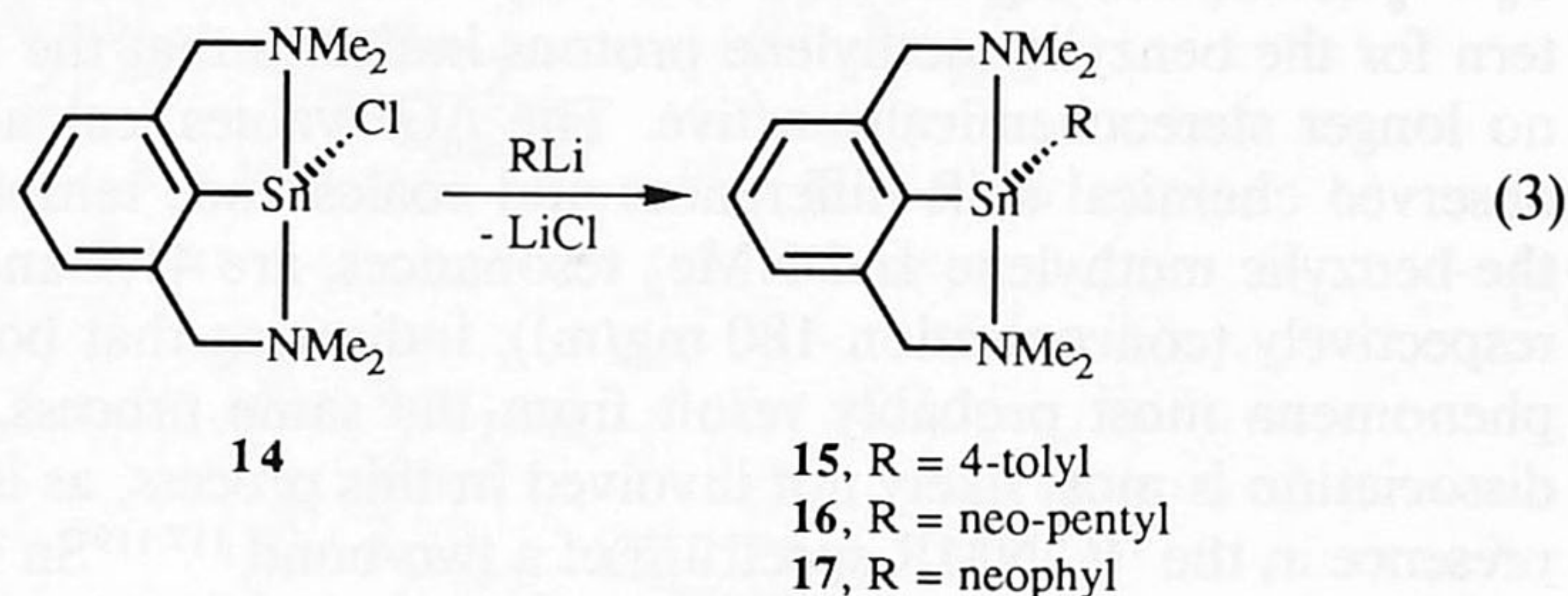
12, X = Cl

13, X = N(SiMe<sub>3</sub>)<sub>2</sub>

FIG. 8. The first examples of heteroleptic divalent organotin compounds.

metal in which the metal, the bound  $C_{\text{ipso}}$  atom, and the two coordinating nitrogen atoms are all in one plane. However, organotantalum compounds in which the tantalum atom has an octahedral coordination geometry containing a pseudo facially bonded 2,6-bis[(dimethylamino)methyl]phenyl ligand have been reported recently (86).

Previously, a Mössbauer spectroscopic study of  $\text{SnCl}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}]$  **14** and some related species that were assumed to be diaryltin(II) compounds were reported, but no further structural information on their structural features was given (87). Recently, the structural features of **14**, both in the solid state and in solution, have been reinvestigated (88). The X-ray structure determination of **14** showed the coordination geometry of this compound to be  $\psi$ -trigonal bipyramidal with the carbon ligand, the chlorine atom, and the lone pair at the equatorial sites and both coordinating nitrogen atoms at the axial positions, schematically shown in Eq. (3).



Remarkable is the acute C—Sn—Cl angle of  $95.0(3)^\circ$  in **14**, most probably for the same reason as found for the C—Sn—C angle in homoleptic divalent organotin compounds in which the tin center has a  $\psi$ -trigonal bipyramidal coordination geometry (*vide supra*).

Further reaction of the organotin(II) chloride **14** with 4-tolyl-, neopentyl-, or neophyllithium affords the unique corresponding mixed aryl—alkyltin(II) compounds **15**, **16**, and **17** respectively [Eq. (3)] (88).

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **14–17** show that in solution at low temperatures ( $-70^\circ\text{C}$  for **14** and  $-25^\circ\text{C}$  for **15–17**), these compounds have structures that are comparable to that found for **14** in the solid state, i.e., a  $\psi$ -trigonal bipyramidal coordination geometry at tin, with the nitrogen atoms at the axial positions and the remaining substituents and the lone pair in the equatorial plane.

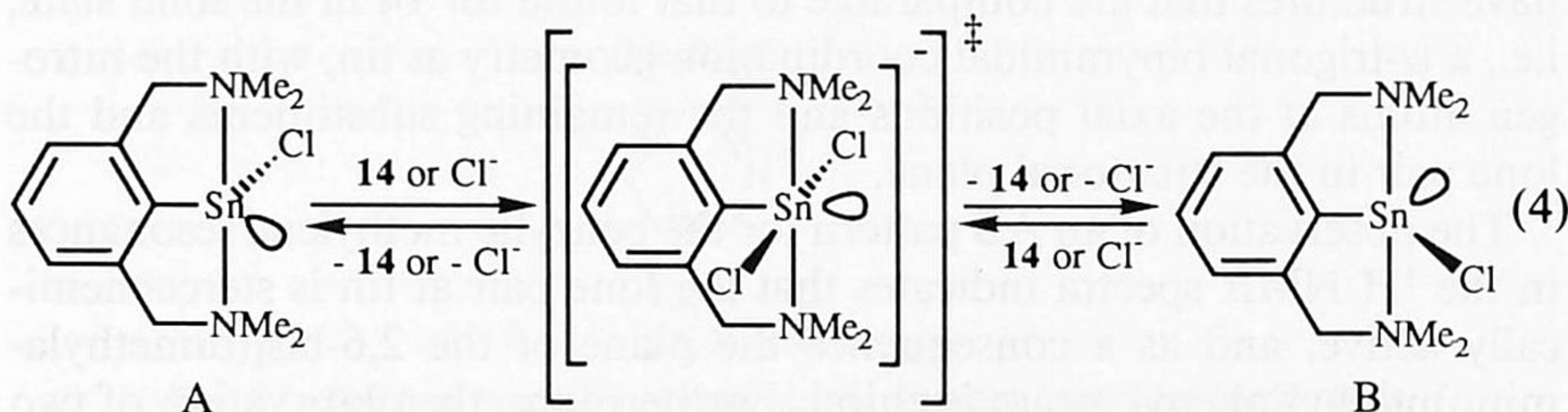
The observation of an AB pattern for the benzylic methylene resonances in the  $^1\text{H}$  NMR spectra indicates that the lone pair at tin is stereochemically active, and as a consequence the plane of the 2,6-bis[(dimethylamino)methyl]phenyl group is chiral. Furthermore, the observation of two

resonances for the  $\text{NMe}_2$  groups indicates that  $\text{Sn}-\text{N}$  coordination is inert at the NMR time scale at these temperatures.

A striking difference between the variable temperature NMR spectra of **14** and of **15-17** is observed. Although, in the heteroleptic diorganotin(II) compounds **15-17** coalescence occurs for the diastereotopic  $\text{NMe}_2$  resonances, the AB pattern of the benzylic methylene resonances remains intact up to  $+120^\circ\text{C}$  (the highest temperature studied). This points to a process involving  $\text{Sn}-\text{N}$  dissociation, while the  $\text{Sn}$  lone pair remains stereochemically active and rotation around the  $\text{C}_{\text{ipso}}-\text{Sn}$  bond is blocked. (Fast rotation around this bond would give rise to loss of the planar chirality and thus would render the diastereotopic benzylic methylene resonances homotopic.)

In the  $^1\text{H}$  NMR spectrum of **14**, however, simultaneous coalescence of both the  $\text{NMe}_2$  and  $\text{CH}_2$  resonances occurs, while the coalescence temperature  $T_c$  is strongly dependent on the concentration of **14** (16 mg/ml,  $T_c = -25^\circ\text{C}$ ; 180 mg/ml,  $T_c = -60^\circ\text{C}$ ). The coalescence of the AB pattern for the benzylic methylene protons indicates that the tin lone pair is no longer stereochemically active. The  $\Delta G^\ddagger$  values, calculated from the observed chemical shift differences and coalescence temperatures  $T_c$  for the benzylic methylene and  $\text{NMe}_2$  resonances, are 41.9 and 42.3 kJ/mol, respectively (concentration 180 mg/ml), indicating that both coalescence phenomena most probably result from the same process.  $\text{Sn}-\text{N}$  bond dissociation is most likely not involved in this process, as is shown by the presence in the  $^{13}\text{C}$  NMR spectrum of a two-bond  $^{117,119}\text{Sn}$  scalar coupling of 30 Hz to the  $\text{NMe}_2$  carbon atoms. This coupling does not change upon raising the temperature of the solution to  $120^\circ\text{C}$  (the highest temperature studied). Apparently, also at high temperature, i.e., in the coalesced situation,  $\text{Sn}-\text{N}$  coordination in **14** is inert at the NMR time scale. It is not unexpected that in **14**,  $\text{Sn}-\text{N}$  coordination is stronger than in **15-17**, since in **14** the  $\text{Sn}$  center has an increased Lewis acidity as a result of the presence of the chlorine atom.

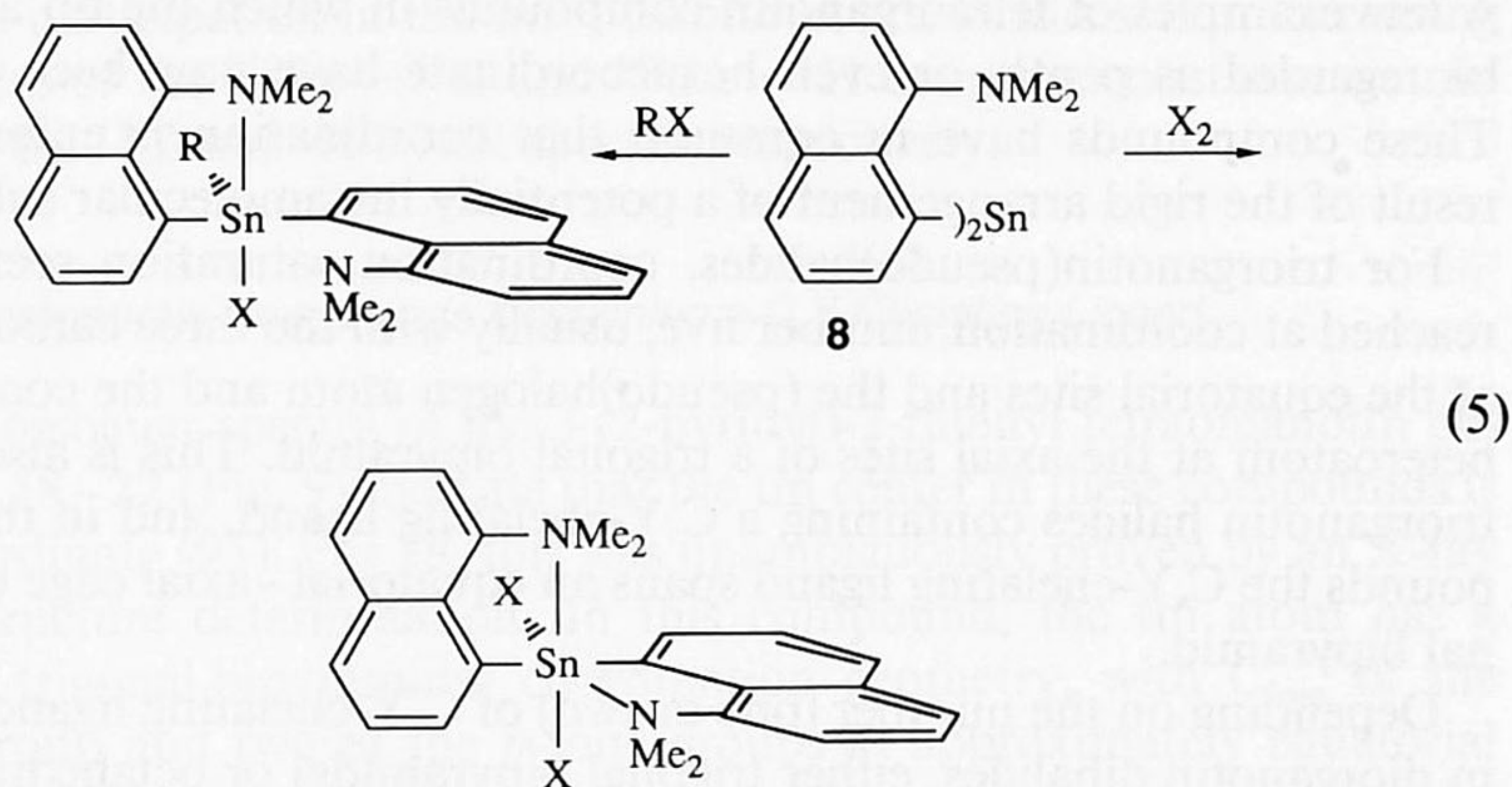
The simultaneous coalescence of the benzylic and  $\text{NMe}_2$  resonances in **14** indicates that on the NMR time scale a fast interconversion between structures A and B (inversion of configuration at tin) occurs.



The observation that the coalescence temperature is dependent on the concentration of **14** points to a bimolecular process. Furthermore, it appeared that addition of LiCl to a solution of **14** lowers the coalescence temperature of the NMe<sub>2</sub> and benzylic resonances. Therefore, ionic species, most probably resulting from initial dimerization of **14**, are proposed to be intermediates in the inversion of configuration at tin.

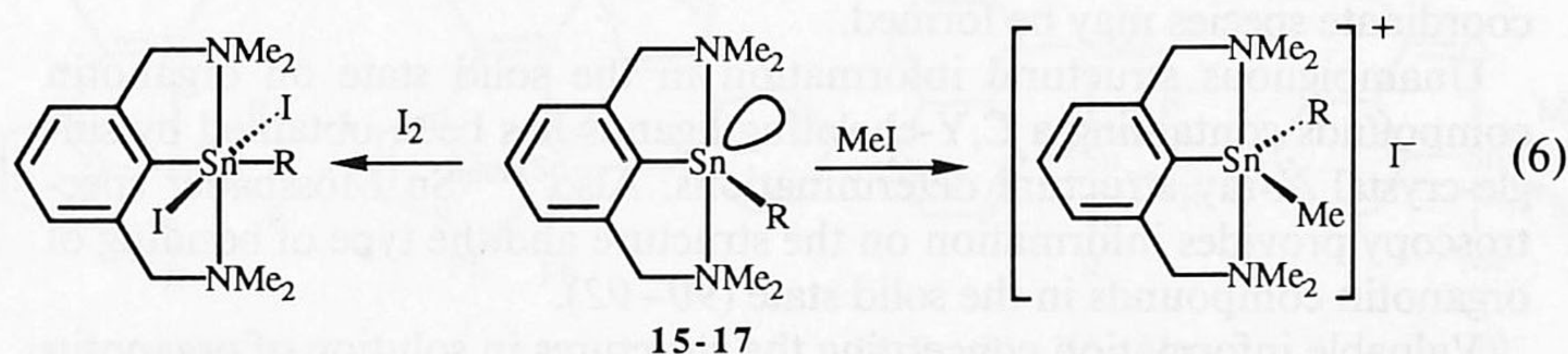
#### D. Reactivity of Divalent Organotin Compounds

It has been recognized that divalent organotin compounds easily undergo oxidative addition reactions (89). Similarly, **8** reacts with alkyl halides and dihalogen to give the corresponding oxidative addition products (75).



These interesting compounds are discussed in Section III.

Similarly, the heteroleptic diorganotin compounds **15-17** react with diiodine and methyl iodide



giving rise to the formation of hexacoordinate diorganotin diiodides and pentacoordinate triorganotin cations, respectively (88). These type of compounds are discussed in Section III.

## III

## TETRAVALENT ORGANOTIN COMPOUNDS CONTAINING A C,Y-CHELATING LIGAND

## A. General

As a consequence of the increasing number of electronegative groups present at the tin atom in the series  $\text{SnR}_4$ ,  $\text{SnXR}_3$ ,  $\text{SnX}_2\text{R}_2$ ,  $\text{SnX}_3\text{R}$  ( $\text{X}$  = halide or pseudo halide), the Lewis acidity at the tin center increases down this series. Due to the poor acceptor properties of the tin atom in tetraorganotin compounds, for a long time these compounds were regarded as being unable to extend their coordination number beyond four. A few examples of tetraorganotin compounds in which the tin atom may be regarded as penta- or even hexacoordinate have now been reported. These compounds have in common that coordination is enforced as a result of the rigid arrangement of a potentially intramolecular substituent.

For triorganotin(pseudo)halides, coordination saturation seems to be reached at coordination number five, usually with the three carbon ligands at the equatorial sites and the (pseudo)halogen atom and the coordinating heteroatom at the axial sites of a trigonal bipyramid. This is also true for triorganotin halides containing a C,Y-chelating ligand, and in these compounds the C,Y-chelating ligand spans an equatorial-axial edge of a trigonal bipyramid.

Depending on the number (one or two) of C,Y-chelating ligands present in diorganotin dihalides, either trigonal bipyramidal or octahedral coordination geometries have been found for the tin center.

Only a very limited amount of data are available for monoorganotin halides containing a C,Y-chelating ligand. In the solid state, a trigonal bipyramidal coordination geometry for the tin center is preferred. However, in solution when external donor molecules are also present, hexacoordinate species may be formed.

Unambiguous structural information in the solid state on organotin compounds containing a C,Y-chelating ligands has been obtained by single-crystal X-ray structure determinations. Also  $^{119\text{m}}\text{Sn}$  Mössbauer spectroscopy provides information on the structure and the type of bonding of organotin compounds in the solid state (90-92).

Valuable information concerning the structures in solution of organotin compounds containing a C,N-chelating ligand is obtained from  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR spectroscopic studies. Furthermore, these studies provide sometimes detailed information on the fluxional processes that are operative in solutions of these compounds. It appears that the  $^{119}\text{Sn}$  chemical



shift value depends on: (i) the type of substituents present at tin and (ii) the coordination number of tin. It is especially the latter property that may cause large changes in chemical shift values. When the coordination number at tin in a given compound is raised from four to five to six, the chemical shift value is shifted downfield by a few hundred parts per million (93). Recently we have reported the  $^{119}\text{Sn}$  spectroscopic parameters of a series of tetra-, tri-, and diorganotin compounds containing several C,N-chelating ligands (94). The observation of one-bond  $^{119}\text{Sn}-^{13}\text{C}$  and two bond  $^{119}\text{Sn}-^1\text{H}$  coupling constants in the  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of organotin compounds provides detailed information on the hybridization of the tin atom in these compounds. The tin—carbon bonds in tetrahedral and trigonal bipyramidal and octahedral arrangements at tin, respectively, proceeds via  $sp^3$ -,  $sp^2$ -, and  $sp$ -like orbitals. As a result of the increasing  $s$ -electron participation in the tin—carbon bonds in this series, increasing magnitudes of the  $^{119}\text{Sn}-^{13}\text{C}$  and  $^{119}\text{Sn}-^1\text{H}$  coupling constants are observed in the  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra, respectively.

#### B. Tetraorganotin Compounds Containing a C,Y-Chelating Ligand

The Mössbauer spectra of the 3-(2-pyridyl)-2-thienyl tetraorganotin derivatives, **18**–**22** (Fig. 9) indicate that the tin center in these compounds is pentacoordinate (95). For **18**, this was unambiguously proven by an X-ray crystal structure determination. In this compound, the tin atom has a distorted trigonal-bipyramidal coordination geometry, with  $\text{C}_{\text{ipso}}$  of the thienyl group and two of the  $p$ -tolyl groups at approximately equatorial positions and the nitrogen atom and one of the  $p$ -tolyl groups at the axial sites. A similar coordination geometry was found for the tin center in

