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Bivalent Tin Analogues of Carbenes

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The structure and certain chemical and physiocochemical properties of bivalent tin compounds (stannylenes) are examined and the electronic, structural and chemical similarity between these compounds and carbenes and their analogues—bivalent compounds of Group IVB elements—is demonstrated. The possibilities of stannylenes in the synthesis of organotin (IV) compounds as well as complexes in which stannylenes are electron-donating ligands, like carbenes, are analysed. The bibliography includes 457 references.

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I. INTRODUCTION

During the last 15–20 years, the chemistry of bivalent tin compounds has developed rapidly; their structural and chemical similarity to compounds of other Group IVB elements in their lowest oxidation state—the bivalent compounds of carbon (carbenes)[1–5] and their closest analogues in the subgroup (silylenes, germylenes, and plumbylenes)[6–24]—is becoming increasingly evident.

Certain questions of the chemistry of tin(II) compounds have been reflected in monographs and reviews devoted mainly to the chemistry of quadrivalent tin[25–33]. The review by Donaldson[34], in which the structure and chemical properties of tin(II) compounds (mainly inorganic) were considered for the first time fairly fully (on the basis of the literature data up to 1966) as well as a series of reviews devoted to individual aspects of the chemistry of these compounds[9,18,35–38] merit special attention. For further information concerning the review literature and various problems of the synthesis, properties, and structure of tin(II) compounds, the reader is recommended to consult the Bibliographic Guide[39].

Numerous data indicating the chemical and structural similarity of carbenes and their analogues were first considered thoroughly in the review of Nefedov and Manakov[6] and later also other reviews[40–42], but they describe the chemistry of tin(II) compounds very briefly and incompletely. With the exception of relatively inaccessible publications in 1977 and 1978,[43,44] there has been hitherto no review analogous to those on silylenes and germylenes which would provide an adequate survey of studies demonstrating the structural and chemical similarity of tin(II) compounds to carbenes and their analogues. This review, which surveys studies published up to 1980, aims to fill this gap to some extent.

II. THE STRUCTURE AND PROPERTIES OF BIVALENT TIN COMPOUNDS

As a Group IVB element, tin has the outer electronic configuration ns^2np^2 in the ground state and, like its nearest neighbours in the subgroup (germanium and lead), can form stable compounds not only in the quadrivalent but also in the bivalent state. The formation of covalent inorganic and organic tin(II) compounds as well as organotin(II) compounds† can take place as a result of the employment of two unpaired p electrons (Fig.1).

Like carbenes and their analogues, in this case tin(II) compounds have the structure in the gas phase which can correspond in the one-electron approximation (i.e. when the fully occupied low-lying and vacant high-lying molecular orbitals are excluded from consideration) to the σ^2, σp, and p^2 configurations (Fig.2). The σp configuration can then be both singlet ($^1\sigma p$) and triplet ($^3\sigma p$), while the σ^2 and p^2 configurations are singlet.

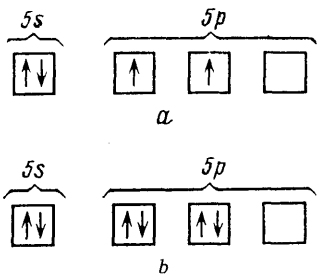


Figure 1. The distribution of electrons in the ground state: *a*) tin atom; *b*) SnX_2 molecule.

In the gas state at high temperatures, tin(II) dihalides are monomeric[45] and the study of their emission spectra under such conditions has shown that the SnX_2 molecules are non-linear[46]. The chemiluminescence emission spectra of SnX_2 in a flame[47] as well as the Raman spectra of the vapours of $SnCl_2$ [48,49] and other compounds of the type SnX_2 [50] at temperatures above 630 °C confirm the non-linearity of the structure of tin(II) dihalides under these conditions. Electron diffraction studies of the vapours of tin(II) dihalides established that the valence angle in their molecules is close to 95°.[50]

The results obtained agree with one another and also with infrared spectroscopic[51,52] and Mössbauer spectroscopic[53] data for tin(II) dihalides fixed in low-temperature inert matrices and make it possible to refine the values of the valence angles in the SnX_2 molecules (90–94°). Comparison of the bond angles and lengths in tin(II) dihalides and the dihalides of other Group IVB elements[9,40,41,50] shows that they are all isostructural and the closeness of the bond angles to 90° suggests that, like other carbene analogues,

† In contrast to organotin(II) compounds having at least one Sn–C bond, there is no direct bond between tin and carbon in organic compounds of tin(II).

stannylenes have a singlet ground state ($^1A_1$).[40,41] The singlet state of dihalogenostannylenes is confirmed by the fact that the energies of their orbitals (between −10 and −11.5 eV), determined from the ionisation potentials[54,55], are close to the energies of the σ orbitals of dihalogeno-derivatives of carbenes, silylenes, germylenes, and plumbylenes[40,41].

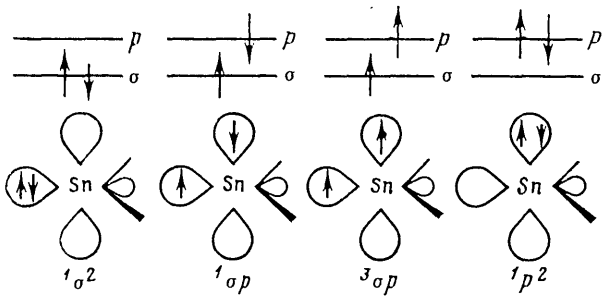


Figure 2. The structure of tin(II) compounds.

The direct determination of the energies of the *p* orbitals of stannylenes is impossible, but they can be estimated from the differences between the energies of the σ and *p* orbitals, which can be determined from the energy of the transition from the ground to the excited state ($^1A_1 \rightarrow {}^1B_1$). It was found that the energies of the *p* orbitals of dihalogeno-stannylenes (−6– −7 eV) are somewhat higher than the energies of *p* orbitals of carbenes but are very close to those of silylenes, germylenes, and plumbylenes. Thus the σ^2 configuration with a vacant *p* orbital makes the dominant contribution to the ground state of dihalogenostannylenes.

As in dihalogenostannylenes, in certain free stannylenes of other types in the gas phase and in the low-temperature matrices the tin orbitals are in a state close to sp^2. Thus spectroscopic investigations support a singlet ground state in a few diorganostannylenes[56] and stannylenes of the type $Sn(NR^1R^2)_2$.[57–59]

In a study of the phosphorescence observed in the GeO, GeS, SnO, and SnS molecules[60] isolated in low-temperature matrices, their lifetimes in the excited triplet states were calculated (3–100 μs).

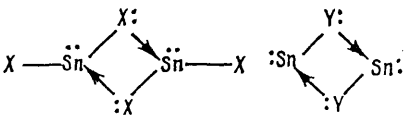


Figure 3. The structure of the dimers $(SnX_2)_2$ and $(SnY)_2$.

Mass-spectrometric studies of tin(II) halides and tin(II) monoxide[61,62] in the vapour phase revealed the presence, together with monomers, of the corresponding dimers, which consist, according to the spectroscopic studies of $(SnX_2)_2$ and $(SnO)_2$ molecules[52,53,63–66] as well as $(SnY)_2$ (Y = S or Se) [67] isolated in matrices at a low temperature, of four-membered rings formed as a result of the coordination interaction of the **free electron pair of halogen, oxygen, sulphur or selenium with the vacant p orbital of the tin atom (Fig.3).**

Structural and other physicochemical studies have shown that in the condensed (liquid or solid) phase many tin(II) compounds with electronegative substituents incorporating heteroatoms having unshared electron pairs are coordination polymers where the tin atoms employ in the hybridisation their own free *p* and *d* orbitals. Thus the X–Sn–X bond angles are somewhat less than 90° in crystalline anhydrous SnF_2,[68] $SnCl_2$,[69,70] $SnBr_2$,[71] and SnI_2 [72] and also in the mixed tin(II) halides[73,74], while their molecules form a coordination polycarbenoid layer structure (Fig.4), in which the free electron pair of the tin atom is involved in the hybridisation of the orbitals. The tetragonal tin monoxide $(SnO)_n$ [75] and tin(II) sulphide[69], selenide, and telluride[76] have similar structures.

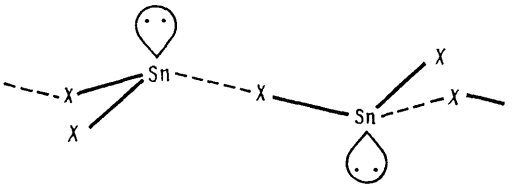


Figure 4. The layer structure of crystalline $(SnX_2)_n$.

The study of the Raman[77] and absorption[78] spectra of a melt of tin dichloride over a wide temperature range showed a gradual breakdown of the $(SnCl_2)_n$ chains with increase of the temperature of the melt. The weaker axial coordinate bonds begin to dissociate first and at a high temperature *in vacuo* free stannylenes can be formed in the gas phase[45,46,48–50]. The coordinate bonds in the polycarbenoid chains $(SnX_2)_n$ can break down also under the influence of electron-donating solvents (Solv) which results in the formation of discrete carbenoid complexes $Solv.SnX_2$, in which the tin atom is an acceptor of the electron pair of the solvent. The synthesis and properties of numerous complexes of this kind have been described in reviews[32,34]. It is of interest to note that the geometry of carbene-like molecules in such complexes differs little from the geometry of the free stannylenes, as shown by the similarity by the geometries of dichlorostannylenes and its complex with dioxan[79].

Organic compounds of tin(II) consists of a large group of compounds in which the organic moieties are linked to the tin atom via a heteroatom (oxygen, nitrogen, sulphur, phosphorus, and others). It has been established mass-spectrometrically that some of these [for example, $Sn(OCOAr)_2$,[80] bis(diketonato)tin(II),[81] and tin(II) amides[57,58]] are monomeric in the gas phase and also in solution. The majority of organic compounds of tin(II) having electron-donating heteroatoms are coordination intra- or inter-molecular complexes in the liquid and crystalline state. The most common types of compounds of this kind are cyclic[82–85] and linear[86–90] tin(II) alkoxides as well as acyloxy-derivatives of tin(II).[91–94]

Chelates with Sn–O bonds, such as bis(1,3-diketonato)-tin(II),[81,95–97] tin tropolonates[98], and many other tin(II) chelates[97,99–101] constitute a large group of organic compounds of tin(II). Their crystal structures have not been established in most cases, but the available X-ray diffraction data for solid bis(benzoylacetonato)tin(II) [101] and bis(1,3-diphenylpropane-1,3-dionato)tin(II) [102] suggest that their

ligands are bidentate and that the tin atom is an sp^3d hybrid (Fig.5*a*). It is believed[95,103] that the tin atom in 1,3-diketonatotin(II) halides is in the sp^3 configuration (Fig.5*b*). The tin atom in the monomeric product $Sn(OCH_2CH_2)_2NCH_3$ is evidently in the same state (Fig.5*c*).[104]

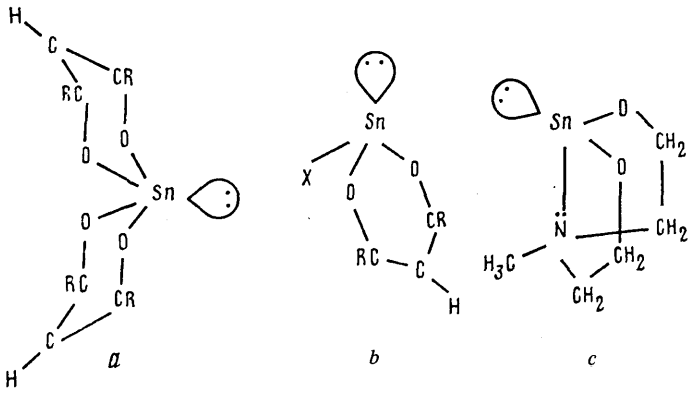


Figure 5. The structures of certain organic compounds of tin(II): *a*) bis (1,3-diketonato)tin(II); *b*) 1,3-diketonatotin(II) halides; *c*) $Sn(OCH_2CH_2)_2NCH_3$.

The crystal structure of bis(*O*-methyl dithiocarbonato)tin(II),[105] bis(diethyldithiocarbamato)tin(II),[106] and diazasilastannetidines[107] are in principle analogous to the structures presented above. The structures of other organic compounds of tin(II), containing the Sn–N,[104,108–111] Sn–P,[112] Sn–As,[113] and certain other bonds[100,103,114] have not been established exactly although it has been suggested that the dimers of some of them, which exist in solutions, have structures analogous to those of the tin(II) dihalide dimers (Fig.3).

Little is so far known about the structures of organotin(II) compounds. The reason for this is in the first place that only few compounds of the type R_2Sn: (the first was obtained as early as 1852 [115]) can retain the tin atom in the bivalent state for a long time. In the vast majority of cases, regardless of the methods of their synthesis, diorganostannylenes polymerise very readily (see Section III). Certain organotin(II) compounds containing specific groups, which prevent the polymerisation of diorganostannylenes to the corresponding polystannanes, constitute an exception. Such compounds include dicyclopentadienyltin(II) [116] and bis-(methylcyclopentadienyl)tin(II),[117] which contain the cyclopentadienyl groups (Cp)—carriers of a closed π-electron system. Gas-phase electron diffraction studies established that the Cp^2Sn molecule has an angular sandwich structure[118] (Fig.6*a*).

Although dicyclopentadienyltin(II) is monomeric in the gas phase and in benzene solution, in the solid state it is a coordination polymer in which the cyclopentadienyl rings form a kind of bridges between the tin atoms (Fig.6*b*). In solid cyclopentadienyltin(II) chloride the coordination polymer is formed as a result of Cl...Sn coordinate bonds (Fig.6*c*). Other more exotic examples of organostannylenes are presented in Fig.7.[119–122]

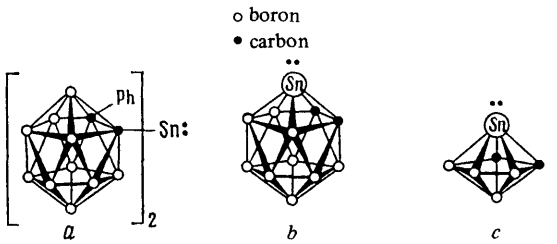


Figure 7. Some examples of organostannylenes: *a*) bis[2-phenyl-1,2-dicarba-*closo*-dodecaboran(12)-1-yl tin(II); *b*) 3-stanna-1,2-dicarba-*closo*-dodecaborane(11); *c*) small tin(II)-containing metallocarbaboranes.