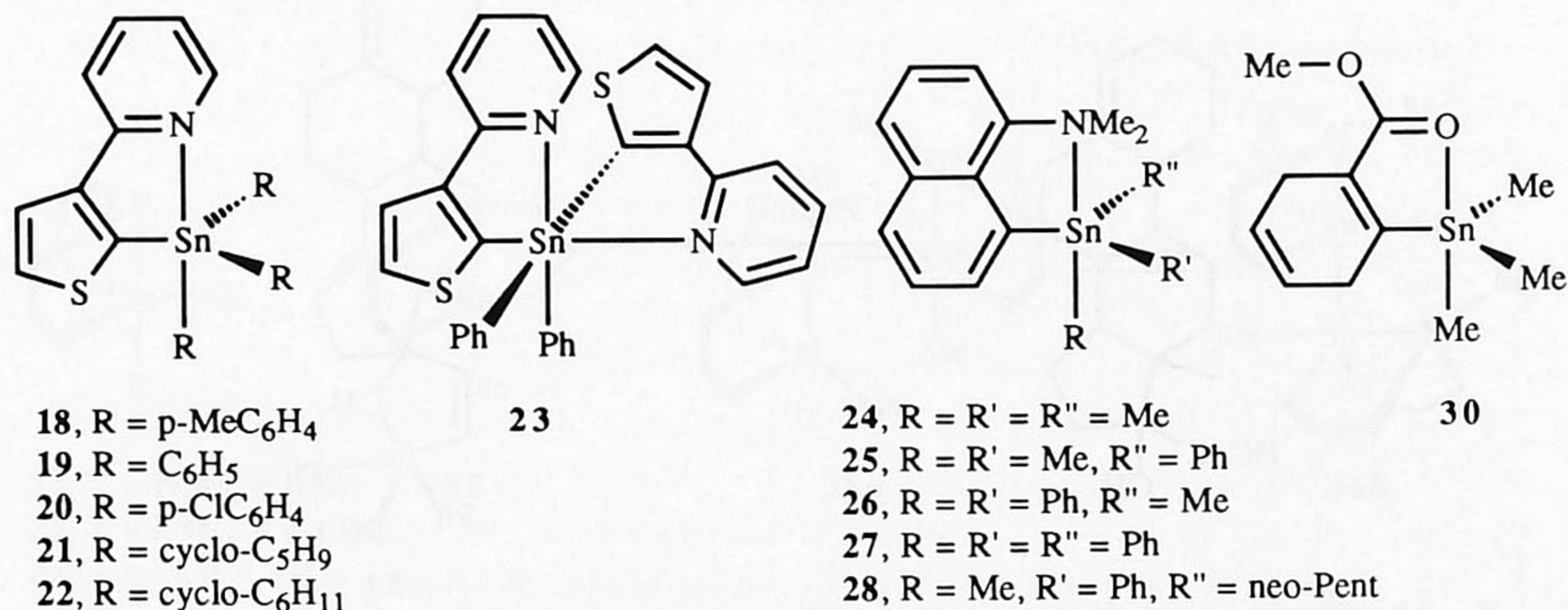


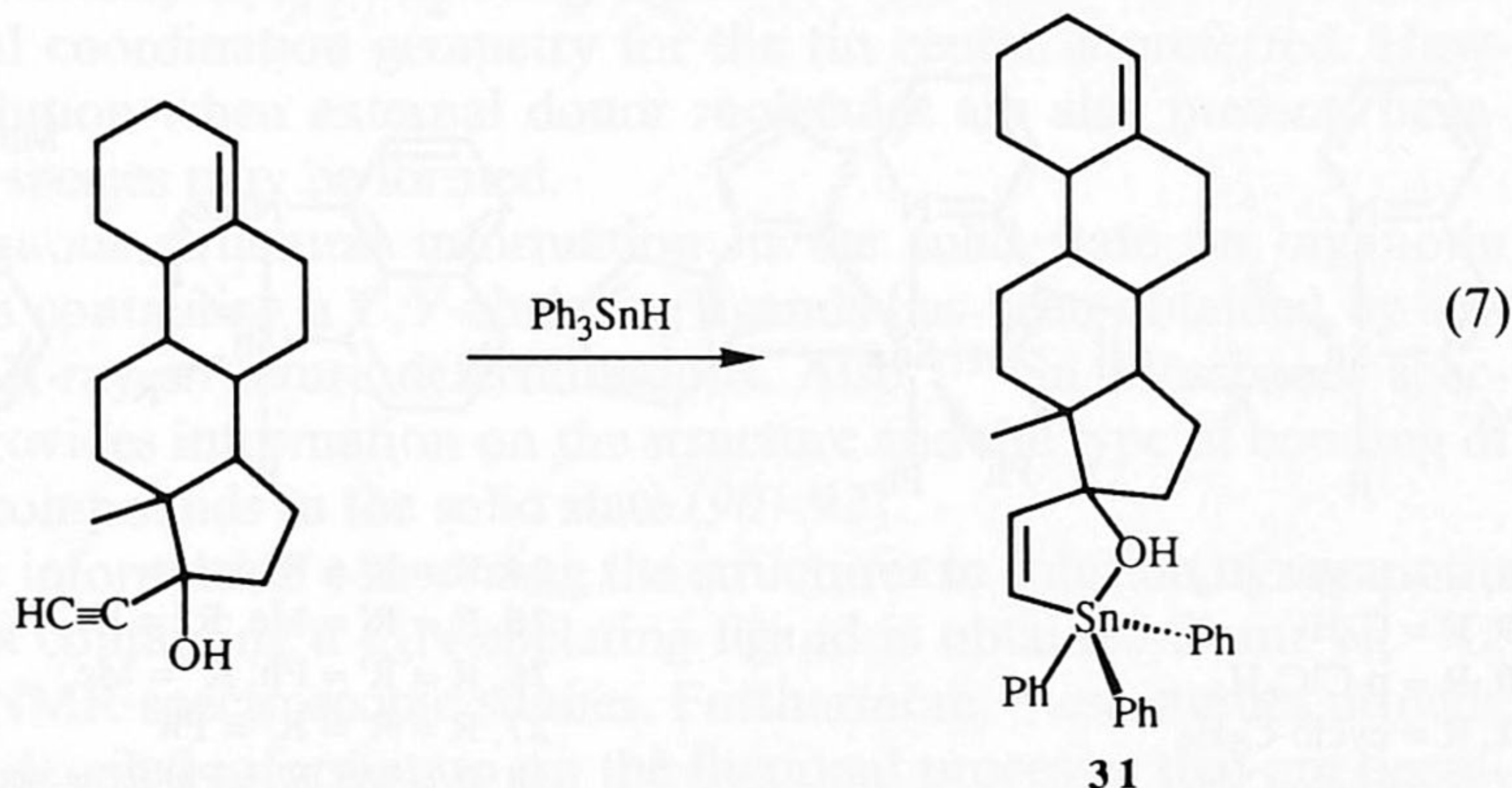
FIG. 9. Tetraorganotin compounds containing a C,N- or C,O-chelating ligand.

[8-(dimethylamino)-1-naphthyl]triphenyltin **27** (96). The Sn—N bond distances of 2.841(7) and 2.884(3) Å, for **18** and **27**, respectively, seem to be rather long, but are nevertheless shorter than those found in  $\text{SnCl}_2\text{Ph}_2 \cdot \text{pyrazine}$  (97), which amount to 2.782(11) and 2.965(11) Å, the latter distance being the longest one ascribed to Sn—N coordination. That in solution the tin centers in **18–22** and **24–28** are pentacoordinate was concluded from (i) the observation of an increase of the  $^1J(^{117,119}\text{Sn}—^{13}\text{C}_{\text{ipso}})$  value in the  $^{13}\text{C}$  NMR spectra and (ii) a high-field shift of the  $^{119}\text{Sn}$  resonance in the  $^{119}\text{Sn}$  NMR spectra (95,96).

An octahedral coordination geometry at the tin center was found by X-ray crystallography in bis[3-(2-pyridyl)-2-thienyl]diphenyltin, **23**; see Fig. 9 (98). The various groups at the tin center have an all-*cis* arrangement. The Sn—N distance of 2.560(2) Å is considerably shorter than that observed in **18**, *vide supra*. That the structure as found for **23** in the solid state is most likely retained in solution was concluded from the comparison of the  $^{119}\text{Sn}$  and  $^{13}\text{C}$  NMR spectra of solutions of **23**, with those of bis(2-thienyl)diphenyltin. Based on the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR spectral data of bis[8-(dimethylamino)-1-naphthyl]dimethyltin, **29**, a distorted octahedral coordination geometry for the tin center in this compound has also been proposed (96).

An X-ray crystal structure determination of (2-carbomethoxy-1,4-cyclohexadien-1-yl)trimethyltin, **30**, revealed that the tin center in this compound is pentacoordinate as a result of intramolecular Sn—O coordination; see Fig. 9 (99). The C(1) atom of the cyclohexadiene moiety and two of the methyl groups are at approximately equatorial positions, and the other methyl group and the coordinating oxygen atom [Sn—O distance 2.781(3) Å] are at the axial sites of a distorted trigonal bipyramid.

The reaction of 17-ethynyl-4-estren-17-ol with triphenyltin hydride



affords selectively the *cis*-addition product **31**, for which the X-ray struc-

ture unambiguously showed that the tin atom has a distorted trigonal bipyramidal coordination geometry, with two phenyl groups and the olefinic carbon atom at approximately equatorial positions, and the coordinating oxygen atom (Sn—O 2.77(1) Å) and one of the phenyl groups at the axial sites (100). It has been proposed that the preferred formation of the *Z*-isomer over the *E*-isomer, which generally are formed in these reactions, is a consequence of the presence of a potentially coordinating group.

The tetraorganotin compounds **18–31** all have in common that the coordinating heteroatom is part of a rather rigid skeleton, which keeps the potentially coordinating heteroatom in close proximity to the tin atom. It is probably this rigid ligand arrangement that enforces coordination of the heteroatom to tin.

Another class of tetraorganotin compounds for which pentacoordination of the tin atom was established are the diptych and triptych compounds, for which the proposed structures are schematically shown in Fig. 10.

That an Sn—Y interaction is present in the diptych compounds **32–34**, resulting in a trigonal-bipyramidal coordination geometry of the tin atom, was concluded from  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR studies (101,102). The low-temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **32** clearly showed the presence of an equatorial and an axial methyl group. The distinct difference between the equatorial and the axial substituent is furthermore illustrated by the observation of relatively large  $^1\text{J}(^{119}\text{Sn}-^{13}\text{C})$  and  $^2\text{J}(^{119}\text{Sn}-^1\text{H})$  values (377 and 54.5 Hz, respectively) for the equatorial methyl group compared with relatively small values for the axial methyl group (197 and 40.1 Hz, respectively). Most likely this is a result of the enhanced *s*-electron participation at the equatorial positions of the trigonal bipyramid.

That Sn—N coordination is present in the triptych compound **35** was unambiguously proven by an X-ray crystal structure determination of this compound (103). The tin atom in **35** has a distorted trigonal bipyramidal

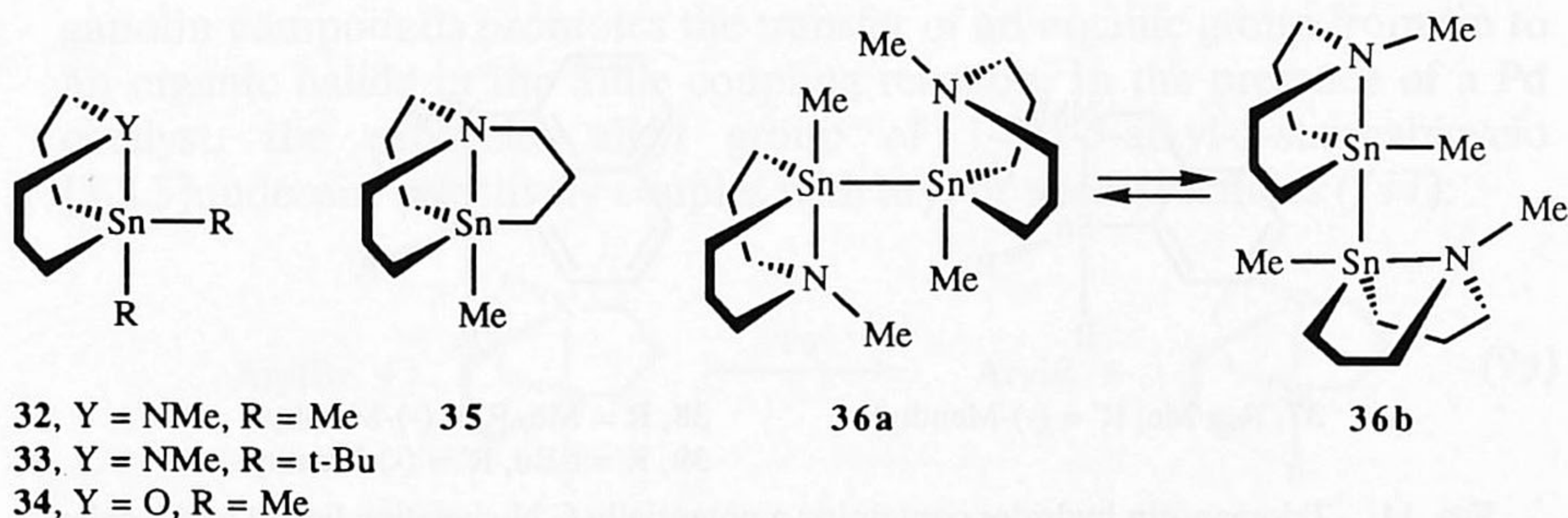


FIG. 10. Diptych and triptych tetraorganotin derivatives with intramolecular Sn—Y coordination.

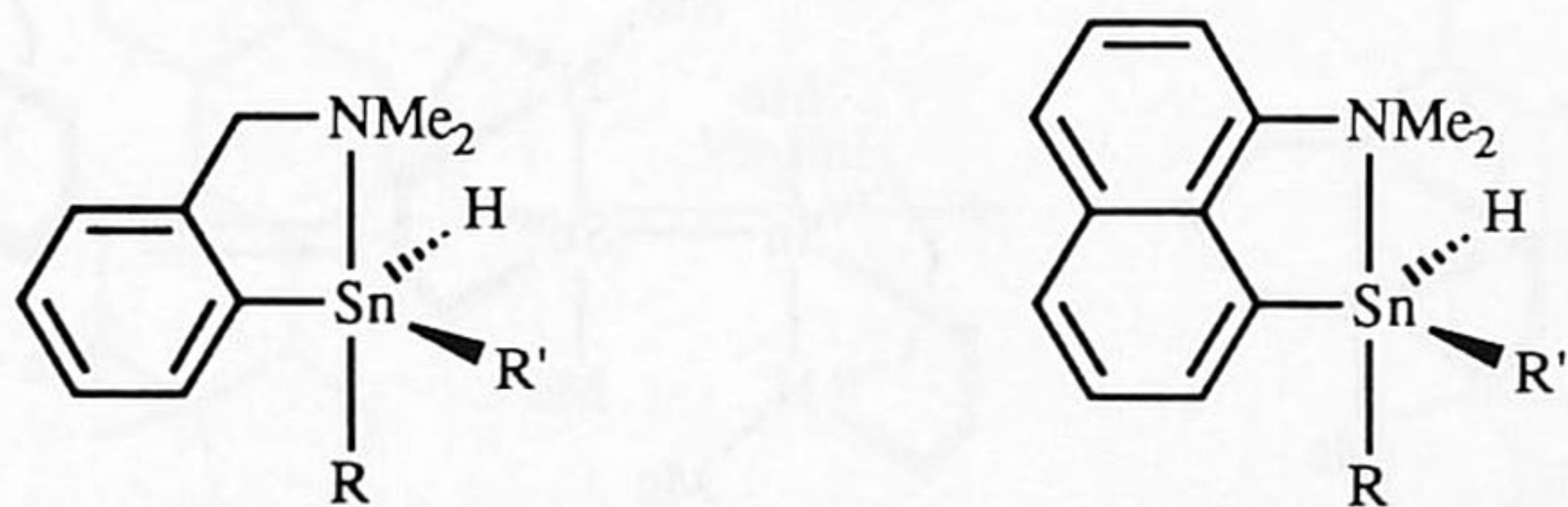
coordination geometry, with the nitrogen atom (Sn—N distance 2.624(8) Å) and the methyl group at the axial positions.

Finally, in the diptych compound **36**, an intramolecular Sn—N interaction was proposed, based on the observed  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR spectra (104). It appeared that in solution an equilibrium exists between at least three isomers for which the proposed structures of the two most abundant ones, **36a** and **36b** (70 and 27%, respectively) are shown in Fig. 10. Furthermore, 2D  $^{119}\text{Sn}$  EXSY spectroscopy (104) showed that these two isomers mutually isomerize via an uncorrelated rearrangement at the tin atom.

A rather unusual series of compounds, which may be regarded as tetraorganotin compounds containing a potentially C,N-chelating ligand, are the triorganotin hydrides **37–39** shown in Fig. 11 (105,106).

These compounds were obtained from the  $\text{LiAlH}_4$  reduction of the corresponding triorganotin bromides (*vide infra*). It should be noted that it is rather unexpected that these compounds are stable, since it is well known that amines catalyze the decomposition of organotin hydrides to ditin compounds and hydrogen (107).

The fact that these compounds were obtained as diastereoisomeric mixtures [the configuration of the (–)-menthyl unit is fixed, the configuration of the tin center may be either (*R*) or (*S*)], varying from 46:54 for **37** to 40:60 for **39** for the two diastereoisomers, indicates that the diastereoselection during the reduction step is small. Evidence for the anticipated intramolecular Sn—N coordination in **37** and **38** was obtained from the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of these compounds. The increased (compared to the values of menthylmethylnaphthyltin hydride)  $^1\text{J}(^{13}\text{C}-^{119}\text{Sn})$  and  $^1\text{J}(^1\text{H}-^{119}\text{Sn})$  values of the menthyl and hydride resonances, respectively, points to an increased *s*-orbital participation in these bonds, while the decreased (again compared to the values of menthylmethylnaphthyltin hydride)  $^1\text{J}(^{13}\text{C}-^{119}\text{Sn})$  and  $^2\text{J}(^1\text{H}-^{119}\text{Sn})$  values for the methyl resonance points to an decreased *s*-orbital participation in this bond. These



**37**, R = Me, R' = (–)-Menthyl

**38**, R = Me, R' = (–)-Menthyl

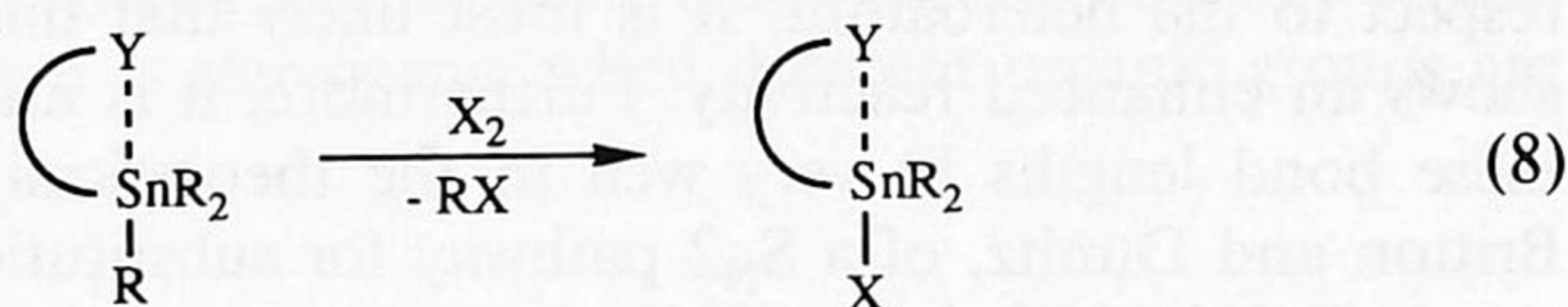
**39**, R = t-Bu, R' = (–)-Menthyl

FIG. 11. Triorganotin hydrides containing a potentially C,N-chelating ligand and a chiral (–)-menthyl group.

observations suggest a distorted trigonal bipyramidal coordination geometry for the tin center in **37** and **38** with the menthyl group and hydride at equatorial positions and the methyl group at an axial site. An X-ray crystal structure determination unambiguously showed such a structure for **39** in which the menthyl group, the hydride and the naphthyl—C<sub>ipso</sub> are at the equatorial sites and the *tert*-butyl group and the coordinating nitrogen atom (Sn—N 2.885(3) and 2.931(3) Å for two independent molecules, respectively) at the axial positions.

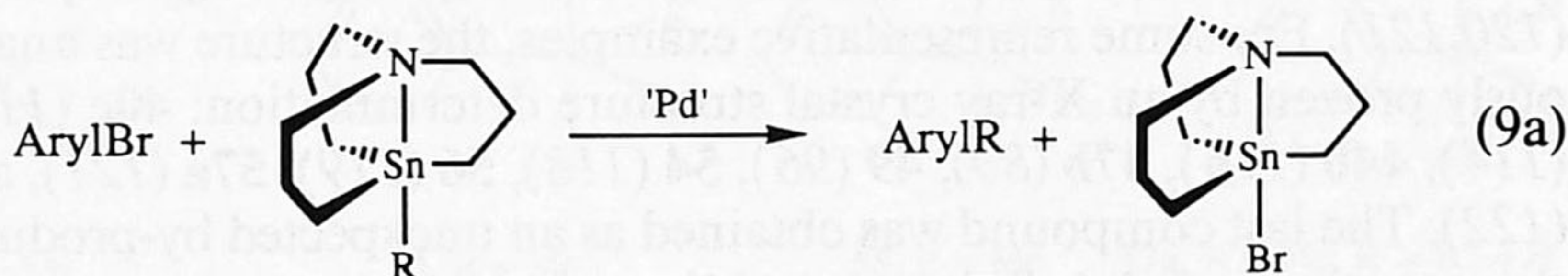
C. *Enhanced Reactivity of the Sn—C Bonds in Tetraorganotin Compounds as a Result of the Enforced Coordination of a Heteroatom-Containing Substituent*

Previously it has been suggested that the reversed reactivity sequence observed in halodemetalation reactions of mixed tetraorganotin compounds, in which a potentially coordinating group (Y) is present in the  $\gamma$ -position with respect to tin, is caused by intramolecular assistance of those groups (108,109):



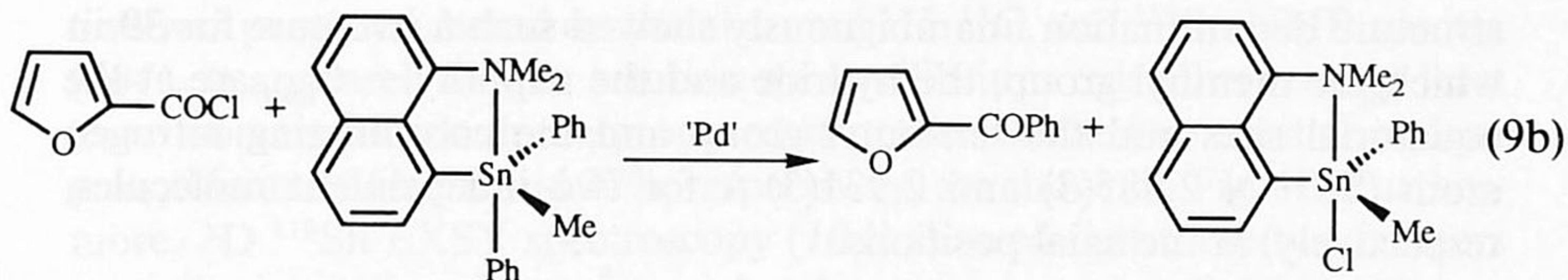
The presence of pentacoordinate tin in such tetraorganotin compounds was confirmed by the X-ray crystal structure determination of (2-carbomethoxy-1,4-cyclohexadien-1-yl)trimethyltin (**99**) *vide supra*. Furthermore, it was shown that tetraorganotin compounds containing the rigid C,N-chelating 8-(dimethylamino)-1-naphthyl ligand show an exceptional reactivity in the redistribution reaction with trimethyltin halide, resulting in the formation of tetramethyltin and a triorganotin halide containing the 8-(dimethylamino)-1-naphthyl ligand (96,110).

Recently it was shown that intramolecular coordination at tin in tetraorganotin compounds promotes the transfer of an organic group from tin to an organic halide in the Stille coupling reaction. In the presence of a Pd catalyst, the exocyclic alkyl group of 1-aza-5-alkyl-5-stannabicyclo [3.3.3]undecane selectively couples with aryl or alkenyl halides (111):



Furthermore, we have recently shown that the rate of the palladium-cata-

lyzed phenyl transfer from [8-(dimethylamino)-1-naphthyl]diphenylmethyltin to 2-furoyl chloride



is enhanced by a factor of  $10^2$  as a result of intramolecular assistance by the intramolecularly coordinating  $\text{NMe}_2$  group in the tetraorganotin compound (112).

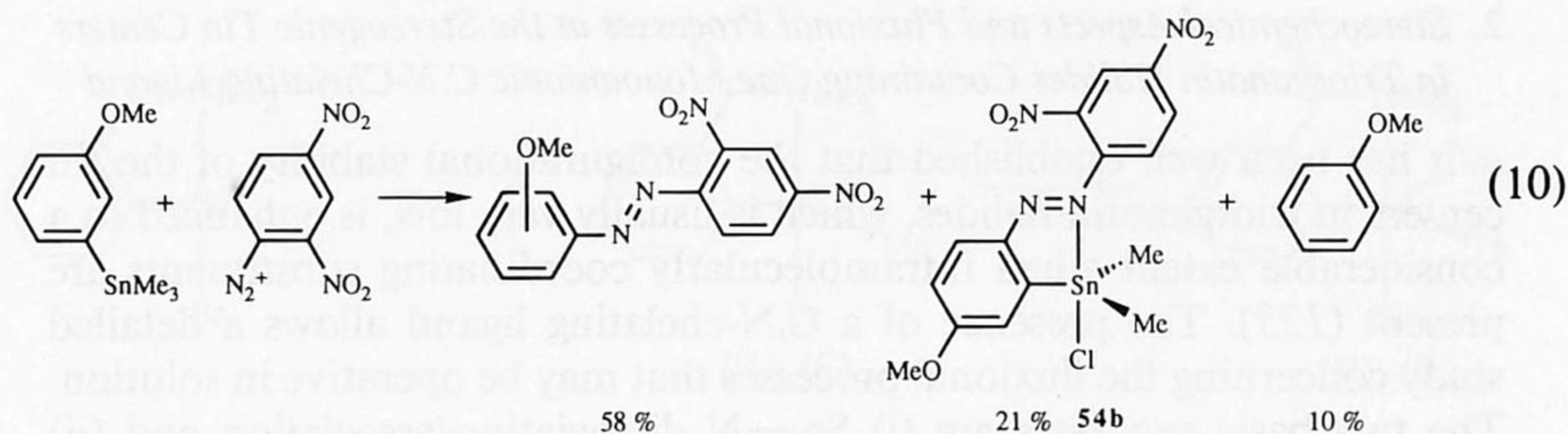
X-ray crystal structure determinations of different tetraorganotin compounds containing a C,Y-chelating ligand have shown that the Sn—Y coordination bonds are extremely long (*vide supra*). That these coordinating heteroatoms, however, have a considerable influence on the electronic situation at Sn is reflected in enlarged C—Sn bonds, *trans*-orientated with respect to the heteroatom. It is most likely that this *trans*-Sn—C bond shows an enhanced reactivity. Furthermore, it is interesting to note that these bond lengths fit very well in the theoretically deduced curve by Britton and Dunitz, of a  $\text{S}_{\text{N}}2$  pathway for substitution with inversion at tetrahedral tin (*vide infra*) (113).