The synthesis of the first stable dialkylstannylene containing two bis(trimethylsilyl)methyl groups, namely $[(Me_3Si_2)CH]_2Sn$:, was reported in 1973.[123] Its structure in the gas phase was not investigated but it was shown mass-spectrometrically that it exists in a free state: it is monomeric in solution and spectroscopic data indicate a singlet

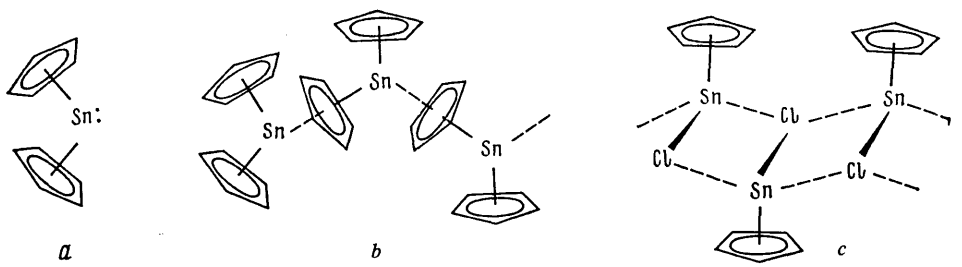


Figure 6. The structure of cyclopentadienyl derivatives of tin(II): *a*) Cp_2Sn in the gas phase; *b*) Cp_2Sn in the solid state; *c*) CpSnCl in the solid state.

ground state of the molecule[56]. This has been confirmed by the study of the crystal structure of the complex $\{Cr(CO)_5 . Sn[CH(SiMe_3)_2]_2\}$ in which the valence angle of the diorganostannylene is close to 98°.[124] According to X-ray diffraction data[125], in the solid state $Sn[CH(SiMe_3)_2]_2$ is a dimer, whose curved bonds are formed as a result of the mutual overlap of the free electron pair of the tin atoms with their unoccupied *p* orbitals[56]. The angle between the C–Sn–C bonds then increase to 112°.

Numerous other compounds, which were believed for a long time to have been diorganostannylenes, proved to be polystannanes with a quadrivalent tin atom. Valuable information, which makes it possible to establish the valence state of the tin atom, is provided by Mössbauer or γ-resonance spectroscopy. The isomer shifts (*IS*) in the Mössbauer spectra of the majority of tin(II) compounds are in the range 3–4 mm s^{-1} (here and henceforth the values of *IS* are quoted relative to SnO_2), which indicates an appreciable *s*-electron density at the tin nuclei. This is a consequence of an appreciable *s* character of the orbital occupied by the free electron pair. When the environment of the resonating nuclei is non-spherical, usually two peaks are observed in the Mössbauer spectrum (quadrupole splitting); on the other hand, when the *s*-electron cloud is fully spherical, there is no quadrupole splitting. Information about the Mössbauer spectroscopy of tin(II) compounds can be found in a number of publications[53,126–129].

The diorganostannylene $[(Me_3Si)_2CH]_2Sn$ has a small isomer shift (*IS* = 2.16 mm s^{-1}) compared with other organotin(II) compounds[123,130], which is consistent with the difference between its structure and those of other diorganostannylenes—Cp_2Sn, CpSnCl, and CpSnBr (Fig.6)—in which the isomer shift (3.76 mm s^{-1},[131] 3.90 mm s^{-1}, and 3.69 mm s^{-1} [103,132] respectively) is only slightly smaller than for $SnCl_2$ (4.07 mm s^{-1}).[133] In solid $[(Me_3Si)_2CH]_2Sn$ the *s* electrons are involved in the formation of a dimer with weak Sn–Sn bonds (see Section III, subsection 1), while cyclopentadienyltin(II) compounds have no Sn–Sn bonds and are characteristic examples of tin(II) compounds with a non-bonding electron pair at each tin atom. Compounds of the type $(R_2Sn)_n$ (R = Bu, Ph, etc.) are polymeric or cyclic with a strong Sn–Sn interaction and their isomer shift (0.72 to 1.55 mm s^{-1}) [131,134] correspond to the quadrivalent state of the tin atom. Their structures have been demonstrated by chemical[25,26,135] and spectroscopic[136–138] methods and also by X-ray diffraction[139].

It is known that under certain conditions (in the vapour phase at the high temperature) carbon, silicon, and germanium form atomic species, which manifest carbene-like properties[4]. As will be shown below, tin in the vapour phase also exhibits similar properties. Metallic tin exists in two allotropic modifications: the α-form (grey tin) and the β-form (white tin). β-Tin is converted into the α-form fairly readily at +18 °C and below, particularly on contact with even very small amounts of α-tin. The shift *IS* in the Mössbauer spectrum is 2.56 mm s^{-1} for β-tin [140] (*IS* = 2.06 mm s^{-1} for α-tin [141]), i.e. it adjoins the region in which the values for tin(II) compounds are located.

In contrast to the tetrahedral configuration of α-tin (Fig.8*a*), in the β-form (Fig.8*b*) each tin atom is in a somewhat distorted octahedral environment characteristic of tin(II) compounds. Since the distance between the nearest tin atoms in the β-form is somewhat greater than in the α-form, the Sn–Sn bonds in β-tin should be weaker. The octahedral environment in β-tin probably entails the involvement of the free electron pair in hybridisation and the occurrence of donor–acceptors interactions (although these may be weak) between the tin atoms. Consequently Sn(II) binding evidently occurs in β-tin and the latter can be regarded as a carbene-like layer polymer with donor–acceptor bonds between the layers. Chemical confirmation of this is provided by the formation of tin(II) dihalides from β-tin and hydrogen halides (see Section III). Tin(IV) tetrahalides are formed from α-tin under analogous conditions[32]. It is noteworthy that atomic tin, fixed in a nitrogen matrix, has *IS* = 3.23 mm s^{-1} in the Mössbauer spectrum[142] and therefore consists of the free stannylene—more precisely the bistannylene $\ddot{S}n$.

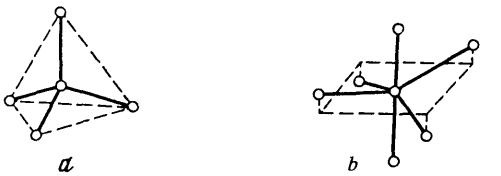


Figure 8. Configurations of α-tin (*a*) and β-tin (*b*).

III. REACTIONS OF STANNYLENES LEADING TO THE FORMATION OF QUADRIVALENT TIN COMPOUNDS

A consequence of the electronic and structural similarity of stannylenes to other carbene-like molecules of Group IVB elements with covalence unsaturation is the ability to form new chemical bonds. The presence of the stereochemically active free electron pair enables stannylenes, like carbenes, silylenes, and germylenes, to polymerise, to become inserted in single bonds, to add to carbon–carbon double bonds, etc. and also to form carbenoid complexes in which stannylenes behave as donors of an electron pair. The high reactivity of carbene-like molecules is determined mainly by the electrophilicity of the vacant *p* orbital, which decreases appreciably from carbenes to silylenes, but changes little in the series of germylenes, stannylenes, and plumbylenes[40,41].

1. Dimerisation and Polymerisation of Stannylenes

One of the main characteristic properties of carbenes, which follows from their covalence unsaturation, is the ability to form one (sp^2) or two (sp^3) new covalent bonds. The carbene-like compounds of Group IVB elements, including stannylenes, are not exceptional in this respect although the formation of a single new covalent sp^2 is energetically less favourable for these elements[40,41]. The possibility of the existence of the dimers of certain organic compounds of tin(II), namely $(R_2P)_2Sn{=}Sn(PR_2)_2$ and $(Me_2N)_2Sn{=}Sn(NMe_2)_2$, has been postulated by some workers[143,144], while the dimer $\{[(Me_3Si)_2CH]_2Sn\}_2$, which has been isolated and characterised in the crystalline state, has, as mentioned above, a weak Sn–Sn bond which readily dissociates on dissolution in benzene[125].