#### D. Triorganotin Halides Containing a C,Y-Chelating Ligand

##### 1. Compounds Containing One Monoanionic C,N-Chelating Ligand

The triorganotin halides containing one monoanionic C,N-chelating ligand that has been studied are depicted in Fig. 12.

These compounds include the following type of C,N-chelating ligands: 2-[(dimethylamino)methyl]phenyl **40a–45** (54,114–117); [2-(dimethylamino)phenyl]methyl **46a–c**, **47a–c** (80); 8-dimethylamino-1-naphthyl **48–50** (110); {2-[(dimethylamino)methyl]phenyl}methyl **51,52** (118), 8-(dimethylamino)methyl-1-naphthyl, **53,54** (118), 2-(4,4-dimethyl-2-oxazoline)-5-(methyl)phenyl **55,56** (119); and 2-(phenylazo)phenyl **57a,57b** (120,121). For some representative examples, the structure was unambiguously proven by an X-ray crystal structure determination: **40c** (115), **41b** (114), **44b** (116), **47b** (80), **49** (96), **54** (118), **56** (119), **57a** (121), and **57b** (122). The last compound was obtained as an unexpected by-product from the reaction of 2,4-dinitrophenyldiazonium cation with (3-methoxyphenyl)trimethyltin (120):



All these compounds have in common that the tin center has a trigonal bipyramidal coordination geometry with the carbon ligands at the equatorial sites and the more electronegative nitrogen and halogen atom at the axial positions. Pentacoordination is attained by the formation of a five- or six-membered chelate ring spanning an equatorial-axial edge of the trigonal bipyramid.

Based on the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR data of these compounds, it is most likely that the structures as found in the solid state are retained in solution. It should be noted at this point that as a consequence of this geometry, the tin atom is stereogenic when different organic groups are present.

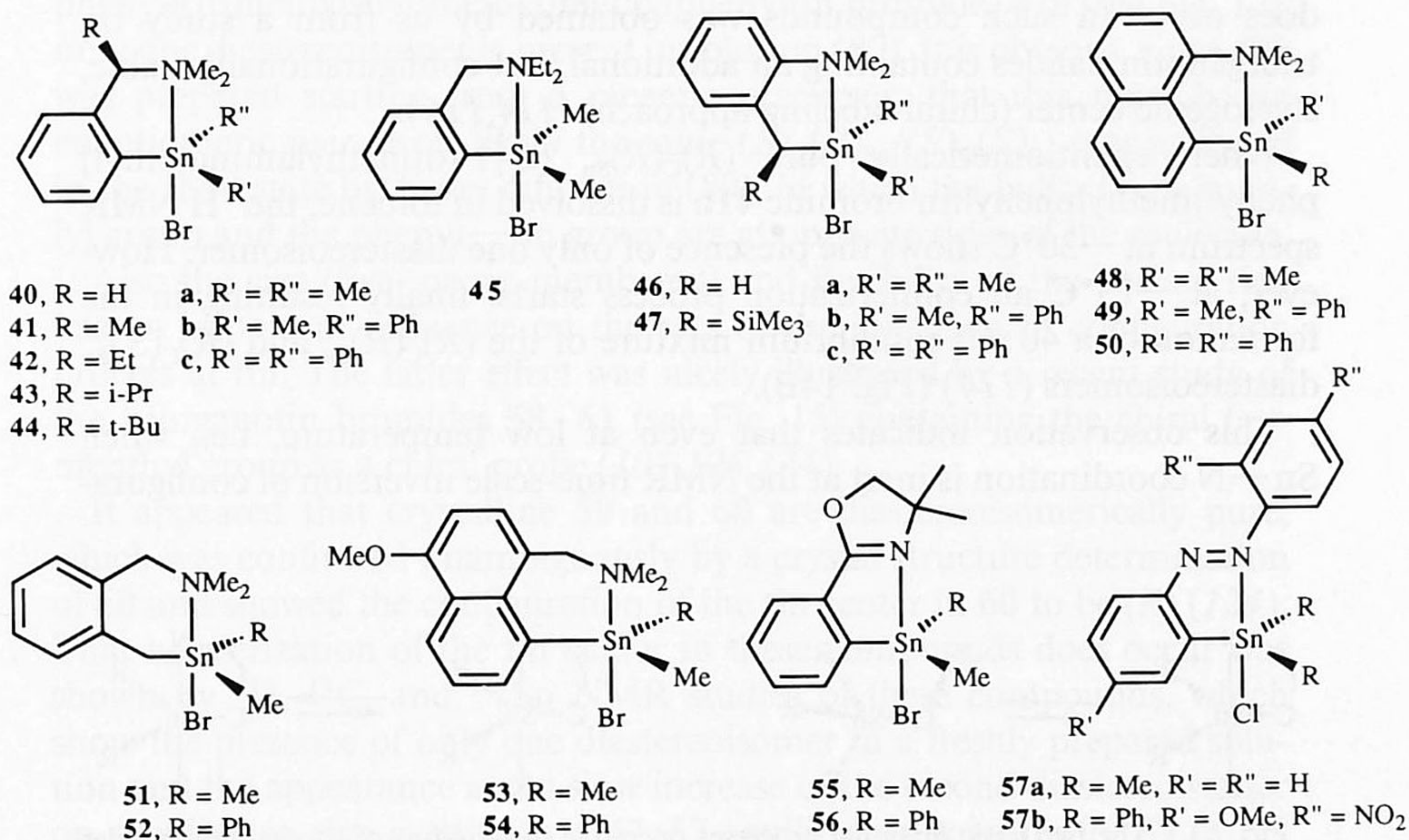


FIG. 12. Triorganotin halides containing one C,N-chelating ligand.

## 2. Stereochemical Aspects and Fluxional Processes at the Stereogenic Tin Centers in Triorganotin Halides Containing One Monoanionic C,N-Chelating Ligand

It has been well established that the configurational stability of the tin centers in triorganotin halides, which is usually very low, is enhanced to a considerable extent when intramolecularly coordinating substituents are present (123). The presence of a C,N-chelating ligand allows a detailed study concerning the fluxional processes that may be operative in solution. The two basic processes are (i) Sn—N dissociation/association and (ii) inversion of configuration of the tin center; see Fig. 13.

That these two processes are operative in solution was concluded by us from the observed  $^1\text{H}$  NMR spectra of chiral {2-[(dimethylamino)methyl]phenyl}methylphenyltin bromide **40b** at different temperature (54) (Fig. 14A). Below  $30^\circ\text{C}$ , the  $\text{NMe}_2$  and the benzylic  $\text{CH}_2$  groups are diastereotopic. Above this temperature, the two methyl resonances of the  $\text{NMe}_2$  group coalesce, indicating that a process involving Sn—N dissociation/association becomes fast on the NMR time scale [a similar conclusion was reached by a temperature-dependent lineshape analysis of the  $^1\text{H}$  resonances of the prochiral  $\text{NEt}_2$  group in **45** (117)]. In contrast, the AB pattern observed for the benzylic  $\text{CH}_2$  group remains unaltered up to at least  $125^\circ\text{C}$  (the highest temperature studied), indicating that configuration inversion of the chiral tin center does not occur or is still slow on the NMR time scale. Evidence that configuration inversion at the tin center does occur in such compounds was obtained by us from a study on triorganotin halides containing an additional, but configurationally stable, stereogenic center (chiral-labeling approach) (114,116).

When enantiomerically pure  $(R)_\text{C}(R)_\text{Sn}$  {2-[1-(dimethylamino)ethyl]phenyl}methylphenyltin bromide **41b** is dissolved in toluene, the  $^1\text{H}$  NMR spectrum at  $-30^\circ\text{C}$  shows the presence of only one diastereoisomer. However, at  $-13^\circ\text{C}$  an epimerization process starts, finally resulting in the formation of a 40:60 equilibrium mixture of the  $(R)_\text{C}(R)_\text{Sn}$  and  $(R)_\text{C}(S)_\text{Sn}$  diastereoisomers (114) (Fig. 14B).

This observation indicates that even at low temperature, i.e., when Sn—N coordination is inert at the NMR time-scale inversion of configura-

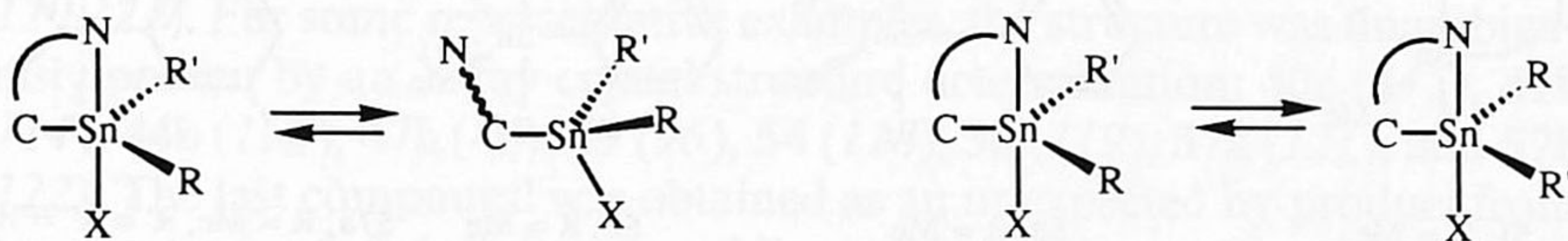


FIG. 13. The two basic fluxional processes operative in solutions of triorganotin halides containing a C,N-chelating ligand.



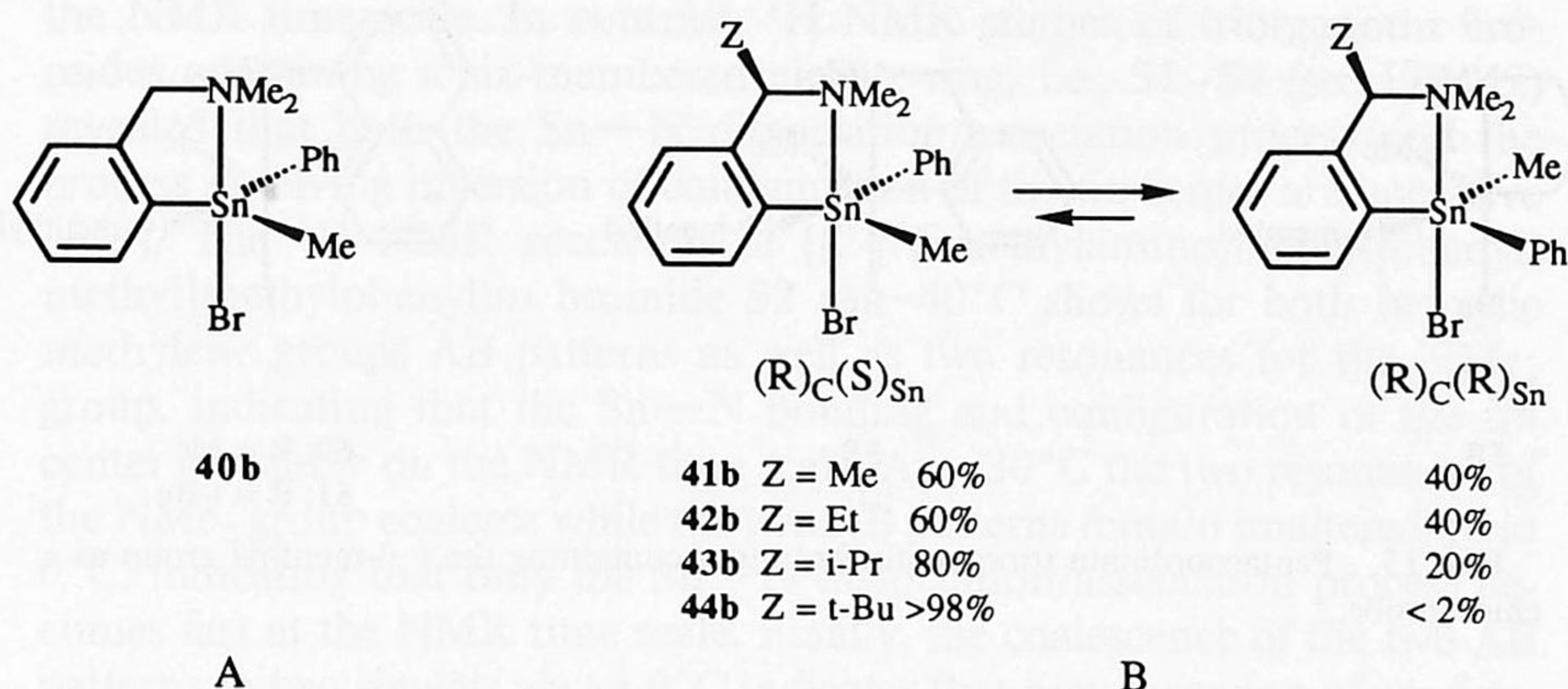


FIG. 14. Sn-chiral (A) and C,Sn-chiral (B) triorganotin halides.

tion of the tin center does occur. Furthermore it was shown that in solution the distribution between the two diastereoisomers is dependent on the bulk of the substituent present at the chiral benzylic carbon center (116), while for **14b** (Z = Me) the  $(R)_C(S)_{Sn}:(R)_C(R)_{Sn}$  ratio is 60:40, and for **44b** (Z = *t*-Bu) only the sterically less crowded  $(R)_C(S)_{Sn}$  diastereoisomer is present in solution; see Fig. 14B. Similarly, for {[2-(dimethylamino)phenyl](trimethylsilyl)methyl]methylphenyltin bromide, **47b** (see Fig. 12), only one diastereoisomer is present in solution (80). It is obvious, since **47b** was prepared starting from a racemic precursor, that this must be an enantiomeric pair, most likely the same  $(R)_C(R)_{Sn}/(S)_C(S)_{Sn}$  pair as found in the solid state by X-ray diffraction (80), in which the bulky trimethylsilyl group and the phenyl—Sn group are at opposite sides of the molecule.

Also the size (five- or six-membered) and flexibility of the chelate ring has an important influence on the rate of the inversion of configuration process at tin. The latter effect was nicely illustrated by a recent study of the triorganotin bromides **58–61** (see Fig. 15) containing the chiral (–)-menthyl group as a chiral probe (105,106,124).

It appeared that crystalline **59** and **60** are diastereoisomerically pure, which was confirmed unambiguously by a crystal structure determination of **60** and showed the configuration of the tin center in **60** to be (*R*) (124). That epimerization of the tin center in these compounds does occur was shown by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR studies of these compounds, which show the presence of only one diastereoisomer in a freshly prepared solution and the appearance and a slow increase of the second diastereoisomer on standing to give eventually a 47:53 equilibrium mixture for **59** in 2.5 days and a 46:54 equilibrium mixture for **60** in 5 days. These observations

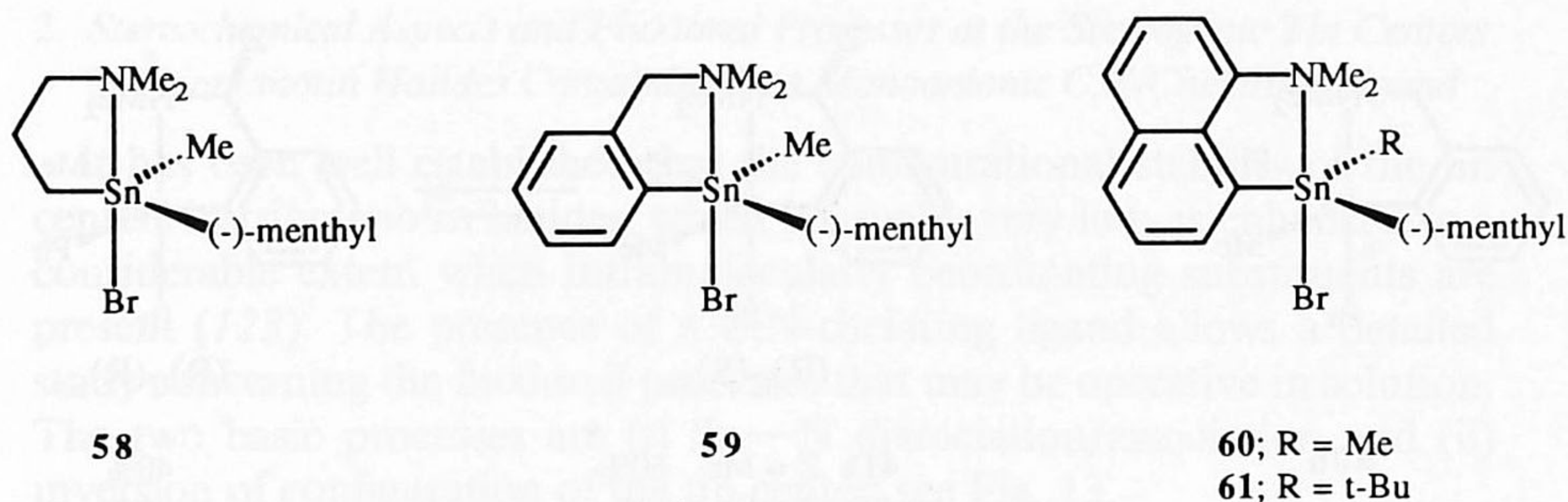


FIG. 15. Pentacoordinate triorganotin bromides containing the (-)-menthyl group as a chiral probe.

were furthermore confirmed by a linear increase of the  $[\alpha]_{20}^D$  values of **59** and **60**, from an initial value of  $-14.8^\circ$  to a constant value of  $-41.5^\circ$  after 2.5 days for **59** and from  $+2.9^\circ$  to a constant value of  $-37.9^\circ$  after 5 days for **60**. For **58**, however,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR studies showed the presence of only one resonance pattern at ambient temperature. At low temperature ( $-60^\circ\text{C}$ ), this single pattern tends to decoalesce in two resonance patterns for the two possible diastereoisomers. This observation indicates that in **58** the inversion of configuration process at tin must be very fast, even on the NMR time scale. Most likely this is a result of the much more flexible chelate ring present in **58** as compared to both **59** and **60**. Surprisingly,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR spectra of freshly prepared solutions of **61** showed the presence of two diastereoisomers in a constant 45:55 molar ratio. Most probably, due to (i) the rigid chelate ring and (ii) the steric constraints around the tin center in **61** (cf. *t*-Bu in **61** versus Me in **60**), the inversion of configuration process at the tin center in **61** is completely blocked, resulting in a constant ratio of the two diastereoisomers in the solid state as well as in solution. An alternative explanation could be the occurrence of an extremely fast epimerization process immediately after dissolution of solid **61**. However, with respect to the observations made for **60**, this seems highly unlikely.

In triorganotin bromides containing the 8-dimethylamino-1-naphthyl C,N-chelating ligand, i.e., **48–50** (Fig. 12) and **60–61** (Fig. 15), even at high temperature ( $125^\circ\text{C}$ ) Sn—N dissociation does not occur at the NMR time scale (106,110,124). Most likely this is the result of the fixed orientation of the N and C donor sites of the rigid 8-dimethylamino-1-naphthyl group, which holds the  $\text{NMe}_2$  substituent always in close proximity to the tin atom.

So far, it appears that triorganotin bromides containing a rigid five-membered chelate ring have a tin center that is configurationally stable on

the NMR time scale. In contrast,  $^1\text{H}$  NMR studies of triorganotin bromides containing a six-membered chelate-ring, i.e., **51**–**54** (see Fig. 12) revealed that both the Sn—N dissociation/association process and the process involving inversion of configuration of the tin center are operative (118). The  $^1\text{H}$  NMR spectrum of [ $\{2-[(\text{dimethylamino})\text{methyl}]\text{phenyl}\}$  methyl]methylphenyltin bromide **52** at  $-40^\circ\text{C}$  shows for both benzylic methylene groups AB patterns as well as two resonances for the  $\text{NMe}_2$  group, indicating that the Sn—N bonding and configuration of the tin center are stable on the NMR time scale. At  $-30^\circ\text{C}$  the two resonances of the  $\text{NMe}_2$  group coalesce while the two AB patterns remain unaltered up to  $0^\circ\text{C}$ , indicating that only the Sn—N dissociation/association process becomes fast at the NMR time scale. Finally, the coalescence of the two AB patterns to two singlets above  $0^\circ\text{C}$  indicates that now inversion of configuration of the tin center has become fast on the NMR time scale. Similar conclusions were drawn from the temperature-dependent  $^1\text{H}$  NMR spectra of **53** and **54** (118). An interesting feature of **54** is the presence in solution of two diastereoisomers as a result of the presence of the stereogenic Sn center in combination with an  $\alpha$ - or  $\beta$ -puckering of the six-membered chelate ring, as schematically shown in Fig. 16. As another consequence of this puckering for achiral **53**, at low temperature ( $-50^\circ\text{C}$ ), two  $\text{NMe}_2$  resonances and an AB pattern for the  $\text{CH}_2\text{N}$  group are observed in the  $^1\text{H}$  NMR spectrum.

That the dissociated form of triorganotin bromides that can form a six-membered chelate ring, i.e., a tetrahedral coordination geometry at the tin center, is abundantly populated at higher temperatures is indicated by the large temperature dependence of the  $^{119}\text{Sn}$  chemical shifts of **51**–**52** (94), e.g.,  $-49.4$  ppm for **51** at  $-85^\circ\text{C}$  versus  $-6.2$  ppm at  $100^\circ\text{C}$ . This conclusion is supported by the largely temperature-independent  $^{119}\text{Sn}$  chemical shift values of triorganotin bromides having a five-membered

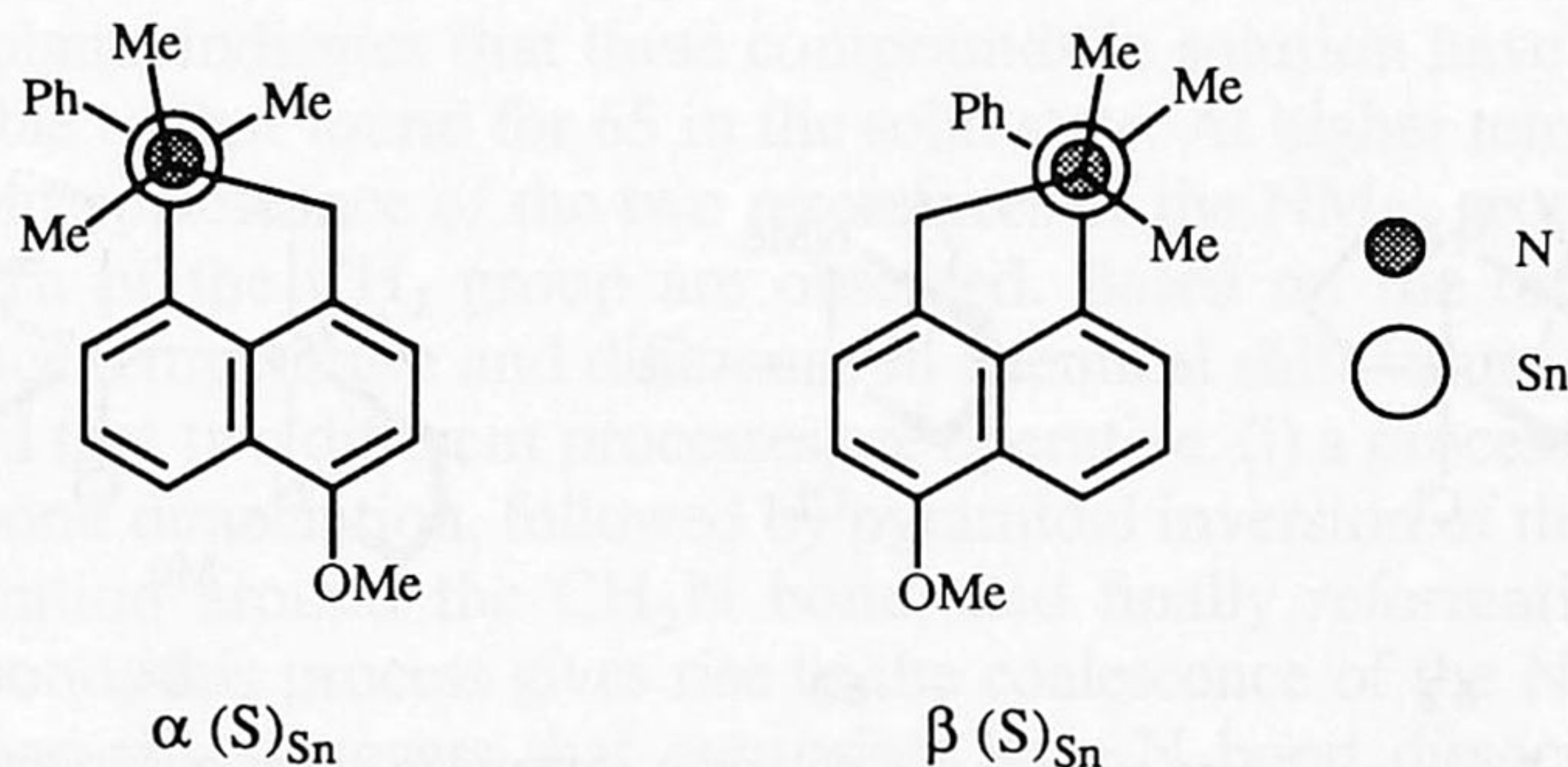


FIG. 16. Schematic projection along the N—Sn bond in **54** showing the two diastereoisomers as a consequence of the  $\alpha$ - or  $\beta$ -puckering of the six-membered chelate ring.

chelate ring (40–50,55,56) or a more rigid six-membered chelate ring (53,54), indicating that for these compounds the population of the dissociated form is infinitely small at higher temperatures (94).

### 3. Compounds Containing Miscellaneous C,N-Chelating Ligands

Interesting structural features are observed for triorganotin halides containing one quadridentate tris-anionic-, cf. 62, terdentate dianionic-, cf. 63,64, quadridentate dianionic-, cf. 70–72, terdentate monoanionic-, cf. 65–69, or two bidentate monoanionic ligands, cf. 73–75. The latter three types of ligands are potential candidates in enforcing hexacoordination in triorganotin halides.

An X-ray crystal structure determination of the triptych compound 62 revealed the trigonal bipyramidal coordination geometry, which is schematically shown in Fig. 17, with the three carbon atoms at the equatorial sites and the coordinating nitrogen atom and the chlorine atom at the axial positions. As a result of the fixed geometry of the quadridentate tris-anionic ligand, the Sn—N coordination bond (2.37(3) Å) is extremely short (125).

Based on  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR spectroscopic studies a trigonal bipyramidal structure for the diptych compound 63 (102) has also been proposed; see Fig. 17.

The diptych compound 64 for which the structure was unambiguously proven by an X-ray crystal structure determination (104), consists of two enantiomorphous units connected via a Sn—Sn bond. In each unit, the tin atoms have trigonal bipyramidal coordination geometries with the two carbon ligands and the connecting Sn atom occupying equatorial sites. Based on  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR spectroscopic studies, it is most likely that the structure as found in the solid state is retained in solution. At low temperature ( $-40^\circ\text{C}$ ), the  $^{13}\text{C}$  NMR spectrum of 64 shows inequivalent

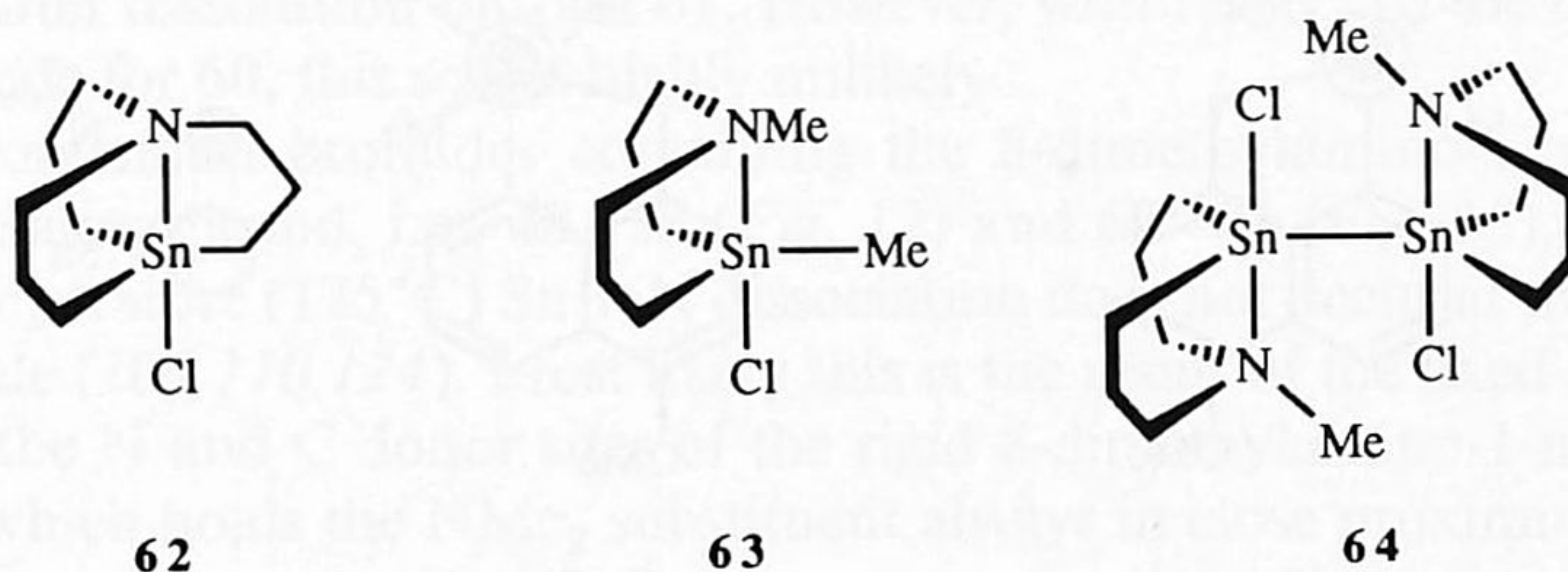


FIG. 17. Pentacoordinate triorganotin chlorides containing either quadridentate tris-anionic 62 or terdentate-dianionic 63 or 64 ligands.

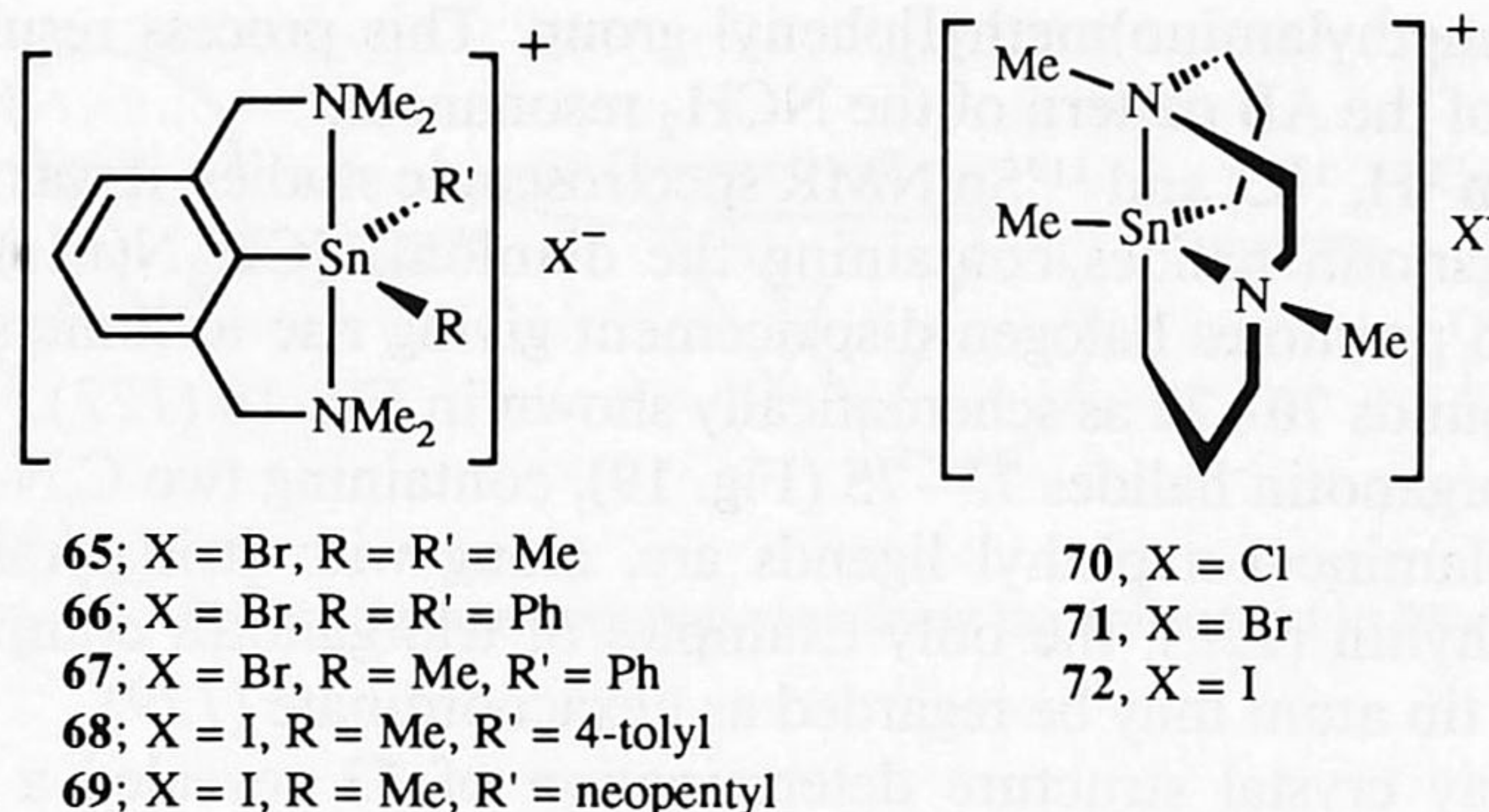


FIG. 18. Pentacoordinate triorganotin cations (stannonium ions) as a result of intramolecular coordination.

methylene carbon atoms in each unit, which was explained in terms of hindered rotation around the Sn—Sn bond (104).

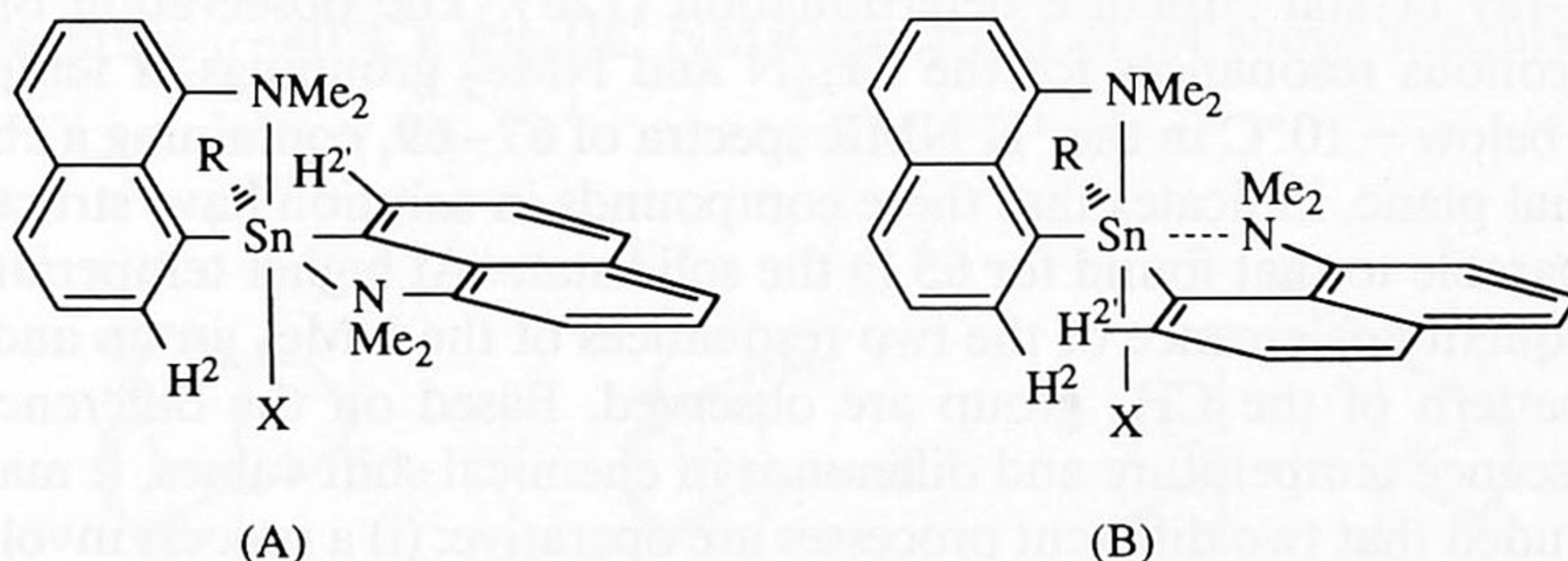
A series of triorganotin halides containing the terdentate monoanionic 2,6-bis[(dimethylamino)methyl]phenyl ligand have been reported (88,126). As mentioned before, compounds **65–69** are potential candidates for hexacoordinate triorganotin halides. However, based on (i) the high solubility in polar solvents (even water), (ii) colligative studies, and (iii) conductivity measurements, it appeared that the presence of the 2,6-bis[(dimethylamino)methyl]phenyl ligand in these triorganotin halides promotes halogen displacement giving rise to the formation of stable ionic compounds **65–69**, which in fact are the first examples of triorganostannonium ions, as is shown schematically in Fig. 18. Moreover, in the case of **65**, the existence of such an ionic structure was unambiguously proven by an X-ray crystal structure determination (126). The observation of anisochronous resonances for the CH<sub>2</sub>N and NMe<sub>2</sub> groupings at temperatures below  $-10^{\circ}\text{C}$  in the <sup>1</sup>H NMR spectra of **67–69**, containing a chiral, trigonal plane, indicates that these compounds in solution have structures comparable to that found for **65** in the solid state. At higher temperatures, subsequent coalescence of the two resonances of the NMe<sub>2</sub> group and the AB pattern of the CH<sub>2</sub> group are observed. Based on the difference in coalescence temperature and difference in chemical shift values, it may be concluded that two different processes are operative: (i) a process involving Sn—N bond dissociation, followed by pyramidal inversion of the nitrogen atom, rotation around the CH<sub>2</sub>N bond, and finally reformation of the Sn—N bond; this process gives rise to the coalescence of the NMe<sub>2</sub> resonances, and (ii) a process that comprises Sn—N bond dissociation followed by rotation of the SnRR' group around the Sn—C bond to the

2,6-bis[(dimethylamino)methyl]phenyl group. This process results in coalescence of the AB pattern of the  $\text{NCH}_2$  resonances.

Based on  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR spectroscopic studies, it was proposed that triorganotin halides containing the dianionic  $[\text{CH}_2\text{N}(\text{Me})(\text{CH}_2)_3]_2$  ligand also promotes halogen displacement giving rise to ionic structures for compounds **70**–**72** as schematically shown in Fig. 18 (127).

The triorganotin halides **73**–**75** (Fig. 19), containing two C,N-chelating 8-dimethylamino-1-naphthyl ligands are, along with [tris(pyrazolyl)borato]trimethyltin (128), the only examples of triorganotin compounds in which the tin atom may be regarded as hexacoordinate (129).

An X-ray crystal structure determination of **73** revealed a structure shown schematically in Fig. 19A. The tin center has a distorted octahedral coordination geometry with the two naphthyl  $\text{C}_{\text{ipso}}$  atoms, one of the nitrogen atoms, and the iodine atom, as well as the other nitrogen atom and the methyl group in mutual *trans*-positions. The  $\text{Sn}-\text{N}$  distance *trans* to the methyl group of  $3.10(1) \text{ \AA}$  is extremely long for a  $\text{Sn}-\text{N}$  coordination bond, but this value is only slightly longer than one of the  $\text{Sn}-\text{N}$  bond lengths found in the diphenyltin dichloride pyrazine complex [ $2.965(11) \text{ \AA}$ ]. The latter  $\text{Sn}-\text{N}$  bond length is the longest one reported so far that has still been ascribed to  $\text{Sn}-\text{N}$  coordination (130). The  $\text{C}_{\text{ipso}}-\text{Sn}-\text{C}_{\text{ipso}}$  angle of  $140.0(5)^\circ$  in **73** deviates considerably from the ideal octahedral value of  $180^\circ$ . Previously, Britton and Dunitz (113) have correlated the structural features of  $\text{SnC}_2\text{X}_2\text{Y}_2$  ensembles with a C,C-transoid arrangement. It was shown that in such species the  $\text{C}-\text{Sn}-\text{C}$  angle is a function of the deviation of the  $\text{C}-\text{X}$  and  $\text{C}-\text{Y}$  distances from the theoretical values. The  $\text{Sn}-\text{N}$  and  $\text{Sn}-\text{C}(\text{methyl})$



**73**, R = Me, X = I

**74**, R = Et, X = I

**75**, R = Benz, X = Br

FIG. 19. Triorganotin halides containing two C,N-chelating ligands in which the tin atom may be regarded as hexacoordinate.

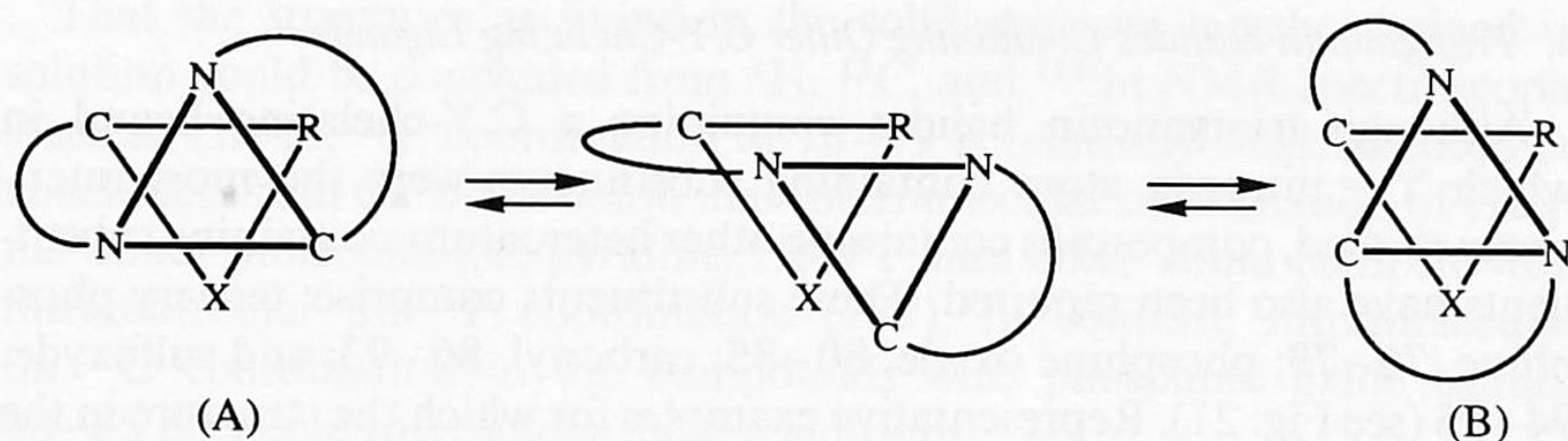


FIG. 20. Schematic representation visualizing the Bailar twist in 73–75.

distances in 73 do fit very well in the theoretically deduced curve; furthermore these distances predict a value of  $141^\circ$  for the  $C_{\text{ipso}}-\text{Sn}-C_{\text{ipso}}$  angle, which is very close to the value of  $140.0(5)^\circ$  found for 73!

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR spectroscopic studies of 73–75 in solution indicated that at low temperature ( $-50^\circ\text{C}$ ) two distinctly different species are present. One has been attributed to structure (A), Fig. 19, as was established for 73 in the solid state, and the other to the isomeric structure (B), Fig. 19. The respective resonance patterns observed in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra could be assigned on the basis of the observed  $^1J(^{119}\text{Sn}-^{13}\text{C})$ ,  $^2J(^{119}\text{Sn}-^1\text{H})$  and  $^3J(^{119}\text{Sn}-^1\text{H})$  values. On the basis of these values, an enhanced *s*-electron participation in the  $C_{\text{ipso}}-\text{Sn}-C_{\text{ipso}}$  bonds in structure (A) and the linear  $C_{\text{ipso}}-\text{Sn}-C(R)$  bonds in structure (B) was proposed. It is well established that in diorganotin compounds in which the tin atom has an octahedral coordination geometry, the *trans*-carbon atoms are bound to tin via *sp*-like orbitals at the tin center (39). At higher temperatures, a process becomes operative at the NMR time scale resulting in a fast interconversion between isomers (A) and (B). Such a stereoisomerization (Bailar twist), visualized in Fig. 20, is known for octahedral arrangements and proceeds via a trigonal prismatic transition state (131).

Alternatively the structures of 73–75 can also be seen as trigonal bipyramidal, with the carbon ligands at the equatorial sites, which undergo intramolecular nucleophilic attack at the tin atom by the noncoordinated nitrogen atom at the equatorial C—C edge opposite the methyl group. Recent *ab initio* calculations of related tin compounds have shown that such processes represent a lower energy reaction path.

It should be noted here that in isostructural silicon compounds, i.e., bis[8-(dimethylamino)-1-naphthyl]silicon dihydrides, difluorides, and hydride fluorides, the tetrahedral configuration at silicon is largely preserved. The hexacoordination at silicon can be seen best as that of a bicapped tetrahedron resulting from a twofold nucleophilic coordination (56).