Presumably the absence in the vast majority of instances of "olefinic" stannylene dimers from the reaction products can be explained by their extremely high reactivity and especially their tendency to polymerise[25,26,28,30,31,33,145,146]:

$$n/2\,[R_2Sn{=}SnR_2] \rightarrow n/2\,[R_2\dot{S}n{-}\dot{S}nR_2] \rightarrow (R_2Sn)_n .$$

The reduced ability to polymerise of a few of the diorganostannylenes presented in Fig.7 can be accounted for primarily by steric factors due to the presence of bulky substituents. Steric factors are not the only cause of the decrease

of the ability of stannylenes to dimerise and polymerise. Thus the reduced capacity for polymerisation of Cp_2Sn molecules agrees with the postulated filling of the unoccupied *p* orbital of the tin atom by the π electrons of the cyclopentadienyl ring (Fig. 6*b*). The polymerisation of Cp_2Sn becomes possible in the presence of dimethylformamide (DMF).[131] Similarly the "filling" of the unoccupied *p* orbital of the tin atom by the free electron pair of a halogen, oxygen, or sulphur atom or another donor of an electron pair in inorganic and organic compounds of tin(II) lowers their ability to polymerise with formation of Sn–Sn bonds. An instance of the copolymerisation of $SnCl_2$ with methylene, generated from CH_2N_2, is known[147]:

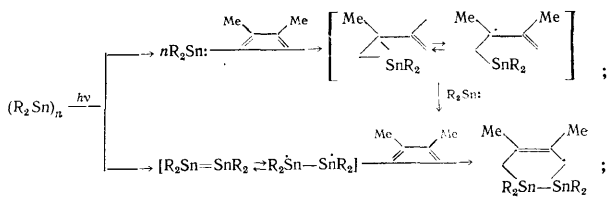
$$:SnCl_2 + :CH_2 \rightarrow [H_2C{=}SnCl_2] \rightarrow [-SnCl_2-CH_2-SnCl_2-CH_2-]_n \ .$$

2. The Reactions of Stannylenes with Unsaturated Compounds

The main and preparatively most interesting reaction of carbene is that with the multiple bonds of unsaturated compounds leading to the formation of cyclopropane or cyclopropene derivatives[1–6]. When carbene analogues, derivatives of Group IVB elements, react with olefins, the products of the further reactions of the corresponding heterocyclopropanes rather than the heterocyclopropanes themselves are isolated.

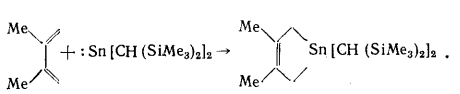
The polymer $(-CF_2-CF_2-SnPh_2-)_n$, the product of the formal addition of diphenylstannylene to the C=C bond, has been obtained in the photolysis of $(Ph_2Sn)_n$ in the presence of tetrafluoroethylene[148].

The photolysis of cyclic polystannanes $(R_2Sn)_n$ in the presence of 2,3-dimethylbutadiene yielded additional products containing two tin atoms in the ring[149]. The formation of these products can be represented as a result of the 1,4-addition of the biradical $R_2\dot{S}n-\dot{S}nR_2$ or the consecutive addition of the stannylenes $R_2Sn:$ to the diene:



R = Me, n-Bu .

The 1,4-cycloaddition of $[(Me_3Si)_2CH]_2Sn$ to 2,3-dimethylbutadiene takes place readily (in hexane at room temperature) and this is perhaps the only example in which it has been shown unambiguously that free diorganostannylenes participate in the formation of the addition product[150]:



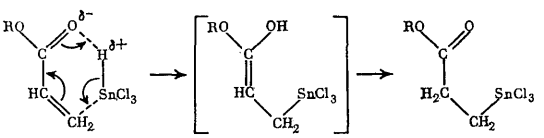
Conflicting data have been obtained in reactions of tin(II) dihalides[151,152], organic compounds of tin(II),[153] and organotin(II) compounds[146] with acetylenedicarboxylate esters: in some cases the formation of the corresponding addition products has been reported, while in others it is claimed that complexes are formed whose Mössbauer spectra contain a doublet in the region characteristic of bivalent tin, which corresponds to a structure with simple donor–acceptor interaction. Analogous complexes are probably formed in reactions of stannylenes with diethyl diazodicarboxylate[103,152] and with tetracyanoethylene[154–156].

It has been established recently that trichlorostannane etherate (see subsection 4 below), which has a structure analogous to trichlorogermane etherate[157–159], interacts with unsaturated compounds having a carbonyl group in the α-position relative to the carbon–carbon bond (acrylates, crotonates, acrylic and methacrylic acids, acryloyl chloride, phorone and others), giving rise to high yields of hydrostannylation products[159–163]:

$$RO-\overset{O}{\overset{\|}{C}}-CH{=}CH_2 + HSnCl_3\cdot 2Et_2O \rightarrow RO-\overset{O}{\overset{\|}{C}}-CH_2CH_2SnCl_3 \ .$$

The etherates of $HSnX_3$ react similarly with the methyl esters of acetylenecarboxylic acids $RC{\equiv}CCO_2CH_3$ (R = H, Me, Ph, or $COOCH_3$), forming the corresponding 1,4-addition products $Cl_3SnCR{=}CHCO_2CH_3$ and the products of their further reactions[164].

The mechanism of these reactions is not altogether clear. The ionic 1,4-addition of $HSnCl_3$ is believed to be the most probable[159,161–163]:



The analogous reaction of the etherates of $HSnX_3$ with unsaturated compounds of the type of acrylonitrile[165], in which the carbon–carbon double bond is activated by conjugation with a C≡N bond, has also been described.

3. The Insertion of Stannylenes in Single Bonds

The insertion in single bonds is a general reaction of those carbenes[1–5] and their analogues[6–24,40,41] although the latter should exhibit a greater selectivity in this process than carbenes, whose electrophilicity is higher. Instances of the insertion of stannylenes in various single bonds are known: C–X, M–X, C–M, M–M, S–S, etc.

(a) The insertion of stannylenes in a carbon–halogen bond. This reaction discovered by Pfeiffer and Heller almost 100 years ago[166] is of great practical importance, since it makes it possible to obtain in a single stage compounds which are usually difficult to synthesise:

$$R-X + SnY_2 \rightarrow RSnY_2X \ .$$

The reactivity of alkyl halides in these reactions decreases appreciably in the sequence RI > RBr > RCl, so that different catalysts are used to achieve a successful reaction with bromides and even more so, chlorides: amines[167], phosphines[168] (and their onium salts), bivalent sulphur and selenium compounds[169], salts of various Group I–III metals[170–173], and tervalent antimony compounds[174,175]. In conformity with the influence of steric factors, the yield of reaction products decreases with increase of the number of carbon atoms in the alkyl group R.[175]

This reaction has been used successfully to develop an industrial method of synthesis of $MeSnCl_3$ [172,176] and also for the development of preparative methods of synthesis of carbofunctional trihalogenostannanes which are difficult to obtain, for example[175,177–179,180–182]:

$$X(CH_2)_nX + SnX_2 \rightarrow X(CH_2)_nSnX_3 \ ;$$

X = Cl, Br; *n* = 1, 3, 4, 5, 6 ;

$$Y_nMe_{3-n}SiCH_2Cl + SnCl_2 \rightarrow Y_nMe_{3-n}SiCH_2SnCl_3 \ ;$$

Y = alkyl, aryl, cyclopropyl, F, Cl, MeO, EtO, RCOO; *n* = 0–3 ;

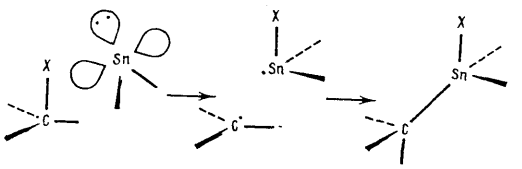
$$R_3SiCH_2Cl + SnO \rightarrow [R_3SiCH_2Sn(O)Cl]_4 + R_3SiCH_2SnCl_3 + (R_3SiCH_2)_2SnCl_2 \ .$$

Different diorganostannylenes R_2Sn, obtained by the thermal, photolytic, or some other method, are also inserted in the carbon–halogen bonds of organohalogen compounds[103,146,149,150,153,184–194] and their reactivity is so high that, for example, $[(Me_3Si)_2CH]_2Sn$ is inserted even in the C_{ar}–Cl bonds of chlorobenzene[184].

The reactivity of organic compounds of tin(II) without the C–Sn bond is somewhat lower than that of diorganostannylenes; nevertheless the products of the insertion of various tin(II) chelates[95,98,103,153,195,196] and also $[(Me_3Si)_2N]_2Sn$ [184,185] and $[(CO)_5M]_2Sn$ (M = Cr, Mo, or W) [197] in the C–I bond in alkyl iodides and in the activated C–halogen bonds of organobromine or organochlorine compounds have been obtained in high yields.

Finally, the reactions of the anions $:SnX_3^-$ and $:Sn(OH)_3^-$, having stereochemically active free electron pairs, with organic halides RX, leading to the formation of the product of the formal insertion in the C–X bond, have been described[198–201]. It has been suggested that the insertion of stannylenes in the C–X single bond in organic halides constitutes the basis of a direct synthesis of organotin halides[202–205]. It has been established that free (in the vapour phase) tin atoms readily react with alkyl halides to form the intermediate [RSnX] (R = Me, Et, or Bu; X = Br or I).[206] It has been shown for the intermediate [BuSnBr], isolated at a low temperature, that these alkylhalogenostannylenes are highly reactive with respect to various reagents and are particularly readily inserted in the C–halogen bonds in alkyl halides to form R_2SnX_2—the desired product of the direct synthesis.

The mechanism of the insertion of stannylenes in the C–halogen bond is not altogether clear[207–209]. Bearing in mind the fact that stannylenes are isostructural with singlet carbenes, silylenes, and germylenes, a common mechanism may be expected for the insertion of these species in single bonds[40,41,43], according to which the electrophilic unoccupied *p* orbital of the carbene or its analogue attacks the corresponding bond. Next the reactive molecules approach one another, which is accompanied by the migration of the halogen to the tin atom and the recombination of the resulting close radical pair.



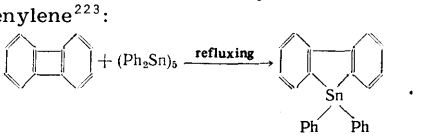
It may be that in the catalytic reactions of SnX_2 or $(R_2Sn)_n$ with R'X the electron-donating catalyst molecules promote the dissociation of the polymer chain of the polystannylene and the formation in solution of discrete stannylene molecules. In some communications the insertion of stannylenes in C–halogen bonds is regarded as a radical-chain process[185,194].

(b) The insertion of stannylene in the C–M, C–C, M–M, and M–H bonds. Like carbenes, diorganostannylenes R_2Sn are readily inserted in the C–Li, C–Na,[210] and C–Mg[211] bonds with formation of compounds of the type R_3SnM (M = Li, Na, or MgX). The appearance of branches in the polymer chain of $(R_2Sn)_n$ [25,26,28,191] and the formation of $(R_3Sn)_3SnLi$ when an attempt is made to isolate R_3SnLi from solution[212,213] can probably be explained by the insertion of diorganostannylenes in the C–Sn bond. This is confirmed by the formation of $Me_3SnSnBu_2Me$ in the reaction of Bu_2Sn with Me_4Sn.[149] One cannot rule out the possibility that the familiar reaction involving the displacement of mercury from its dialkyl and particularly diaryl derivatives by tin(II) dihalides and diorganostannylenes also proceed via the initial insertion of stannylenes in the C–Hg bond:[214–218]

$$R{-}Hg{-}R + SnY_2 \rightarrow [R{-}Hg{-}SnY_2{-}R] \xrightarrow{-Hg} R_2SnY_2 \ ;$$
Y = halogen, alkyl, or aryl.

Stannylenes are inserted just as readily in carbon–transition metal bonds. The insertion of $Sn(NR_2)_2$ [219] and SnX_2 (X = Cl or Br) [220–222] in the Fe–C bond and also of $[(Me_3Si)_2CH]_2Sn$ [150] in the Mo–C and Fe–C bonds has been described.

So far only one example of the insertion of stannylene in a carbon–carbon bond is known, namely in the strained C–C bond of biphenylene[223]:



Like the carbonoid molecules of other Group IVB elements, paricularly germylenes[20–22], stannylenes are readily inserted in metal–metal bonds. In particular, the insertion of diorganostannylenes in the Sn–Na [6,224,225] and Sn–Sn [149,188,192,226–228] bonds and also the insertion of $SnCl_2$ in the B–Hg bond[229] are known. However, this reaction is represented most widely by instances of the insertion of stannylenes in the M–M bonds of dinuclear compounds of transition metals [L is a ligand of the type CO, Cp, PR_3, $P(OR)_3$, etc.]:

$$L_xM{-}ML_x + SnY_2 \rightarrow L_xM{-}SnY_2{-}ML_x \ .$$

Examples of the insertion of stannylenes in the Fe–Fe,[230–232] Ni–Ni,[233] Co–Co,[118,233–239] Cr–Cr, Mo–Mo, W–W,[240] Mn–Mn, and Re–Re [241–243] bonds have been described. The synthesis by this method of tin-containing carbonyl complexes of iron, cobalt, rhenium, and rhodium fixed on a carrier has been reported[244]. Mössbauer spectroscopic data are available for certain products of insertion in M–M bonds, showing that the tin atom in such products is in the quadrivalent state of oxidation (*IS* = 1.27–1.99 mm s^{-1}).[231–237,245–247] It is believed [248] that the formation of $Sn[Co(CO)_4]_4$ from metallic tin and $Co_2(CO)_8$ also involves the insertion in the Co–Co bond initially of the Sn atom and then of the intermediate stannylene $[Co(CO)_4]_2Sn$:.

A few examples indicating the ability of stannylenes to be inserted in the Sn–H [6,149] and Mo–H [124,150,249] bonds are also known.

(c) Insertion of stannylenes in M–X bonds. There are very few examples of the insertion of stannylenes in a non-transition metal–halogen bond. In particular, reactions involving the insertion of diorganostannylenes in the Sn–Cl bond[226,228] and also of metallic tin[217], dihalogenostannylenes[250], and di(permethylcyclopentadienyl)tin(II) [251] in the Hg–X bond have been described. The reaction involving the insertion of stannylenes in a transition metal–halogen bond is more general. Examples of the insertion of dihalogenostannylenes in the Fe–Hal,[130,150,231,232,246,252–256] Cr–Hal, Mo–Hal, W–Hal,[40,257] Co–Hal,[258,259] Rh–Cl,[124,140] Pd–Cl,[260–262] Pt–Cl,[255,263–265] Ir–Cl,[140,255,266] Mn–Hal,[266] Ni–Cl,[267] and Ru–Hal [255,268,269] bonds and also of $[(Me_3Si)_2CH]_2Sn$ in the Pt–Cl,[130] Fe–Cl,[130,150] and Rh–Cl [124] bonds are now known.