## 4. Triorganotin Halides Containing Other C,Y-Chelating Ligands

Although triorganotin halides containing a C,Y-chelating ligand in which Y = nitrogen atom containing substituents were the most intensively studied, compounds containing other heteroatom-containing substituents have also been reported. These substituents comprise: tertiary phosphine, 76–79; phosphine oxide, 80–85; carbonyl, 86–93; and sulfoxide, 94–95 (see Fig. 21). Representative examples for which the structure in the solid state was established by X-ray crystallographic studies are 79 (132), 83 (133), 84 (134), 85 (135), 90–93 (136), 94, and 95 (137), while for the other compounds 76–78 (138), 80–82 (133), and 86–89 (139,140), the structure was established on the basis of IR and Mössbauer spectroscopic studies. Like in the triorganotin halides containing a C,N-chelating ligand, also in these compounds the tin atom has a trigonal bipyramidal coordination geometry, as schematically shown in Fig. 21, with the three carbon atoms at equatorial positions and the more electronegative halogen and heteroatom at axial sites.

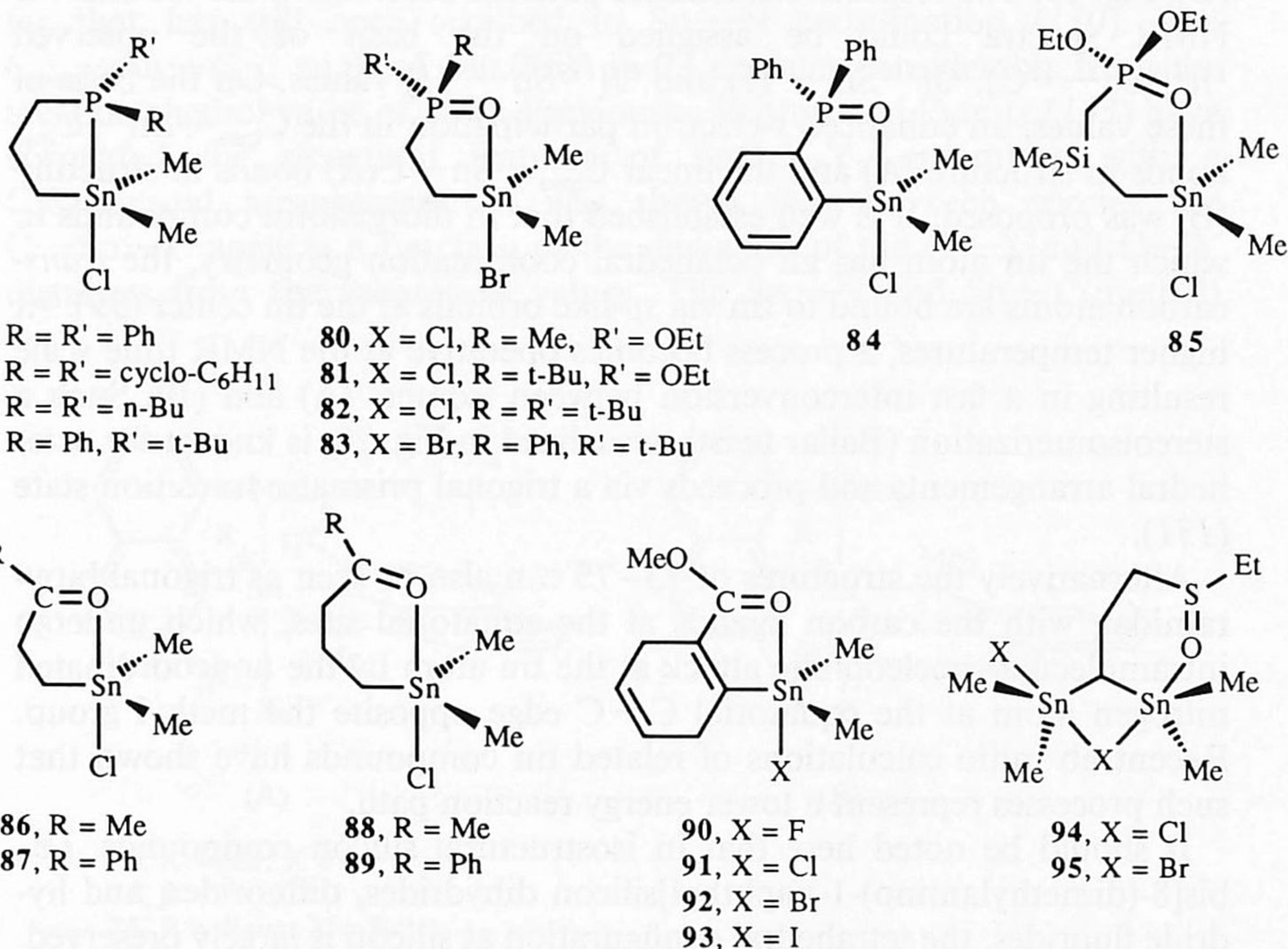


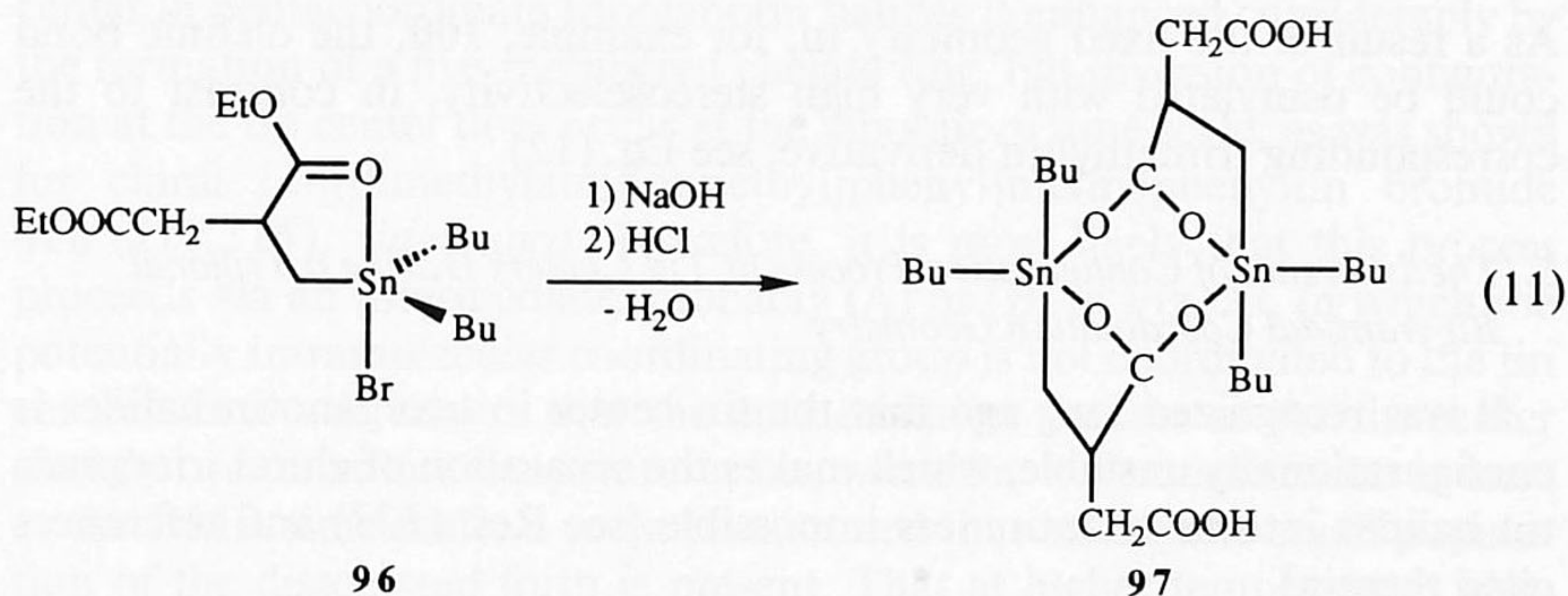
FIG. 21. Triorganotin halides containing an intramolecular coordinating phosphine, phosphine oxide, carbonyl, or sulfoxide ligand.



That the structures as found in the solid state are largely retained in solution could be concluded from  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR spectroscopic studies. The Sn—P coordination in **76–79** is relatively weak as could be concluded from the observation that intermolecular coordination of external donor molecules like pyridine, HMPT, and DMF could compete with intramolecular Sn—P coordination (132). In contrast, intramolecular Sn—O coordination in the compounds with phosphine oxide ligands **80–85** appeared inert under these conditions.

Also in compounds **86–89**, intramolecular Sn—O coordination is relatively weak as was shown by replacement of the intramolecular coordinating oxygen atom by external ligands like pyridine (139,140).

A rather exotic example of a triorganotin compound in which penta-coordinate tin centers are proposed as a result of intramolecular coordination is the product **97**, obtained from the hydrolysis reaction of the ester-tin compound **96**. For the latter compound, the presence of a pentacoordinate tin center as a result of intramolecular Sn—O (carboxyl) coordination was proposed (141):



Nice examples of intramolecular Sn—O coordination are the six-membered carbocyclic tin compounds **98–100**; see Fig. 22 (142). The 1,3-diaxial conformation of these compounds is stabilized by the intramolecular Sn—O interaction.

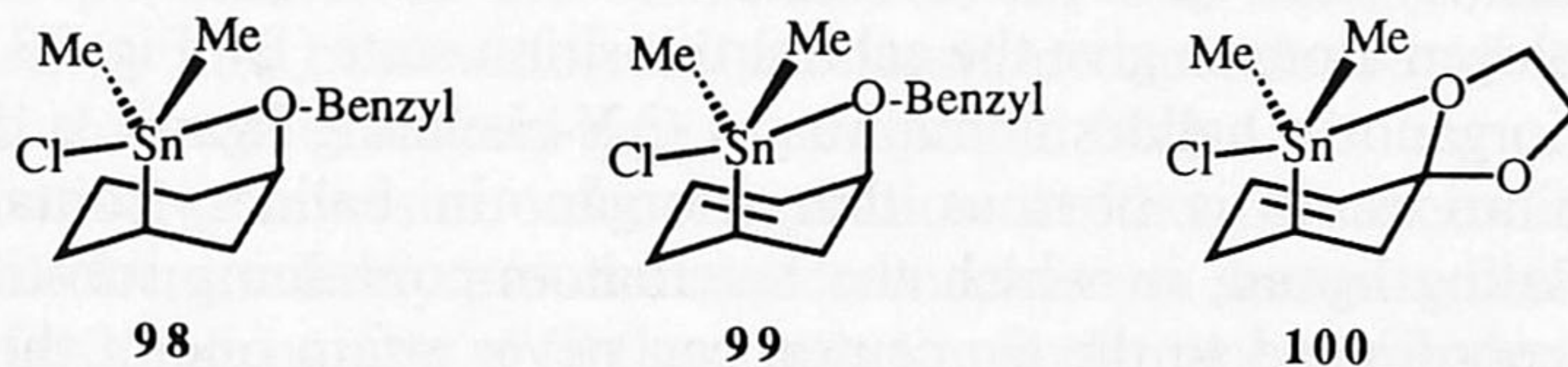
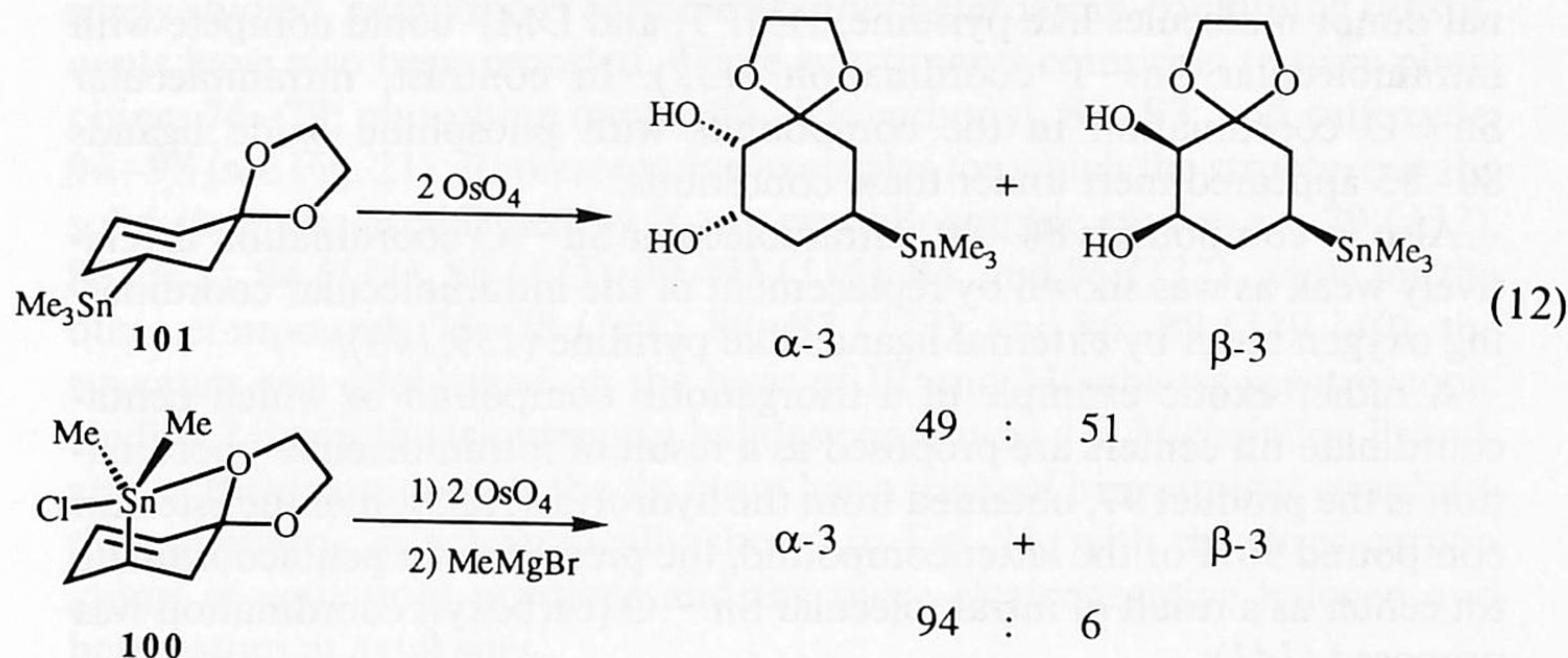


FIG. 22. Stabilization of 1,3-diaxial conformation in carbocyclic triorganotin chlorides by intramolecular O—Sn coordination.

In contrast, the corresponding trimethyltin derivatives (tetraorganotin compounds that lack O—Sn coordination) exist predominantly as diequatorial conformers, e.g., **101** in



As a result of the fixed geometry in, for example, **100**, the olefinic bond could be osmylated with very high stereoselectivity, in contrast to the corresponding trimethyltin derivative; see Eq. (12).

##### 5. The Inversion of Configuration Process at Tin Centers Having a Trigonal Bipyramidal Coordination Geometry

It was recognized long ago that the tin center in triorganotin halides is configurationally unstable, which makes the separation of chiral triorganotin halides into its enantiomers impossible [see Ref. (123) and references cited therein].

For simple triorganotin halides it has been established that the rate of the inversion process is accelerated if external nucleophiles, e.g., pyridine, are present (123). Based on the fact that the inversion process is second order in nucleophile, two possible mechanisms have been proposed: (i) addition of a nucleophile to the metal center, followed by addition of a second nucleophile and displacement of the halogen atom giving the achiral transition state (A) (see Fig. 23) or (ii) addition of two nucleophiles without loss of the halogen atom to give the achiral transition state (B), Fig. 23 (123).

For triorganotin halides containing a C,Y-chelating ligand, a different situation arises. It is obvious that triorganotin halides, containing a C,Y-chelating ligand, in which the heteroatom-containing substituent is already coordinated to the tin center, can never attain one of the transition-state structures (A) or (B), Fig. 23. This could explain why the configurational stability of triorganotin halides containing such a ligand is in-

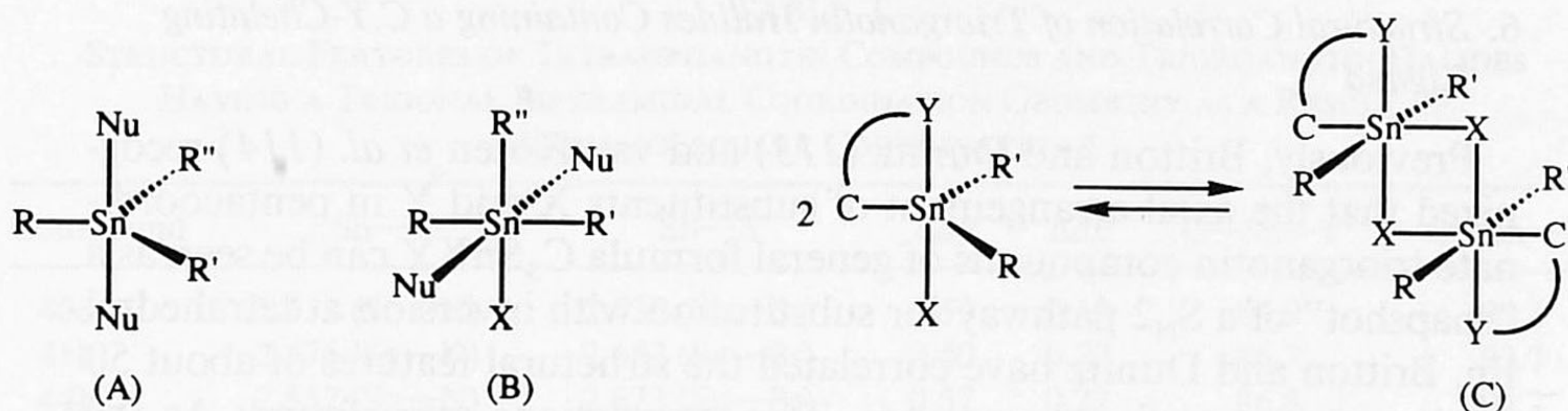


FIG. 23. Transition states (A) and (B) proposed for the inversion of configuration at tin.

creased to such an extent (114). It has been suggested that an alternative dimerization process may occur in solution, giving rise to structures shown schematically in Fig. 23C (114).

As has been mentioned before, the configurational stability of the tin center in pentacoordinate triorganotin halides is enhanced considerably by the formation of a five-membered chelate ring, but inversion of configuration at the tin center does occur at the laboratory time scale, as was shown for chiral {2-[(dimethylamino)methyl]phenyl}methylphenyltin bromide **41b** (114,116), *vide supra*. Therefore, it is most likely that this process proceeds via an intermediate, probably (A) or (B) in Fig. 23, in which the potentially intramolecular coordinating group is not coordinated to the tin center. As it was shown that the epimerization process at the tin center already occurs at low temperature, i.e., when Sn—N coordination is inert at the NMR time scale, it must be assumed that an infinite small population of the dissociated form is present. That at higher temperatures also, i.e., when a process involving Sn—N dissociation/association becomes fast on the NMR time scale, the population of the dissociated form is infinitely small was concluded from the observed temperature-independent  $^{119}\text{Sn}$  chemical shift values (94). Further evidence for such a process is the observation that the Sn center in triorganotin halides containing a six-membered chelate ring is configurationally less stable (118), indicating an increased population of the dissociated form. The latter conclusion is supported by the observation of temperature dependence of the  $^{119}\text{Sn}$  chemical shift values for this type of compound (94).

Alternatively, inversion of configuration at the pentacoordinate tin center involving a Berry pseudorotation mechanism seems to be energetically unfavorable in view of (i) the strong site preference of the electronegative halogen and nitrogen atoms for axial positions (143) and (ii) the geometric constraints of the five-membered chelate ring.

### 6. Structural Correlation of Triorganotin Halides Containing a C,Y-Chelating Ligand

Previously, Britton and Dunitz (113) and van Koten *et al.* (114) recognized that the axial arrangement of substituents X and Y in pentacoordinate triorganotin compounds of general formula  $C_3SnXY$  can be seen as a "snapshot" of a  $S_N2$  pathway for substitution with inversion at tetrahedral tin. Britton and Dunitz have correlated the structural features of about 50 of these triorganotin compounds. Two correlations were found: As the Sn—Y distance  $d_y$  becomes shorter, the Sn—X distance  $d_x$  tends to become longer and the average X—Sn—C angles tend to become smaller.

A theoretical curve showing these bond distance variations could be deduced using the simple relationship between bond length and bond order proposed by Pauling (144), where  $d(n)$  is the bond length,  $d(1)$  is the single bond length, and  $c$  depends on the type of bond:

$$\Delta d(n) = d(n) - d(1) = -c \log n \quad (13)$$

The value of  $c$  for any particular Sn(IV) ensemble could be obtained from

$$\sum n = \sum 10^{-\Delta d/c} = 4 \quad (14)$$

by assuming that the sum of the bond orders is constant.

The second correlation, between distance and angle, can be expressed in terms of the average C—Sn—X angle ( $\alpha_x$ ). For the dependence of bond order on bond angle, Bürgi (145) proposed

$$n_x = (1 - 3 \cos \alpha_x)/2 \quad (15a)$$

$$n_y = (1 + 3 \cos \alpha_x)/2 \quad (15b)$$

so that  $n_x = 1$  when  $\alpha_x$  is the tetrahedral angle and  $n_x = \frac{1}{2}$  when  $\alpha_x$  is  $90^\circ$ .

It is remarkable that the experimental data of the structures investigated by Britton and Dunitz fit so well with the calculated values using these simple models.

In Table I, the experimental data, obtained from X-ray crystal structure determinations of all triorganotin halides known so far in which the tin atom has a trigonal bipyramidal coordination geometry as a result of intramolecular coordination, are compiled (also the data for pentacoordinate tetraorganotin compounds are included). Figure 24 shows the interdependence of the derived  $\Delta d_x$  and  $\Delta d_y$  values of these compounds, while in Fig. 25, the interdependence of the  $\Delta d$  values and the averaged C—Sn—X ( $\alpha_x$ ) and C—Sn—Y ( $\alpha_y$ ) angles are given. The experimental data fit the theoretically deduced curves very well, the only exceptions being the  $\alpha_x$  and  $\alpha_y$  values of 62 and the  $\alpha_y$  value of 35. Probably this is a

TABLE I  
STRUCTURAL FEATURES OF TETRAORGANOTIN COMPOUNDS AND TRIORGANOTIN HALIDES  
HAVING A TRIGONAL BIPYRAMIDAL COORDINATION GEOMETRY AS A RESULT OF  
INTRAMOLECULAR COORDINATION.<sup>a</sup>

Compound	Sn—Y	Sn—X	$\Delta dy$	$\Delta dx$	C—Sn—Y <sup>b</sup>	C—Sn—X <sup>c</sup>
40c	2.511 (Sn—N)	2.630 (Sn—Br)	0.53	0.18	84.9	95.1
41b	2.476 (Sn—N)	2.683 (Sn—Br)	0.50	0.23	86.7	93.7
44b	2.552 (Sn—N)	2.673 (Sn—Br)	0.57	0.22	86.8	94.2
47b	2.492 (Sn—N)	2.663 (Sn—Br)	0.51	0.21	84.8	95.3
49	2.496 (Sn—N)	2.667 (Sn—Br)	0.52	0.22	85.3	95.0
54	2.401 (Sn—N)	2.739 (Sn—Br)	0.42	0.29	88.3	91.7
56	2.414 (Sn—N)	2.678 (Sn—Br)	0.43	0.23	85.0	94.9
57a	2.560 (Sn—N)	2.445 (Sn—Cl)	0.58	0.16	82.7	97.0
57b	2.674 (Sn—N)	2.433 (Sn—Cl)	0.69	0.15	81.8	98.5
60 (A) <sup>d</sup>	2.55 (Sn—N)	2.641 (Sn—Br)	0.57	0.19	85.3	95.3
60 (B) <sup>d</sup>	2.55 (Sn—N)	2.630 (Sn—Br)	0.57	0.18	85.2	95.2
62	2.372 (Sn—N)	2.613 (Sn—Cl)	0.39	0.32	80.5	99.5
64	2.448 (Sn—N)	2.560 (Sn—Cl)	0.47	0.27	86.3	93.7
83	2.324 (Sn—O)	2.684 (Sn—Br)	0.42	0.23	85.7	94.4
85	2.371 (Sn—O)	2.518 (Sn—Cl)	0.47	0.23	86.7	93.3
90	2.52 (Sn—O)	1.974 (Sn—F)	0.62	0.14	83.4	96.8
91	2.470 (Sn—O)	2.432 (Sn—Cl)	0.57	0.14	81.2	98.8
92	2.470 (Sn—O)	2.588 (Sn—Br)	0.57	0.14	80.8	99.2
93	2.391 (Sn—O)	2.830 (Sn—I)	0.49	0.14	81.1	98.9
94	2.301 (Sn <sub>2</sub> —O)	2.572 (Sn <sub>2</sub> —Cl <sub>1</sub> )	0.40	0.28	89.3	90.7
	2.925 (Sn <sub>1</sub> —Cl <sub>1</sub> )	2.478 (Sn <sub>2</sub> —Cl <sub>2</sub> )	0.63	0.18	82.7	97.3
95	2.287 (Sn <sub>2</sub> —O)	2.748 (Sn <sub>2</sub> —Br <sub>1</sub> )	0.39	0.30	89.5	90.5
	3.065 (Sn <sub>1</sub> —Br <sub>1</sub> )	2.626 (Sn <sub>2</sub> —Br <sub>2</sub> )	0.62	0.18	83.7	96.3
98	2.720 (Sn—O)	2.438 (Sn—Cl)	0.82	0.15	81.9	98.2
18 <sup>e</sup>	2.841 (Sn—N)	2.183 (Sn—C)	0.86	0.08	76.5	103.8
27 <sup>e</sup>	2.884 (Sn—N)	2.183 (Sn—C)	0.78	0.08	78.4	102.1
30 <sup>e</sup>	2.781 (Sn—O)	2.150 (Sn—C)	0.88	0.05	74.7	105.4
31 <sup>e</sup>	2.770 (Sn—O)	2.190 (Sn—C)	0.87	0.09	77.0	104.0
35 <sup>e</sup>	2.624 (Sn—N)	2.214 (Sn—C)	0.64	0.11	74.7	105.2
39 <sup>e</sup> (A) <sup>d</sup>	2.931 (Sn—N)	2.212 (Sn—C)	0.95	0.11	74.7	106.0
39 <sup>e</sup> (B) <sup>d</sup>	2.885 (Sn—N)	2.212 (Sn—C)	0.91	0.11	73.4	107.1

<sup>a</sup> Data of all known structures so far (July 1992).

<sup>b</sup> Averaged value of the three C—Sn—Y angles.

<sup>c</sup> Averaged value of the three C—Sn—X angles.

<sup>d</sup> Two molecules in the asymmetric unit.

<sup>e</sup> Tetraorganotin compounds.

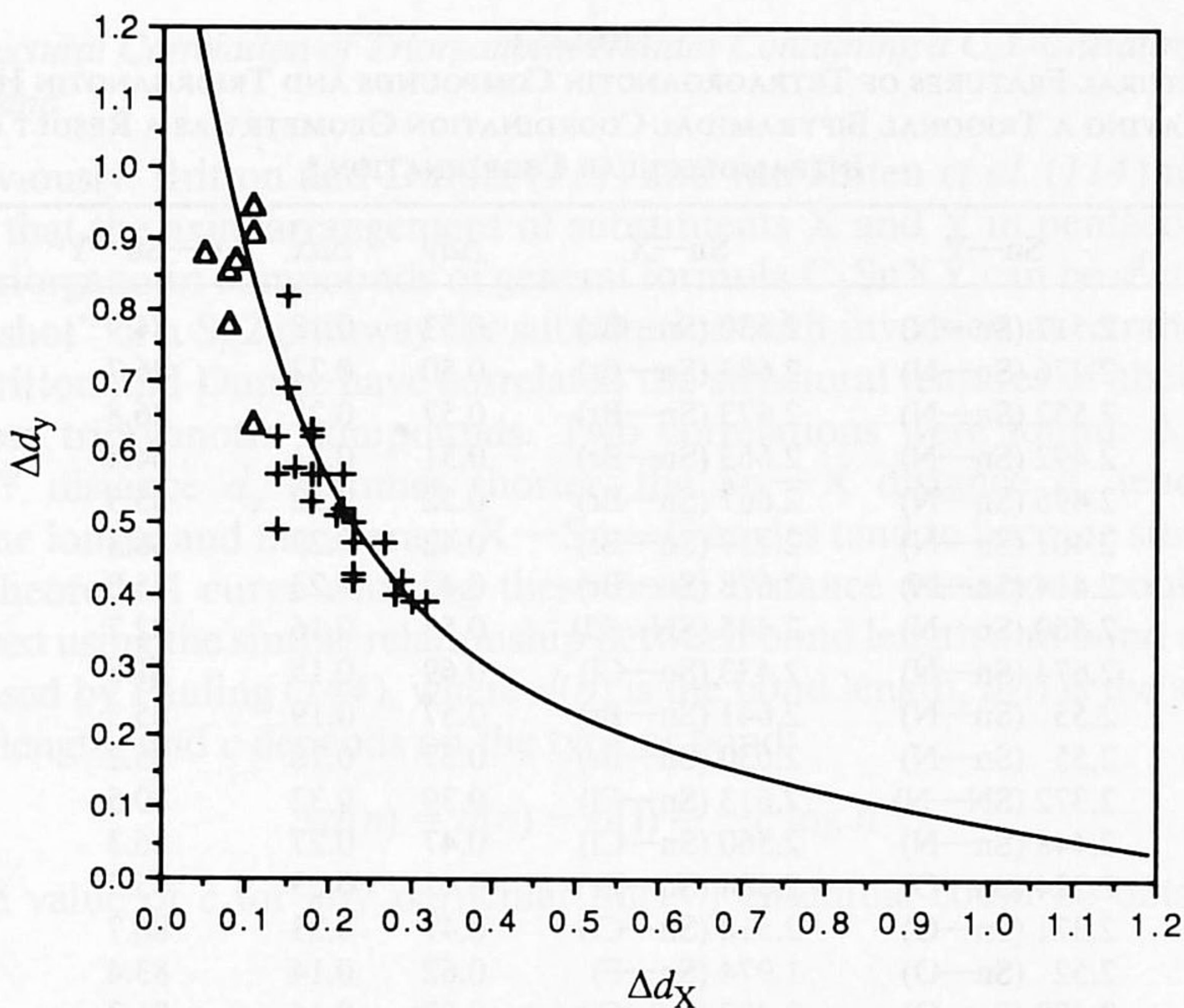


FIG. 24.  $\Delta d_x$  vs  $\Delta d_y$  for the triorganotin halides (+) and tetraorganotin compounds ( $\Delta$ ) having a trigonal bipyramidal arrangement at the tin center as a result of intramolecular coordination. The curve shows the bond order conservation function  $10^{-\Delta d_x/c} + 10^{\Delta d_x/c} = 1$ , with  $c = 1.20 \text{ \AA}$ .

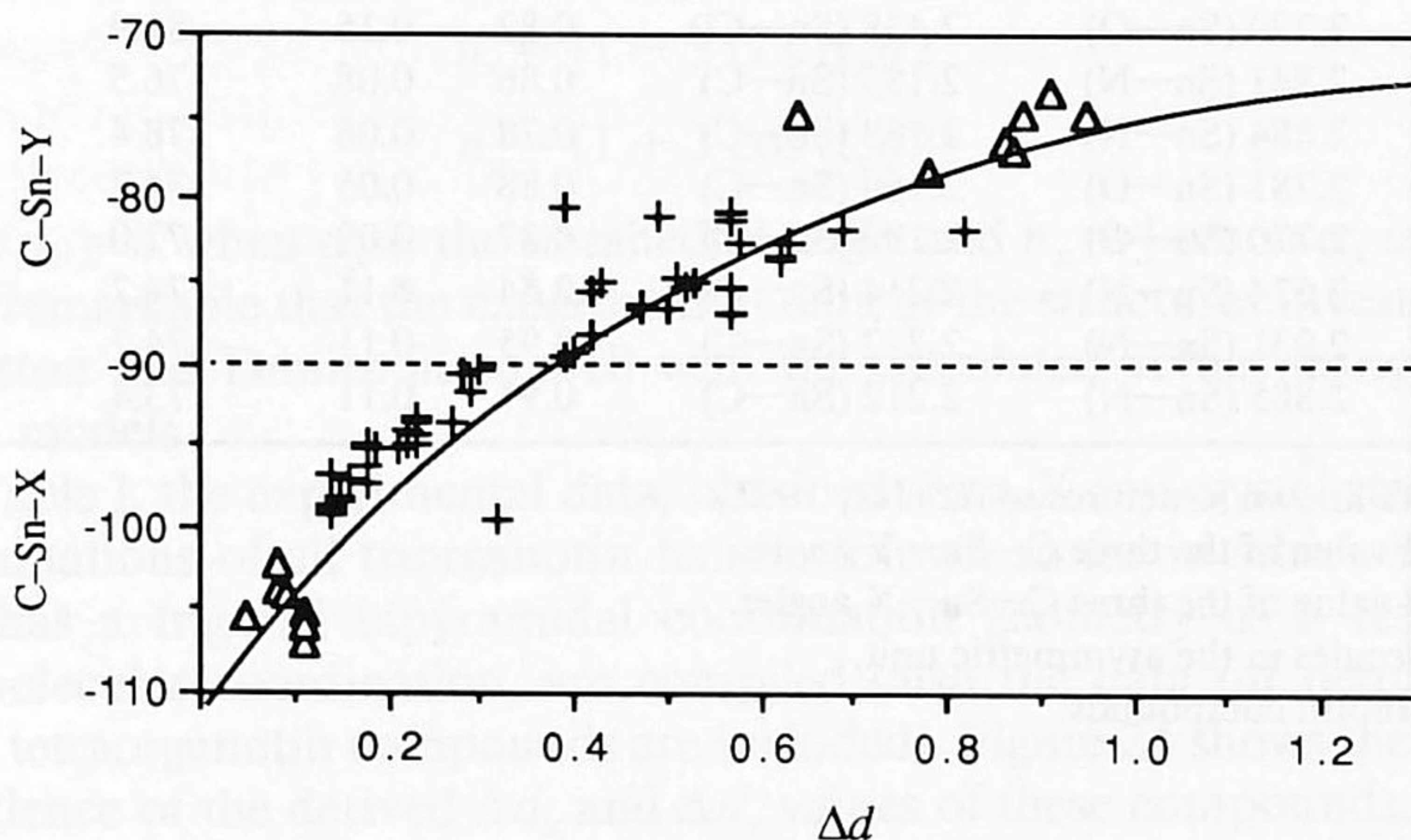


FIG. 25.  $C-Sn-X$  ( $\alpha_x$ ) and  $C-Sn-Y$  ( $\alpha_y$ ) vs  $\Delta d_x$  and  $\Delta d_y$  for the triorganotin halides (+) and tetraorganotin compounds ( $\Delta$ ) having a trigonal bipyramidal arrangement at the tin center as a result of intramolecular coordination. The curve gives the combination of Eqs. (13), (14), and (15) with  $c = 1.20 \text{ \AA}$ .

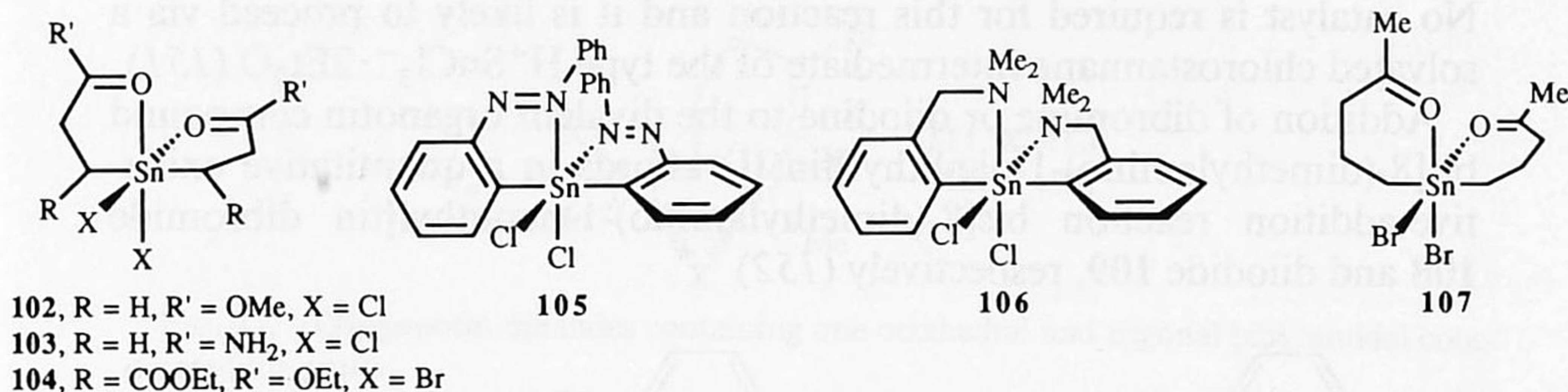


FIG. 26. Diorganotin dihalides having an octahedral arrangement at the tin atom.

consequence of the prefixed geometry of the tris-anionic tetradentate ligand present in these compounds, causing extremely short intramolecular Sn—N distances (see Table I). It is remarkable that the data for the pentacoordinate *tetra*-organotin compounds **18**, **27**, **30**, **31**, **35**, and **39** in which a carbon atom is in *trans*-position with respect to the intramolecular coordinating heteroatom fit so well.

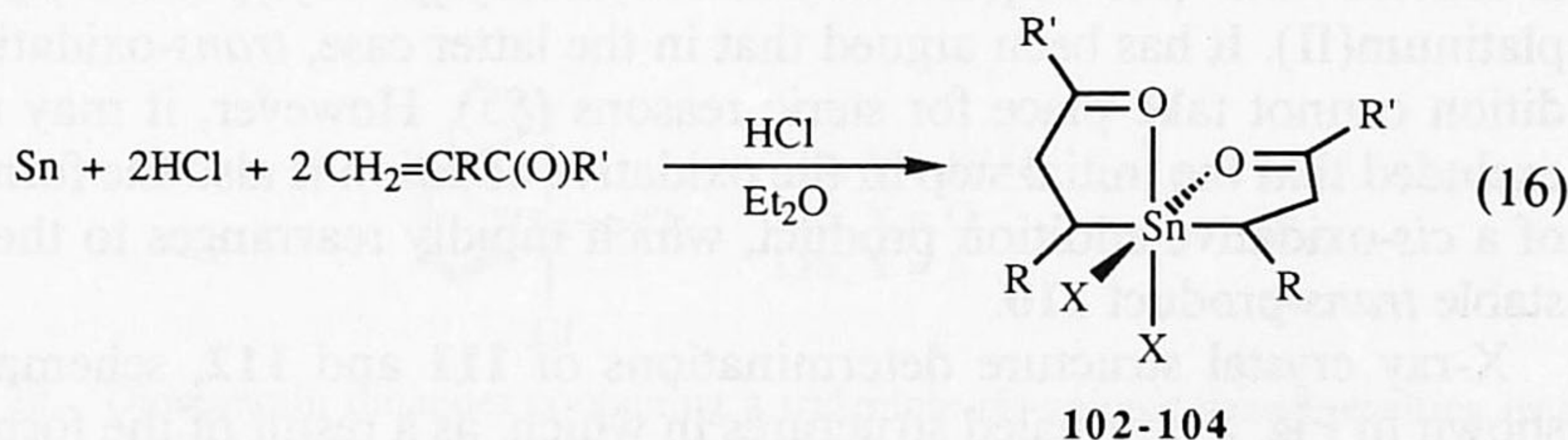
#### E. Diorganotin Dihalides Containing a C,Y-Chelating Ligand

##### 1. Compounds Having an Octahedral Arrangement at the Tin Atom

The structures of diorganotin dihalides containing two C,Y-chelating ligands are given schematically in Fig. 26. The structures of compounds **102**, **103** (146), **104** (147), and **105** (148) were unambiguously proven by X-ray crystal structure determinations. The tin centra have a distorted octahedral coordination geometry, with the two carbon ligands in *trans*-position and both coordinating heteroatoms and the two halogen atoms in *cis*-position.

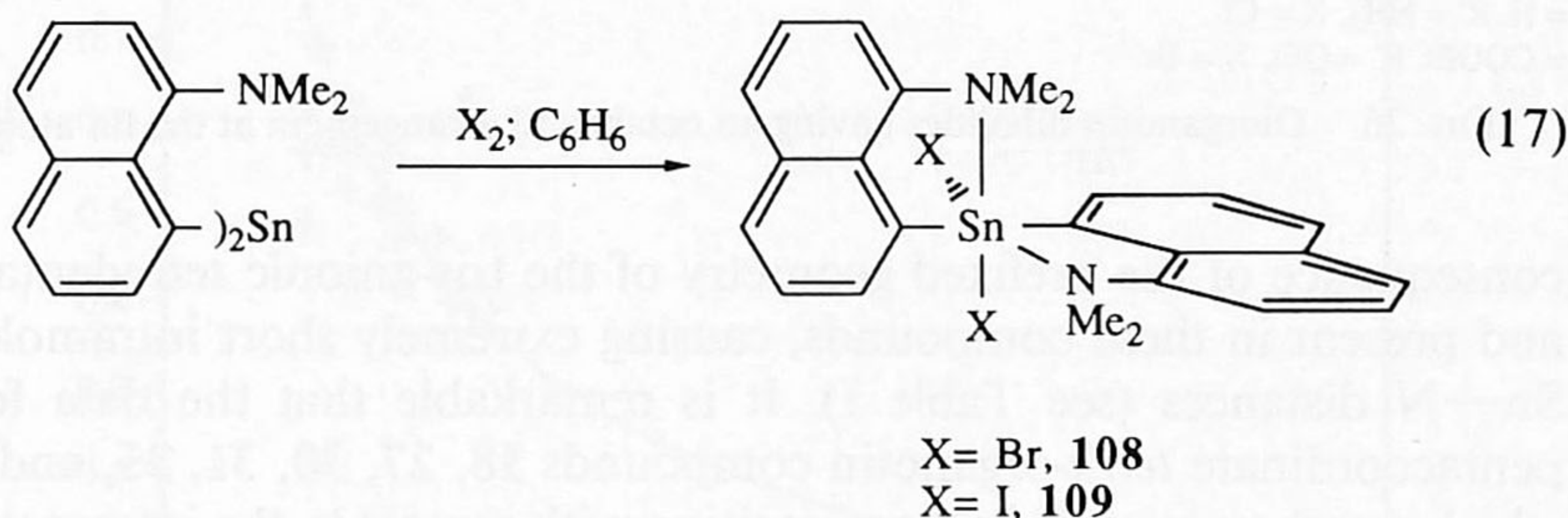
On the basis of <sup>1</sup>H NMR spectroscopic data for **106** (149) and Mössbauer spectroscopic data for **107** (139), similar structures for these two compounds were proposed.

It is interesting to note that the functionally substituted organotin compounds **102**–**104** are easily prepared by direct methods starting from tin powder and an  $\alpha,\beta$ -unsaturated carbonyl compound (150).



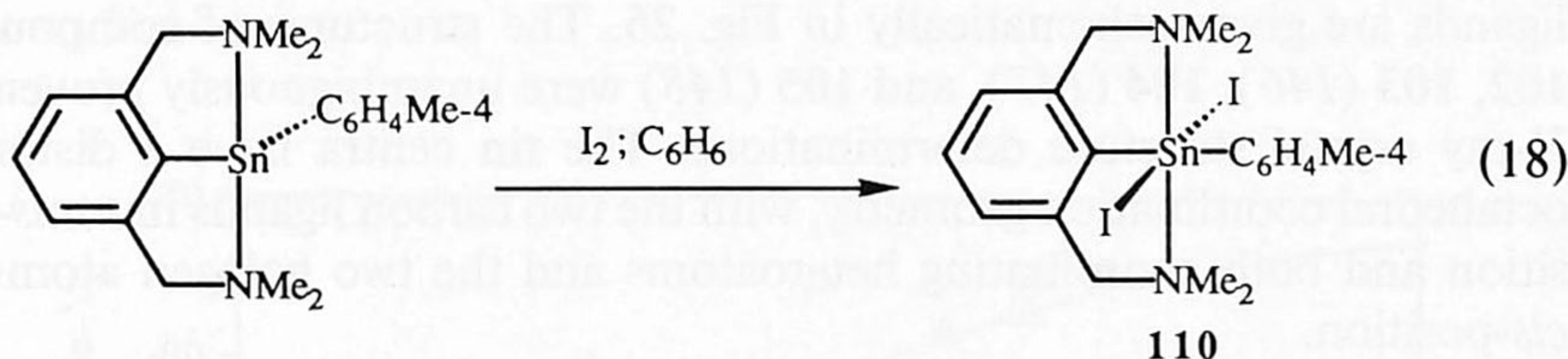
No catalyst is required for this reaction and it is likely to proceed via a solvated chlorostannane intermediate of the type  $\text{H}^+\text{SnCl}_3^- \cdot 2\text{Et}_2\text{O}$  (151).

Addition of dibromine or diiodine to the divalent organotin compound bis[8-(dimethylamino)-1-naphthyl]tin(II) affords in a quantitative oxidative-addition reaction bis[8-(dimethylamino)-1-naphthyl]tin dibromide **108** and diiodide **109**, respectively (152)



An X-ray crystal structure determination of **108** revealed an octahedral arrangement at the tin center, with the two carbon ligands in *trans*-position and both coordinating nitrogen and bromine atoms in *cis*-position.

Similarly the oxidative addition of diiodine to {2,6-bis[(dimethylamino)methyl]phenyl}(4-tolyl)tin(II) gives {2,6-bis[(dimethylamino)methyl]phenyl}(4-tolyl)tin(IV) diiodide **110**



Its X-ray crystal structure determination showed the tin center to be hexacoordinate, with the two carbon ligands, both coordinating nitrogen atoms, and both iodine atoms in *trans*-position (152).

The formation of a *trans*-oxidative-addition product in this case contrasts with the formation of a *cis*-oxidative-addition product when diiodine is reacted with {2,6-bis[(dimethylamino)methyl]phenyl}(4-methylphenyl)platinum(II). It has been argued that in the latter case, *trans*-oxidative-addition cannot take place for steric reasons (85). However, it may not be excluded that the initial step in the oxidative addition is also the formation of a *cis*-oxidative-addition product, which rapidly rearranges to the more stable *trans*-product **110**.