The reactions are usually carried out in polar or non-polar solvents at room temperature or with slight heating; sometimes the process is initiated photolytically. The isomer shifts *IS* in the Mössbauer spectra of the products of the insertion of stannylenes in the M–X bonds are 1.54–2.02 mm s^{-1},[130,140,150,231,246,253,256,258,259,270] which corresponds to the quadrivalent oxidation state of the tin atoms. However,

in certain similar instances the isomeric shift for the formal products of the insertion of stannylenes in a transition metal–halogen bond are in the intermediate range or even in the range characteristic of bivalent tin. Such products, containing discrete SnX_3^- anions as electron-donating ligands, are formed via an ionic mechanism and are discussed below (in Section IV).

(d) The insertion of stannylenes in the S–S bonds of disulphides, the O–O bonds of peroxides, and certain other bonds. Different types of stannylenes are extremely readily inserted in the S–S bonds of diorganodisulphides:

$$Y_2Sn + RS{-}SR \rightarrow RS{-}SnY_2{-}SR ,$$

where Y = Me, Bu, Ph,[149,253] Cp, OMe, SPh, chelate[103,153], oxinate (Ox),[271] or halogen[152,272,273] and R = alkyl, phenyl, Br, Py, or (iso-Pro)$_2$P(S).

The insertion of tin(II) dihalides[152], diarylstannylenes[253], dialkylstannylenes[149,274,275], and tin(II) oxinates[271] in the O–O bonds of organic peroxides ROOR [R = alkyl or C(O)Ph] takes place just as readily, sometimes exothermically.

Examples of the insertion of dihalogenostannylenes in the P–O–P bond in diethylphosphoric and diphenylphosphinic acid anhydrides[276] and also in the N–Cl bond of *N,N*-dichloro- or *N*-chloro-*N*-methyldialkylphosphoramides[277] and the *N,N*-dichloramides of arenesulphonic acids[278] are known.

4. Reactions of Stannylenes with Oxygen, Sulphur, Phosphorus, Halogens, Hydrogen Halides, and Other Similar Compounds

One of the first reactions of diorganostannylenes discovered is their oxidation by atmospheric oxygen[25,26,31,33,150,225]:

$$R_2Sn + O_2 \rightarrow R_2SnO .$$

Organohalogenostannylenes RSnX [206] and organic compounds of tin(II) [81,97,279] are also readily oxidised in air. The capacities of inorganic tin(II) compounds for oxidation are different: tin(II) monoxide is oxidised in air only on heating[32]; tin(II) sulphate $SnSO_4$ is very resistant to oxidation[34]; solid tin(II) halides are slowly oxidised in air but in solutions the reaction is greatly accelerated[152]. In a study of the products of the reaction of atomic tin with oxygen in the vapour phase by the matrix isolation method, it was shown that the initial step in the formation of the main products (SnO_2, SnO, Sn_2O_2, Sn_3O_3, etc.) is the insertion of atomic tin in the O–O bond of the O_2 molecule[280].

Stannylenes react analogously with sulphur, forming the corresponding sulphides $(R_2SnS)_x$.[253,281–283] Diorganostannylenes react just as readily with white phosphorus[284,285] and tellurium[286] forming the corresponding insertion products $(Me_2Sn)_nE_m$ (E = P or Te; n = 3, 5, or 6; m = 2, 3, or 4).

When stannylenes react with halogens, a wide variety of halogenostannanes are formed very readily[6,98,99,103,150,153,186,206,251,271,281,287,288] (Y = halogen, alkyl, aryl, chelate, etc.):

$$Y_2Sn + X_2 \rightarrow Y_2SnX_2 .$$

Free diorganostannylenes react readily with hydrogen halides:

$$R_2Sn + HX \rightarrow R_2Sn(H)X .$$

where R = $(Me_3Si)_2CH$ [150] or t-Bu [289] and X = F or Cl.

On the other hand, protolytically unstable stannylenes undergo various reactions under the influence of hydrogen halides. Thus the cyclopentadienyl groups in Cp_2Sn are readily split off under the influence of HX to form CpSnX or SnX_2,[103,132] while the P–Sn bond in $(t\text{-Bu})_2P{-}Sn{-}Cl$ dissociates on treatment with HCl and $[(t\text{-Bu})_2\overset{+}{P}H_2]SnCl_3$ is formed[290].

In contrast to the analogous carbon, silicon, and germanium compounds, trihalogenostannanes $HSnX_3$, formed when SnX_2 reacts with dry hydrogen halides, are unstable[157]. However, in ethereal solution the $HSnX_3$ are stabilised as a result of the formation of relatively stable etherates $[Et_2O \rightarrow H...OEt_2]^+ . SnX_3^-$,[158] for which the more complex structure $H_nSnX_{2+n} . mEt_2O$ (m/n = 1.1–1.5) has been postulated[159]. The aminates of trihalogenostannanes $[R_3NH]^+SnX_3^-$ proved to be more stable[291,292].

Evidently the formation of SnX_3 from metallic β-tin and HX can also be regarded as a carbenoid reaction, although the formation of the extremely unstable intermediates [HSnX] and $[H_2SnX_2]$ still awaits confirmation:

$$\beta\text{-}Sn + HX \rightarrow [HSnX] \xrightarrow{HX} [H_2SnX_2] \xrightarrow{-H_2} SnX_2 .$$

IV. STANNYLENES AS ELECTRON-DONATING LIGANDS IN COMPLEXES

One of the characteristic properties of carbenes and their analogues is their ability to form complexes with various compounds of non-transition and transition metals[9,36,42,293–299]. By virtue of the presence of the σ orbital, which is a carrier of a nucleophilic free electron pair, stannylenes can also play the role of electron-donating ligands in complexes where the tin atom is in the lowest oxidation state. In connection with the increased interest in complexes of carbenes and their analogues, there has been a recent appreciable increase of the number of publications on the corresponding complexes of tin(II) compounds[18,33,34,36–38,42,44,300–308].

Treatment of tin(II) dihalides with an excess of organolithium, organosodium, organomagnesium, or organozinc compounds is known to result in the formation of the corresponding compounds of the type R_3SnM:[33]

$$Y_2Sn: + 2R{-}M \rightarrow R_2Sn: \xrightarrow{R-M} R_3SnM ;$$
$$M = Li, Na, MgX, ZnX .$$

As early as 1952, it was suggested that Rh_3SnLi is 20% dissociated in solution[309]:

$$Ph_3SnLi \rightleftarrows Ph_2Sn: + PhLi .$$

Later equilibrium between R_3SnLi, R_2Sn:, and RLi,[310,311] and also in the analogous reactions involving magnesium [312] and zinc [313,314] compounds, possibly with participation of stannylene–salt complexes of the type $R_2Sn.MR$, was frequently confirmed chemically, although Mössbauer spectroscopic data have shown that the values of *IS* in such cases correspond, with rare exceptions[315], to the quadrivalent state of the tin atom[211,313].