X-ray crystal structure determinations of **111** and **112**, schematically shown in Fig. 27, revealed structures in which, as a result of the formation



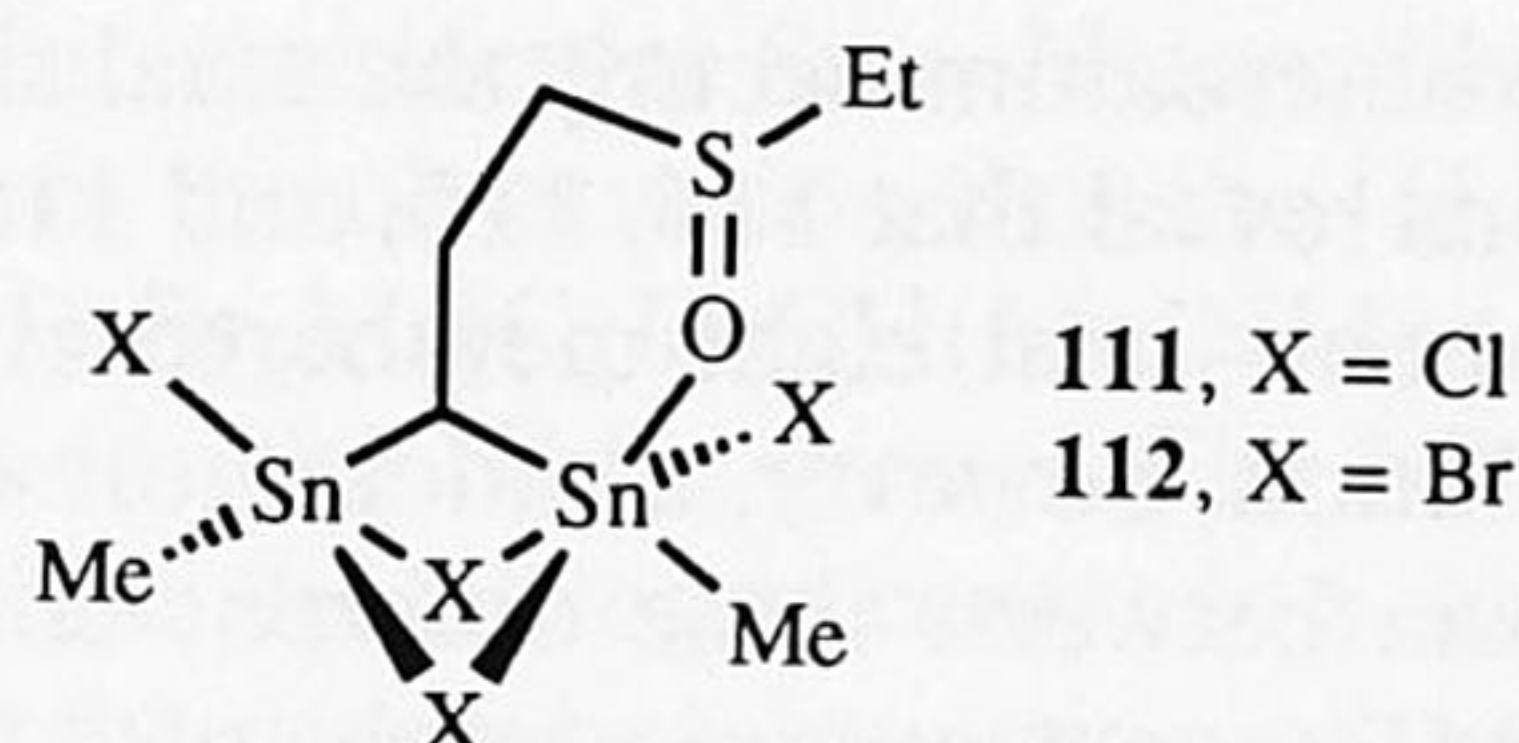
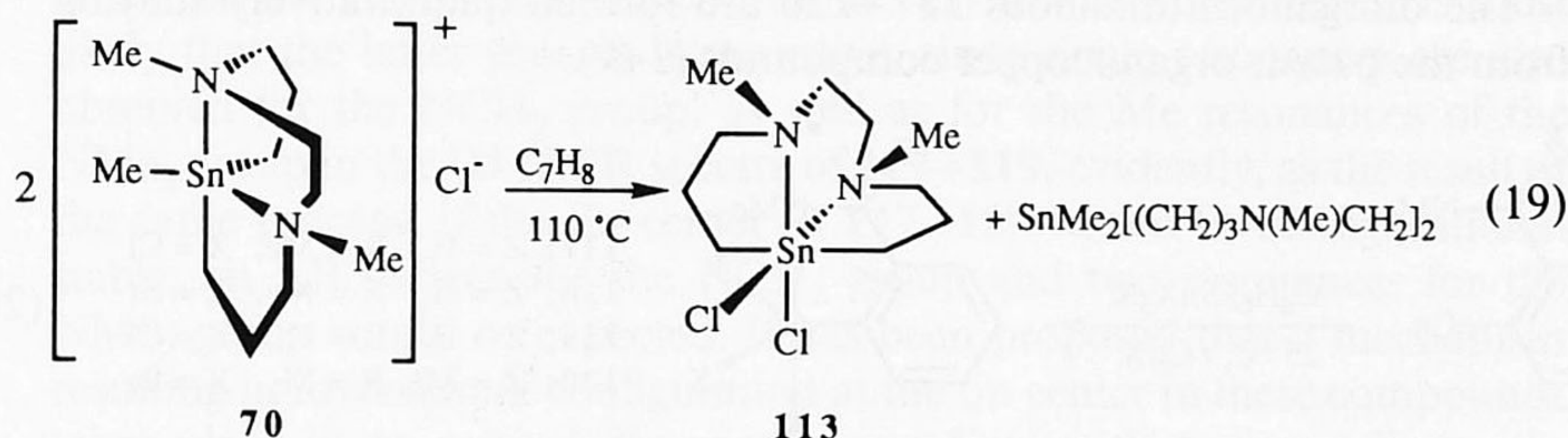


FIG. 27. Diorganotin dihalides containing one octahedral and trigonal bipyramidal coordinated tin center.

of two intramolecular halogen bridges and intramolecular coordination of the oxygen sulfoxide atom, one of the tin atoms has a trigonal bipyramidal and the other tin atom an octahedral coordination geometry (137).

Finally, the disproportionation reaction of the triorganotin chloride **70** into the novel diorganotin dichloride **113** has been reported. On the basis of its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, an octahedral coordination geometry has been proposed, schematically shown in Eq. (19)



for the tin atom that carries *trans*-carbon ligands (127).

## 2. Compounds Having a Trigonal Bipyramidal Arrangement at the Tin Atom

X-ray crystal structure determinations of **114–116**, cf. Fig. 28, have shown that in the solid state the tin atom in these compounds has a trigonal bipyramidal coordination geometry, with the two carbon ligands and one of the chlorine atoms at equatorial positions, while the other

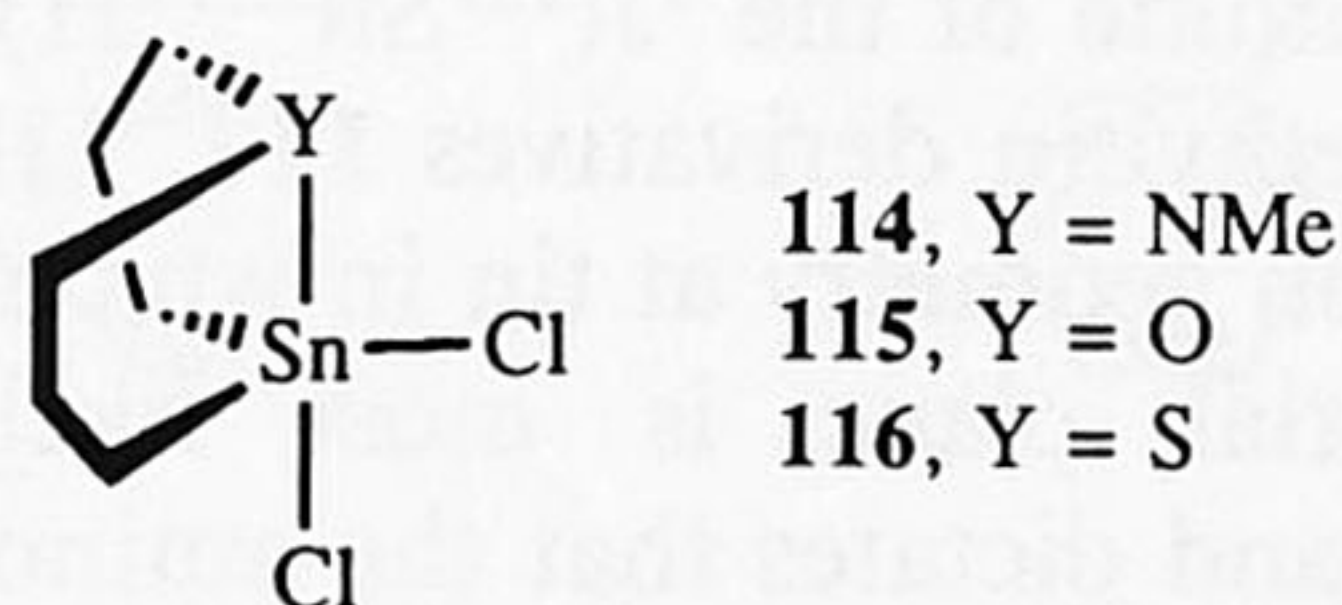
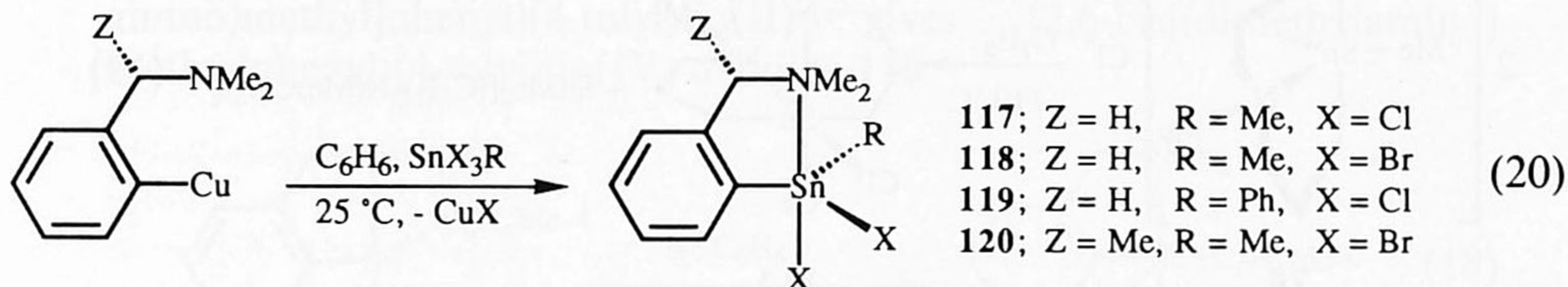


FIG. 28. Diorganotin dihalides containing a tridentate bis-anionic ligand resulting in a trigonal bipyramidal coordination geometry at the tin centers.

chlorine atom and the heteroatom occupy the axial sites. Furthermore, the solid-state investigations reveal that **114**, **115**, and **116** adopt a boat-chair, a chair-chair, and a boat-boat eight-membered ring conformation, respectively (102). In solution, however, a much more complicated situation arises because equilibria between these different conformations must be considered. A  $^{13}\text{C}$  NMR spectroscopic study of **114**–**116** showed both five-membered rings in each compound symmetry equivalent (at least on the NMR time scale), as was indicated by the observation of only one resonance for each type of methylene group.

A series of diorganotin dihalides containing the potentially intramolecularly coordinating 2-[(dimethylamino)methyl] group have been studied. It is well known that the direct alkyl or arylation of tin(IV) halides to organotin halides may be achieved with many organometallic reagents ( $\text{MgXR}$ ,  $\text{LiR}$ ,  $\text{NaR}$ ,  $\text{AlR}_3$  etc.), but that, even when precise reaction stoichiometries are used, a mixture of the three possible halides  $\text{R}_n\text{SnX}_{4-n}$  usually results (107). It was shown however, that aryl-copper compounds are much more selective arylating agents (153).

The diorganotin dihalides **117**–**120** are formed quantitatively starting from the parent organocopper compounds (149).



Because diorganotin dihalides generally are stronger Lewis acids than triorganotin halides (39), the intramolecular Sn—N coordination that was observed in the corresponding triorganotin halides containing the 2-[(dimethylamino)methyl]phenyl group (*vide supra*) must also be expected to occur in **117**–**120**. The observed molecular weight data in solution (**117**–**120** are monomers) exclude the possibility of intermolecular Sn—halogen coordination (143). On this basis, the Sn atom in **117**–**120** is pentacoordinate. Additional evidence for pentacoordinate tin centers in these compounds are (i) the observed absolute  $^{119}\text{Sn}$  NMR chemical shift values (*vide infra*) and (ii) the magnitude of the  $^2J(^{119}\text{Sn}-^1\text{H})$  coupling constants of about 80 Hz for the methyltin derivatives **117**, **118**, and **120**. A trigonal bipyramidal coordination geometry at tin in which the aryl and R groups reside in the equatorial plane is most likely. The bite of the  $\text{C}_6\text{H}_4\text{CH}(\text{Z})\text{NMe}_2$ -2 ligand dictates that the amino ligand will occupy an axial position, leaving one equatorial and one axial position for the two halogen atoms as schematically shown in Eq. (20).

The occurrence of intramolecular Sn—N coordination has been unambiguously deduced from the observation that the  $^1\text{H}$  NMR spectrum of the C-chiral compound  $\text{SnBr}_2\text{Me}[\text{C}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2\text{-}(S)\text{-}2]$ , **120**, at  $25^\circ\text{C}$  shows two resonances for the  $\text{NMe}_2$  group. The  $\text{NMe}_2$  methyl groups are only diastereotopic when the nitrogen center is a stable pyramidal assembly. This will only be the case when inversion of configuration is blocked by Sn—N coordination.

Since the diorganotin dihalide,  $\text{SnBr}_2\text{Me}[\text{C}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2\text{-}(S)\text{-}2]$  **120**, contains two chiral centers, in principle two different diastereoisomers should exist (Fig. 29). The configuration of the chiral benzylic carbon atom is fixed (*S*), the configuration of the chiral tin center may be either (*S*) or (*R*).

The observation of only one resonance pattern in the  $^1\text{H}$  NMR spectrum of **120** over the whole temperature range studied ( $-80$  to  $100^\circ\text{C}$ ) may be caused by two reasons: (i) the energy difference between these two diastereoisomers is so large that in solution only one of them is present or (ii) a process is operative that results in inversion of configuration at tin, which is fast on the NMR time scale, even at very low temperature. It is most likely that the latter process is operative, since single resonances are also observed for the  $\text{NCH}_2$  group, as well as for the Me resonances of the  $\text{NMe}_2$  group in the  $^1\text{H}$  NMR spectra of **117–119**, evidently, as the result of the same process. If the Sn center in **117–119** would be configurational stable, an AB pattern for the  $\text{NCH}_2$  group and two resonances for the  $\text{NMe}_2$  group would be expected. It has been proposed that a mechanism resulting in inversion of configuration at the tin center in these compounds takes place in an achiral dimeric intermediate with hexacoordinate tin centers (Fig. 30) (114).

Additional evidence for such an intermediate was obtained from  $^1\text{H}$  NMR studies of a mixture of the diorganotin dichloride, **117**, and the diorganotin dibromide, **118**. The  $^1\text{H}$  NMR spectrum of a mixture of **117** and **118** in toluene- $d_8$  shows only one resonance pattern, of which the Sn—Me resonance appears at 0.90 ppm, a value in between those of the pure compounds, 0.80 and 1.00 ppm, respectively. Below  $-80^\circ\text{C}$ , the

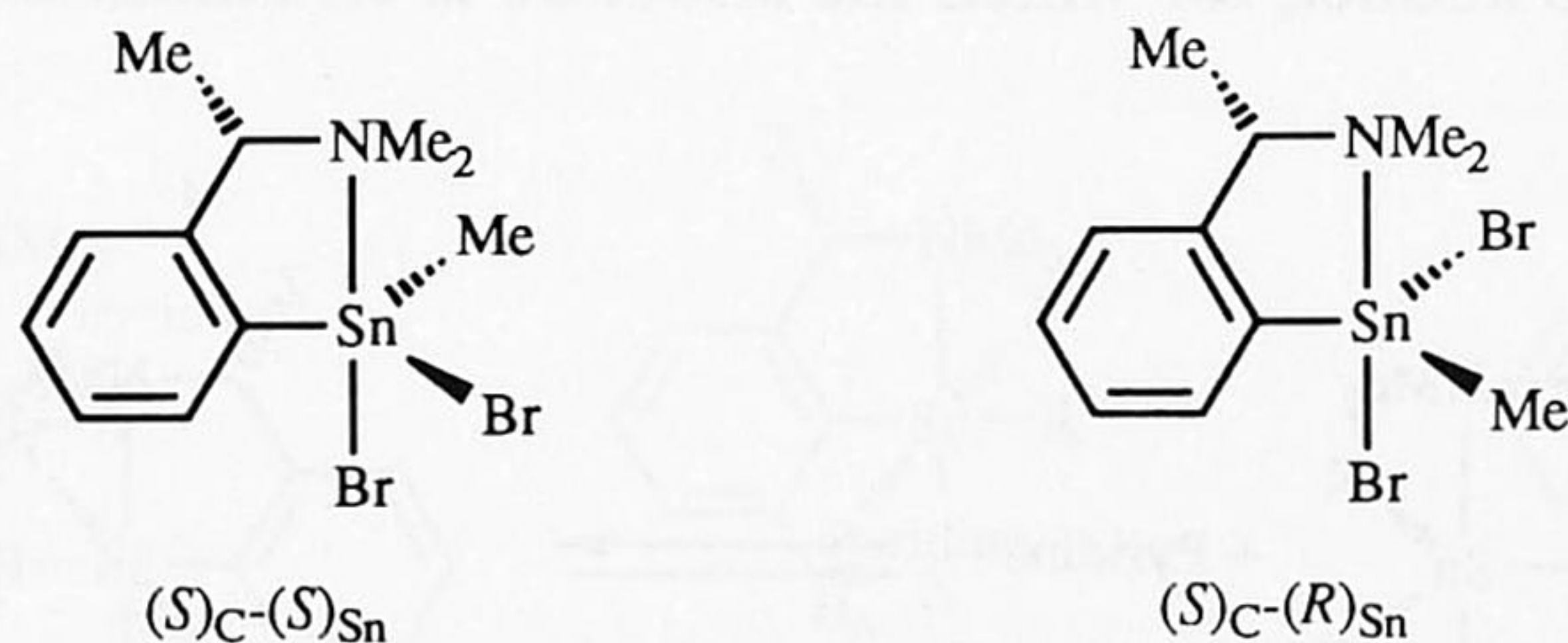


FIG. 29. The two possible diastereoisomers of **120**.

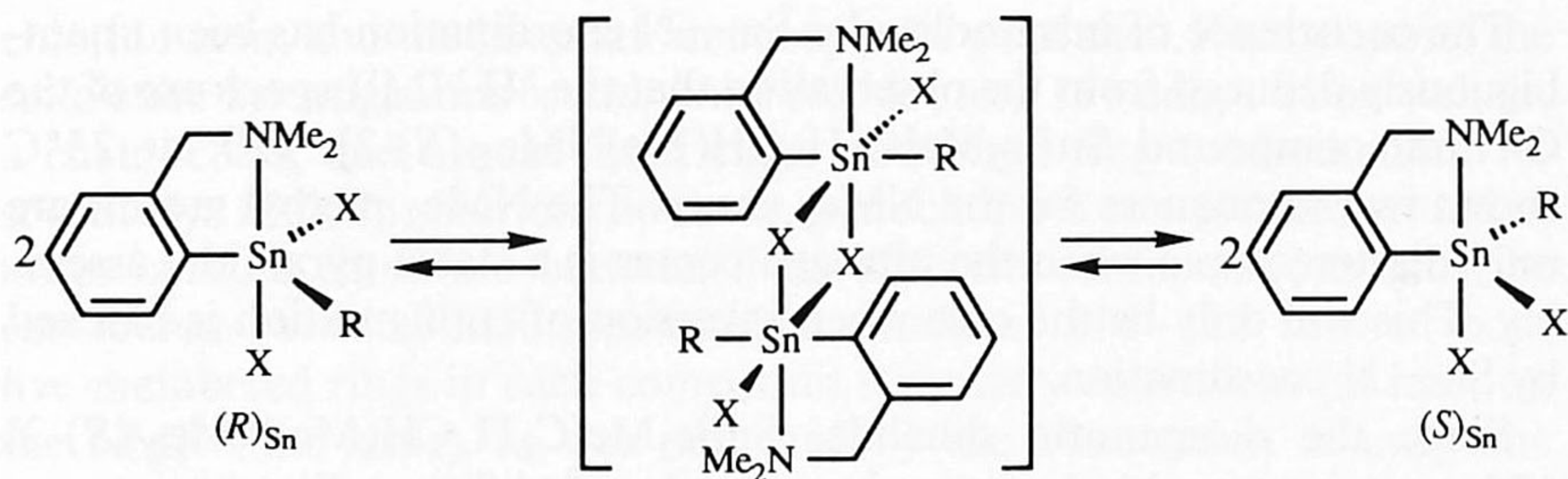


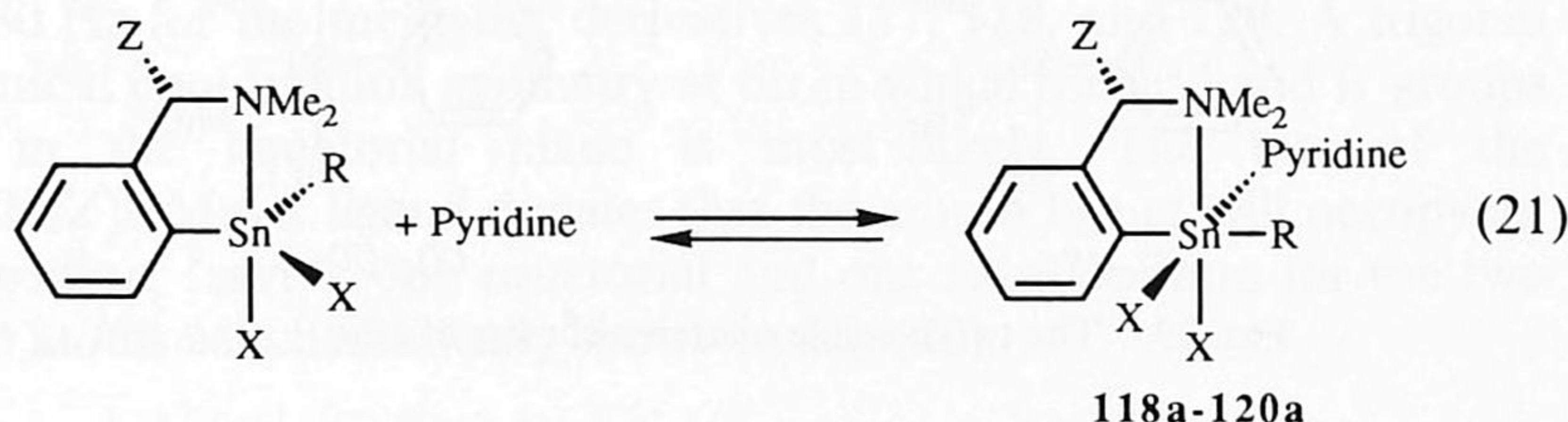
FIG. 30. Proposed mechanism for the inversion of configuration at tin in pentacoordinate-diorganotin dihalides.

Sn—Me resonance splits up into two resonances at positions of the pure compounds. Moreover, at this temperature the NMe<sub>2</sub> and NCH<sub>2</sub> resonances start to split up, which indicates that under these conditions the tin center is becoming configurationally stable on the NMR time scale.

In view of the well-documented tendency of diorganotin dihalides to form complexes in which the tin center has an octahedral coordination geometry (39,107), an <sup>1</sup>H and <sup>119</sup>Sn NMR study of compounds **118–120** in the presence of donor molecules was carried out (94).

When half an equivalent of pyridine is added to a toluene-*d*<sub>8</sub> solution of one of the diorganotin dihalides **118–120**, the <sup>1</sup>H NMR spectra at 25°C remain unchanged as compared to those of the pure diorganotin dihalides. However, at –40°C the <sup>1</sup>H NMR spectra of these solutions show the presence of two resonance patterns in a one-to-one ratio; one pattern is identical to that of the original pentacoordinate diorganotin dihalide while the second resonance pattern has been ascribed to the pyridine adduct (**118a**, **119a** and **120a**, respectively) of the corresponding diorganotin dihalide.

From these observations it was concluded that in solution in the presence of pyridine the diorganotin dihalides **118–120** are in equilibrium with their respective pyridine adducts. At room temperature the equilibrium lies completely to the side of the pentacoordinate species, while at –40°C, this equilibrium has shifted completely to the side of a hexacoordinate pyridine adduct, for which the structure is schematically shown in Eq. (21).



The tin center in these pyridine adducts **118a**–**120a** is hexacoordinate, which is not the result of a simple ligand displacement of the intramolecularly coordinating amino substituent by a pyridine molecule. This is reflected by the observation of two resonances for the NMe<sub>2</sub> group in the <sup>1</sup>H NMR spectrum of C-chiral SnBr<sub>2</sub>Me[C<sub>6</sub>H<sub>4</sub>CH(Me)NMe<sub>2</sub>-(*S*)-2], **118a**, indicating that coordination of the amino substituent to tin is inert on the NMR time scale (*vide supra*).

Further evidence for hexacoordinate tin in **118a**–**120a** is the increase in the value of the <sup>2</sup>J(<sup>117,119</sup>Sn—<sup>1</sup>H) from approximately 78 Hz in the methyltin compounds **118** and **120** to about 105 Hz in **118a** and **120a**. This increase in coupling constant is indicative for an increase in the coordination number at tin (143). The <sup>119</sup>Sn NMR spectra of the pyridine adducts **118a**–**120a** show a 150 ppm shift to higher field compared to the values of **118**–**120** (94). This high-field shift is also indicative of an increase in the coordination number at tin (93). Furthermore the observed absolute <sup>119</sup>Sn chemical shift values obtained for **118a**–**120a** (–293.8, –339.7, and –290.5 ppm, respectively) are in the same range as that observed for other diorganotin dihalides, for which hexacoordination at tin was established independently (*vide supra*).

Although in principle the pyridine adducts **118a**–**120a** can exist as various geometrically different isomers, those isomers having a *cis*-geometry of the two organic groups can be excluded. (It has been well established that the two organic groups in R<sub>2</sub>SnX<sub>2</sub>·2L complexes are invariably, to date, anyway *trans*.) The two halide and the two donor molecules, however, can adopt either *cis*- or *trans*-configuration [see Ref. (39) and references cited therein], thus leaving three possible different geometrical isomers A–C, which are shown schematically in Fig. 31.

As has been outlined above, in structures A and B the two organic groups are in *trans*-position, while both coordinating nitrogen atoms and both halogen atoms have a *cis*-arrangement. In structure C, the two nitrogen atoms, and as a consequence the two halogen atoms, are in *trans*-position.

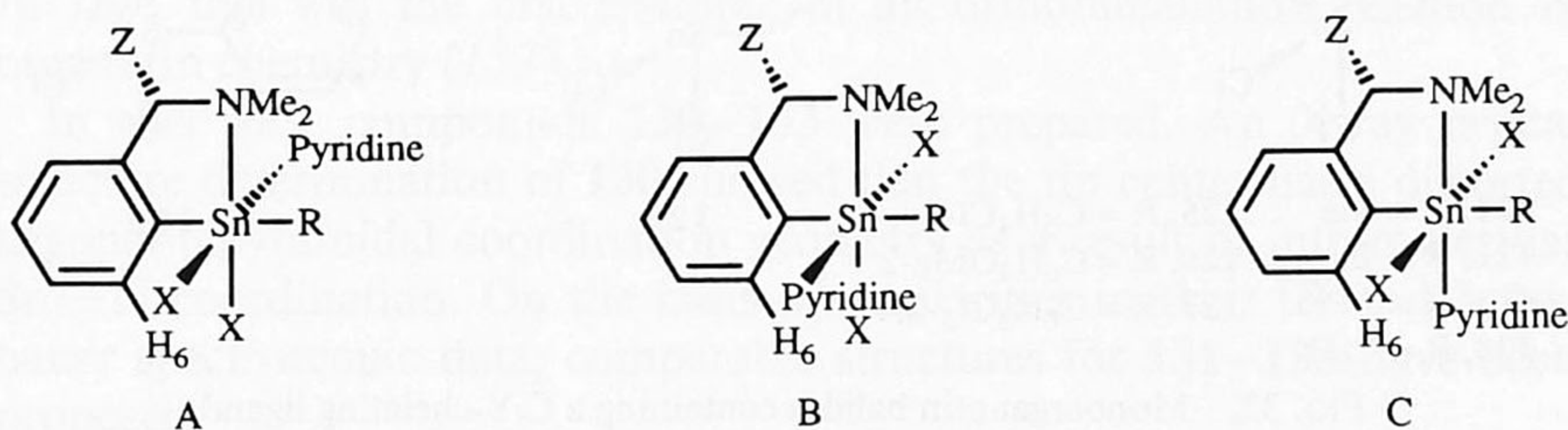


FIG. 31. The three possible different geometrical isomers of **118a**–**120a**.

Based on  $^1\text{H}$  NMR spectra of **118a**–**120a**, structure A or B (if  $Z = \text{H}$ , **118a** and **119a**, A and B are identical; see Fig. 31) seems to be most likely for these complexes. When the  $^1\text{H}$  NMR spectra of these pyridine adducts are compared with those of **118**–**120**, it appeared that major changes in chemical shift have occurred for the protons present in the  $\text{CH}(Z)\text{NMe}_2$  substituent, as well as for those in the  $\text{Me}-\text{Sn}$  group in **118a** and **120a**. Most likely these changes in chemical shift are caused by the anisotropy of the pyridine ring, present in *cis*-position with respect to both the substituted phenyl group and the  $\text{Me}-\text{Sn}$  group, (cf. Fig. 31A and 31B). This is furthermore supported by the observation that the chemical shift values of the  $\text{H}_6$  protons in **118a**–**120a** are almost identical to those in **118**–**120**. A pyridine group present in *trans*-position with respect to the coordinating  $\text{CH}(Z)\text{NMe}_2$  group, cf. Fig. 31C, would have had a major effect on the chemical shift of the  $\text{H}_6$  proton, while it would have little effect on the chemical shift values of the protons in the  $\text{CH}(Z)\text{NMe}_2$  substituent. Based on the observed  $^1\text{H}$  NMR data of **120** and **120a**, it is not possible to conclude which structure, A or B, is correct for **120a**; however, for steric reasons structure B seems to be more likely.

#### F. Monoorganotin Halides Containing a C,Y-Chelating Ligand

Only a few examples of monoorganotin trihalides in which a C,Y-chelating ligand is present are known. Because of their importance as precursors for PVC stabilizers, some structural investigations on ester—tin trihalides have been carried out.

X-ray crystal structure determinations of **121** (146), **123** (154), and **128** (155) show that the tin centers in these compounds have a trigonal bipy-

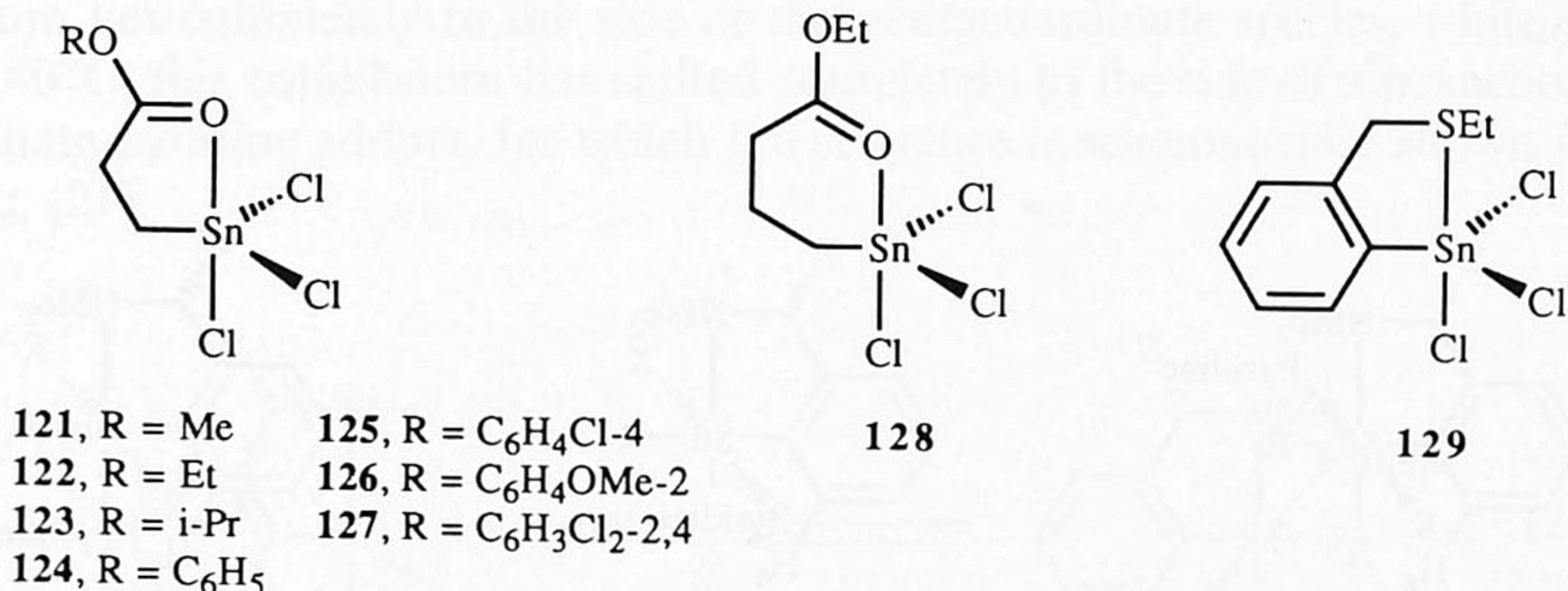
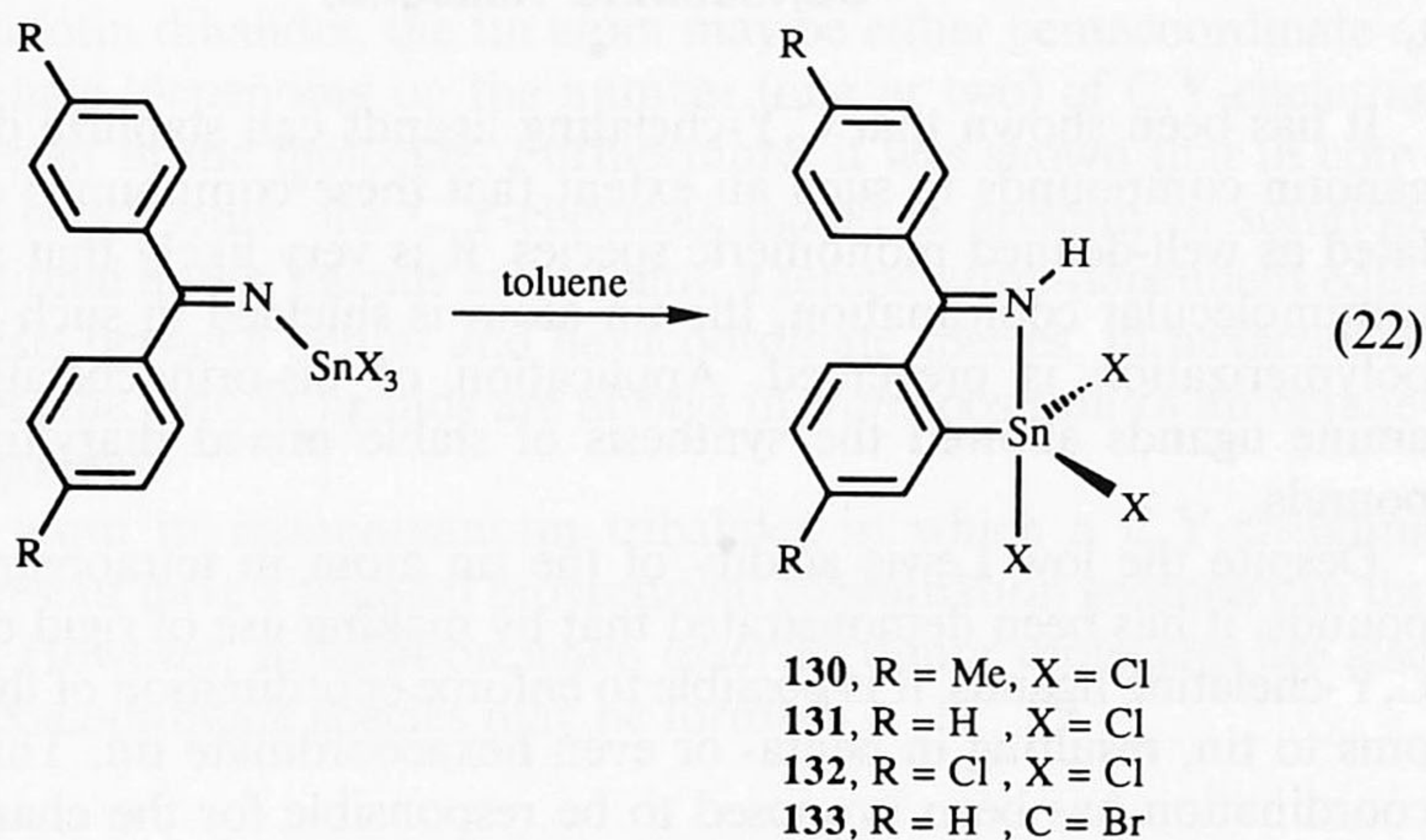


FIG. 32. Monoorganotin halides containing a C,Y-chelating ligand.

ramidal coordination geometry as a result of intramolecular coordination of the carbonyl oxygen atom (cf. Fig. 32). On the basis of IR spectroscopic studies of **122** and **124–127**, a similar structure was proposed (154). These compounds form 1 : 1 adducts with bidentate donor molecules like bipyridine; i.e., in these complexes, intramolecular Sn—O coordination is no longer present. However, with monodentate ligands like pyridine, an equilibrium exists between a 1 : 1 adduct, in which intramolecular coordination is still present, and a 1 : 2 adduct (154, 155). Furthermore it was shown that Sn—O coordination in the compounds in which a five-membered chelate ring is present (**121–127**) is much stronger than that in **128** in which a six-membered chelate ring is present.

In the thioether compound **129**, Sn—S coordination was established on the basis of a temperature-dependent lineshape analysis of the  $^1\text{H}$  NMR resonances of the diastereotopic S<sub>Et</sub> group (156).

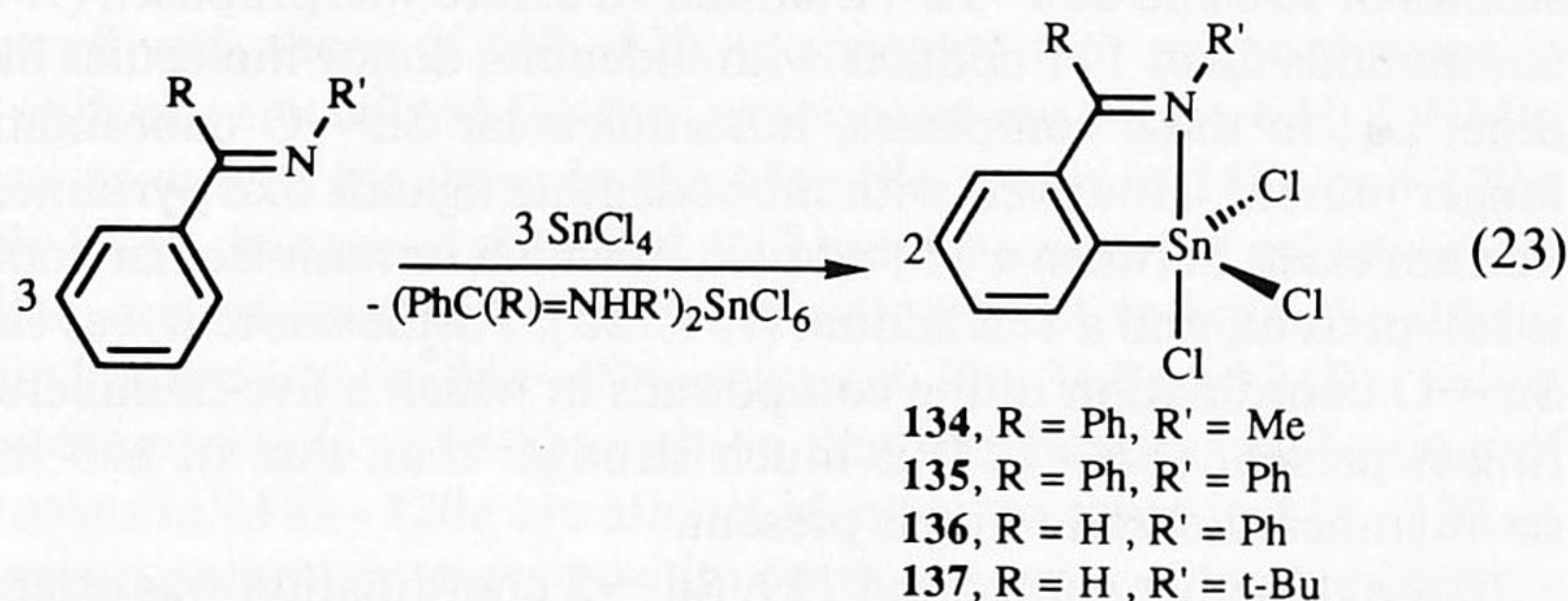
Wade *et al.* have found that ketaminotin trihalides  $\text{SnX}_3\text{N}=\text{CR}_2$  spontaneously rearrange to form a product in which a tin—carbon bond is formed.



In fact, this was the first example of an orthometallation reaction in organotin chemistry (157).

In this way, compounds **130–133** were prepared. An X-ray crystal structure determination of **130** showed that the tin center has a distorted trigonal-bipyramidal coordination geometry as a result of intramolecular Sn—N coordination. On the basis of similarities in their IR and Mössbauer spectroscopic data, comparable structures for **131–133** have been proposed.

As an extension of this work, the same authors recently reported the direct orthometallation of several Schiff's bases according to (158):



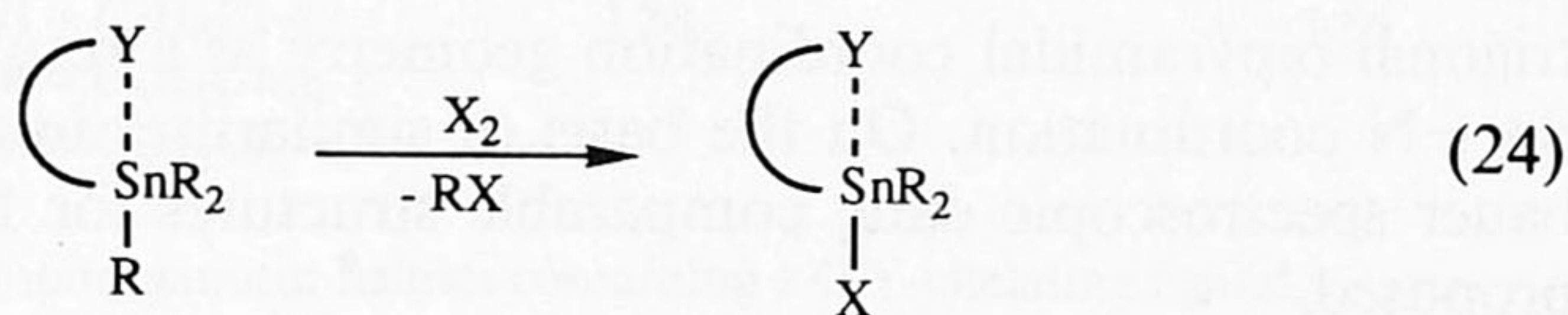
An X-ray crystal structure determination of **134** showed that these compounds have structural features that are comparable to those of **130**.

#### IV

#### CONCLUDING REMARKS

It has been shown that C,Y-chelating ligands can stabilize divalent organotin compounds to such an extent that these compounds can be isolated as well-defined monomeric species. It is very likely that as result of intramolecular coordination, the tin atom is shielded in such a way that polymerization is prevented. Application of bis-ortho-chelating aryldiamine ligands allowed the synthesis of stable mixed diaryltin(II) compounds.

Despite the low Lewis acidity of the tin atom in tetraorganotin compounds, it has been demonstrated that by making use of rigid or cage-like C,Y-chelating ligands, it is possible to enforce coordination of the heteroatoms to tin, resulting in penta- or even hexacoordinate tin. This enforced coordination has been proposed to be responsible for the changes in the reactivity sequence observed in halodemetalation reactions of mixed tetraorganotin compounds, in which potentially coordinating groups (Y) are present in the  $\gamma$ -position with respect to the tin. It is thought that intramolecular assistance by those groups facilitates the cleavage of tin—carbon bonds *trans* to them:





It is anticipated that this concept of intramolecular assistance by heteroatom-tin coordination will be shown to be extremely useful in reactions comprising metal-mediated group transfer from tin to an organic substrate by C—C bond formation (111,112). In this context similar reactivity of tetraorganosilicon compounds with intramolecular heteroatom coordination can be expected.

In triorganotin halides containing a C,Y-chelating ligand, normally the tin atom has a trigonal bipyramidal coordination geometry, as a result of intramolecular coordination. The carbon ligands are at the equatorial sites, while the more electronegative halogen atom and the coordinating heteroatom reside at axial positions. This class of compounds are excellent model compounds for a study of the inversion process at the tin atom and chiral triorganotin halides. Our study on triorganotin halides containing the C,N-chelating 2-[(dimethylamino)methyl]phenyl ligand was the first example in which this was demonstrated (54). In triorganotin halides containing two potentially coordinating heteroatoms either halogen displacement occurs, resulting in the formation of pentacoordinate triorganostannonium cations, or a species is formed in which the coordination geometry of the tin atom may be regarded as distorted octahedral.

In diorganotin dihalides, the tin atom may be either pentacoordinate or hexacoordinate, depending on the number (one or two) of C,Y-chelating ligands present in the molecule. Furthermore, it was shown that in compounds in which only one C,Y-chelating ligand is present, in solution, when additional donor ligands are present, a temperature-dependent equilibrium exists between penta- and hexacoordinate species. In hexacoordinate species, the carbon ligands are always in *trans*-position of an octahedral arrangement.

The tin atom in monoorganotin trihalides in which a C,Y-chelating ligand is present have a trigonal bipyramidal coordination geometry in the solid state. However, in solution when external donor molecules are also present, hexacoordinate species may be formed.

#### ACKNOWLEDGMENTS

Thanks are due to the excellent practical work of a large number of graduate and undergraduate students participating in our research project concerning organotin compounds containing potentially intramolecular coordinating substituents. The X-ray crystallographers, Drs. A. L. Spek, C. H. Stam, and K. Goubitz and Professor J. Kroon are thanked for the continued interest in our studies and generous support with invaluable information concerning the structures of organometallic compounds in the solid state. Drs. J. Boersma and D. M. Grove are kindly acknowledged for their interest in this part of the research of the Utrecht group. The Netherlands Foundation for Chemical Research (SON), the Netherlands Organization for Scientific Research (NWO), and the Universities of Amsterdam (1977–1985) and Utrecht (1986–1992) are thanked for financial support.

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