The possibility of the existence of such carbene-salt complexes has been postulated in the mechanism of Simmons–Smith reactions[315–318] and also in the explanation of numerous data concerning the appreciable influence of alkali metal salts present in the reaction medium on the properties of independently generated carbenes (the salt effect).[4,42,299,319,320]

In their reactions with stronger electron pair acceptors such as the trihalides of Group III elements, stannylenes form the stable complexes $Y_2Sn.MX_3$ [M = B or Al; Y = Cp, MeCp, $(Me_3Si)_2CH$, halogen, or chelate].[98,150,204,321–323] In a number of instances such complexes are formed as a result of the displacement of weaker ligands from their complexes with MX_3:[98,204,322,323]

$$Y_2Sn: + BX_3 \cdot OEt_2 \rightarrow Y_2Sn \cdot BX_3 + Et_2O .$$

The Mössbauer parameters of these complexes (*IS* = 3.71 to 3.83 mm s^{-1}) [98,204,323] correspond to the bivalent state of the tin contained in them. The possibility of the formation

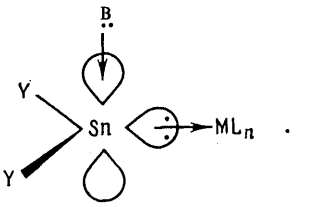
of the ionic complexes $[CpSn]^+MX_4^-$ or the **bridged complexes** $CpSn-X-MX_3$, in which there is no Sn–M σ-bond, has been discussed for organohalogenostannylenes of the type CpSnX in reactions with MX_3 (M = B or Al).[323–327]

As in carbene chemistry[42,293–299], complexes of stannylenes with various transition metal compounds are the most stable and have been investigated more than others. One of the main reactions involved in the synthesis of complexes of this kind is the displacement (photolytic or thermal) by stannylenes of other ligands, for example, carbon monoxide molecules, from transition metal carbonyls:

$$Y_2Sn: + LM(CO)_x \rightarrow CO + Y_2Sn\cdot M(CO)_{x-1}\cdot L \ ;$$
$$M = Fe, Cr, Mo, W, Mn;\ L = CO, Cp, MeCp, PhCN \ .$$

This reaction is common to different types of stannylenes—diorganostannylenes[38,123,124,150,328,329], organic compounds of tin(II) such as tin(II) chelates[330–332], $Sn(NMe_2)_2$,[144] $Sn[N(SiMe_3)_2]_2$,[37] $Me_2Si\begin{matrix}NR\\ \diagup\ \diagdown\\ NR\end{matrix}Sn$,[283] and 1,2,3-$SnC_2B_4H_4Me_2$,[122] as well as inorganic tin(II) compounds, in particular dihalogenostannylenes[331,333–336]. The more electrophilic ligand $[(Me_3Si)_2CH]_2Sn$ displaces norbornadiene ligands[124,150], Ph_3P,[124] and Et_3P [124,150] from transition metal complexes.

In some cases stannylene complexes are stabilised by the additional coordination interaction of the tin atom with the electron pair of a base B:[144,334,335]



Similar complexes are known also for silylenes and germylenes, where stabilisation as a result of coordination to a base B̈ evidently constitutes an essential condition for their stability[42,337–342]. An instance of a carbene complex with additional stabilisation by a base is also known, namely the complex $(CO)_5W.CPh_2.PMe_3$.[343]

Complexes of stannylenes stabilised by a base can also be obtained by the cleavage of complexes whose structure is based on the four-membered ring M_2Sn_2.[144,328,344–348] These complexes are readily cleaved by bases B̈ and the ability of the latter to split the Sn–M bond in the four-membered ring M_2Sn_2 decreases in the sequence[346,348] pyridine > dimethyl sulphoxide (DMSO) > acetone > tetrahydrofuran (THF) > diethyl ether. Weak bases in such complexes can be displaced by stronger bases:[349]

$$(CO)_5W\cdot SnCl_2\cdot THF + (Me_3C)_3P \rightarrow (CO)_5W\cdot SnCl_2\cdot P(CMe_3)_3 + THF \ .$$

The additional coordination interaction with the base B makes the stannylenes more nucleophilic and stabilises the stannylene complex to such an extent that various reactions involving the substitution of chlorine atoms in dichlorostannylene complexes become possible[197,350–352]:

$$(CO)_5M\cdot SnCl_2\cdot THF + Me_3Si{-}X \rightarrow (CO)_5M\cdot Sn\begin{matrix}X\\ \diagup\\ \diagdown\\ Cl\end{matrix} + Me_3SiCl + THF;$$
$$M = Cr, Mo, W;\ X = \ t\text{-}Bu_2E(E = P, As), \quad t\text{-}BuS \ .$$
$$(CO)_5M\cdot SnCl_2\cdot THF \xrightarrow{ROH} (CO)_5M\cdot Sn(OR)_2 \ ;$$
$$M = Cr, Mo, W;\ R = H, Et \ .$$
$$(CO)_5M\cdot SnCl_2\cdot THF + Me_3SnOH \rightarrow (CO)_5M\cdot Sn(OH)_2 + Me_3SnCl \ ;$$
$$(CO)_5M\cdot SnCl_2\cdot THF + NaM'(CO)_5 \rightarrow (CO)_5M\cdot Sn[M'(CO)_5]_2 + NaCl + THF \ ;$$
$$M, M' = Cr, Mo, W \ .$$

The stannylene complex evidently can be stabilised also by the coordination interaction of the stannylene with the free electron pair of a halogen atom which functions as the base B̈. Tin(II) dihalides and also certain other stannylenes with electronegative substituents X (electron pair donors) are known[32,34,129] to be capable of forming intermolecular coordinate bonds Sn–X–Sn (Figs. 3 and 4) and to be able to react with electron-donating solvents (Solv.) to form discrete complexes $SnX_2.Solv.$[32,34] The electron pair donor X can be abstracted also from other metal halides, which entails the formation of discrete stable complex anions X_3Sn^- (Fig. 9*a*). The ions X_3Sn^- have a trigonal-pyramidal structure in which all three atoms X and the free electron pair are involved in the sp^3 hybridisation of the tin(II) orbitals[322,323,353].

The high nucleophilicity of the stannylene stabilised by coordination to an anion X^- and the extremely high stereochemical activity of its free electron pair make it possible to obtain stable complexes of the type $M^{n+}(SnX_3)_n$ (Fig. 9*b*) from SnX_2 and alkaline earth metal salts $M^{n+}X_n$ (n = 1 or 2; X = halogen[354–361], acetate[94,353,362], or other anions[32,34,363,364]) and also quaternary oniom salts[133,361,363,365–368]. A characteristic feature of these complexes is the largely ionic character of the Sn–M bond and the high density of the *s* electrons at the tin nuclei and hence also high Mössbauer *IS* values (2.83–4.03 mm s^{-1}).[94,133,355,357–359,365,367–370]

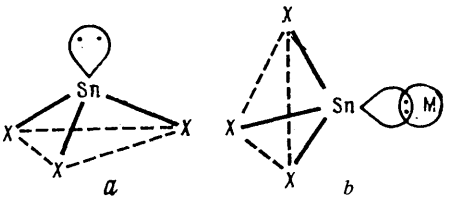


Figure 9. The structures of the anion X_3Sn^- (*a*) and the complex $M^+SnX_3^-$ (*b*).

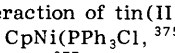
Taking into account the stereochemical activity of the free electron pair in X_3Sn^-, an attempt was made to obtain its complex with BF_3,[371] but it was shown later that in this case a different process takes place[372]:

$$SnCl_3^- + BF_3 \rightarrow (BF_3Cl)^- + SnCl_2 \ .$$

As electron pair donors, the anions SnX_3^- form stable complexes with various transition metal compounds. One of the commonest and simplest methods of synthesis of complexes of the type $X_3Sn.M$ is the reaction of dihalogenostannylenes with transition metal halides, particularly those which contain electron-donating ligands L:

$$SnX_2 + MX\cdot L \rightarrow X_3Sn\cdot M\cdot L \ .$$

Such reactions, which involve the insertion of SnX_2 in a covalent bond M–X, were described above (Section III). When the M–X bond in metal halides is ionic, the interaction of the latter with SnX_2 is ionic, as happens for alkali and alkaline earth metal salts, and also in the reaction of $SnCl_2$ with $(Ph_3P)_3MCl$ (M = Cu, Ag, or Au) in organic solvents[255] or in water[373]. The interaction of tin(II) dihalides with MF_2 (M = Fe, Co, or Ni),[374] $CpNi(PPh_3Cl$,[375,376] $[RuI(CO)_3.(PPh_3)_2]I$,[268] $CpFe(dppe)X$,[377] $(R_3P)_2Pt(CL)H$,[263,378,379,380] and other halogeno-derivatives of transition metals[250,381,382] takes place similarly:



As in the case of stannylenes, one of the methods of synthesis of complexes of type $X_3Sn.M$ involves the displacement of other ligands by X_3Sn^- anions:

$$ML_n + SnX_3^- \rightarrow [ML_{n-1} \cdot SnX_3]^- + L\ ;$$
$$M = Cr, Mo, W, Fe, Co, Ni, Mn, V\ .$$

CO molecules,[257,383–389] π-arene ligands (mesitylene, cycloheptatriene, and benzene),[385,386] acetonitrile[386] and PF_3 [390, 391] molecules, and also halide anions[255,392–399] are displaced in this way. Solutions of mixtures of SnX_2 with R_4EX (E = N, P, or As) or with HX in water or organic solvents[255, 393–399], for example, in ether where the corresponding etherates are formed from SnX_2 and HX,[158,159] can serve in this instance as sources of the ligands X_3Sn^-. The etherates of $HSnX_3$, which are convenient sources of the X_3Sn^- anions, can be obtained successfully by reducing SnX_4 with lithium tetrahydrolaluminate[400]. Other methods of synthesis of complexes of the type $X_3Sn.M$ from quadrivalent tin compounds are also known[268,401–404].

The few available literature data indicate the similarity of the structures of a series of stannylene and carbene complexes[42]. Thus according to structural studies[38], the valence angle of stannylene in the complex $[(Me_3Si)_2CH]_2Sn.Cr(CO)_5$, which is 98°, differs little from the valence angles of free stannylenes, i.e. the tin(II) atom retains the sp^2 configuration. Mössbauer spectroscopic data confirm this conclusion; the isomer shifts *IS* of the free and complexed diorganostannylenes are similar and amount to 2.16 and 2.21 mm s^{-1} respectively[130]. The coplanarity of the stannylene fragment C–Sn–C with the transition metal atom in such complexes ensures the possibility of an additional π-interaction between the occupied 3*d* orbitals of the transition metal and the unoccupied *p* and *d* orbitals of the tin atom, as a result of which the Sn–M bond length is always smaller than the sum of the covalent radii of the atoms of these elements, as in the carbene complexes[42].

Unfortunately there are so far no structural data on complexes of inorganic and organic compounds of tin(II) of the type $SnX_2.ML_n$ (X = halogen or chelate; M = transition metal). Nevertheless it has been suggested on the basis of spectroscopic studies that they have analogous structures and that the anomalous *IS* values in the Mössbauer spectra of these complexes can be accounted for by the synergistic Sn → M σ-interaction and the M → Sn $(d-p)\pi$- or $(d-d)\pi$-interactions along the Sn–M axis (Fig.10).[328,330,405]

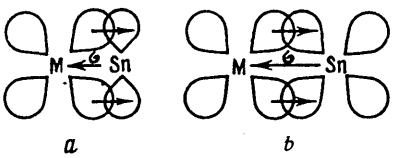


Figure 10. The $(d-p)\pi$-interaction (*a*) and the $(d-d)\pi$-interaction (*b*) of the *p* and *d* orbitals of the tin atom and a transition metal M.

This is confirmed by the absence of appreciable differences between the *IS* values for stannylenes (even dihalogenostannylenes) and their complexes with BX_3 or AlX_3,[98,204,323] which do not have occupied *d* orbitals. However, one cannot rule out the possibility that the appreciable decrease of *IS* in certain complexes of dihalogenostannylenes with transition metals can be accounted for by their ylide structure.

Analogous effects are probably observed in stannylene complexes stabilised by a base B. In the complex $Py(t\text{-}Bu)_2Sn.Cr(CO)_5$, the tin atom projects by only 0.44 Å from the plane passing through the carbon atoms and the chromium

The results of vibrational and Mössbauer spectroscopic and structual studies of certain complexes of the type $Cl_3Sn.M$.

Complex*	*IS*, mm s^{-1}	References	$\alpha(Cl\text{-}Sn\text{-}Cl)^0_{av,s}$	$l(Sn\text{-}Cl)_{av}$, A	l-(Sn–M), Å	References	$\nu(Sn\text{-}Cl)$, cm^{-1}	References
$(SnCl_2)_x$ (crystalline)	4.07	[133]	79	2.74	—	[34, 69]	195	[77]
$H^+[SnCl_3]^-$ (etherate)	3.46—3.54	[140, 159]	—	—	—	—	297, 256	[419]
$Cs^+[SnCl_3]^-$	3.40	[355, 358]	89.8	2.52	4.569	[410]	304, 258	[255]
$[(en)_3Co][SnCl_3]Cl_2$	—	—	92.7	2.488	5.0	[399]	—	—
$SnCl_2$ (monomer in Ar matrix)	3.17	[53]	95±2	2.42	—	[50, 53]	354, 334	[51]
$[(dppe)_2CoCl(SnCl_3)]$	3.10	[382]	94.5	2.444	7.6	[382, 411]	—	—
$[(Me_2PhP)_2AuSnCl_3]$	2.92	[408]	94.9	2.450	2.881	[412]	—	—
$[(chtr)Mo(CO)_2SnCl_3]$	—	—	95.0	2.411	2.72	[413]	—	—
$[(Me_2PhP)_2(nbd)IrSnCl_3]$	2.08—2.16**	[408]	95.5	2.406	2.587	[414]	—	—
$[(cod)_2IrSnCl_3]$	2.06	[408]	96	2.395	2.64	[415]	317, 300, 290	[420]
$[CpFe(CO)_2SnCl_3]$	1.77	[267]	98.3	2.360	2.466	[416]	346, 322	[247]
$[(CO)_5MnSnCl_3]$	1.73	[266]	100.4	2.344	2.59	[417]	345	[421]
$SnCl_4$	0.85	[409]	109.5	2.31	—	[418]	407, 368	[422]

*Notation: en = ethylenediamine, dppe = diphenylphosphinoethane, chtr = cycloheptatrienyl, cod = cyclo-octadienyl, and nbd = norbornadiene.

**The values of *IS* are quoted for isostructural complexes with the phosphine ligand Ph_3P or $(MeO)_2PhP$.

atom linked to tin. The stabilisation of the complex by the base is accompanied by some alteration of the configuration of the tin(II) atom ($sp^2 \rightarrow sp^3$) and a corresponding increase of the C–Sn–C valence angle[406].

In the complexes $X_3Sn.M$, where the role of the base B is assumed by the anion X^-, analogous structural changes should be observed in the dihalogenostannylene fragment. The available data on the Mössbauer spectra, structures, and vibrational spectra of a series of complexes of the type $Cl_3Sn.M$ are compiled in the Table. The large differences between the Sn–M bond lengths in complexes of this type and also the available conductimetric data for solutions of some of them in CH_2Cl_2 or nitromethane[375,376,407] indicate different types of the Sn–M bond, which changes from ionic in complexes of the type $Cs^+[SnCl_3]^-$ to a σ-bond in many complexes with transition metals. In ionic complexes with discrete $SnCl_3^-$ anions, in which the tin(II) atom has a pyramidal sp^3 configuration (Fig. 9*a*), the high value of *IS* is determined by the high density of the *s* electrons at the tin atom, which are not involved in the formation of the Sn–M bond.

A satisfactory correlation between the *IS* values in the Mössbauer spectra, the stretching vibration frequency ν of the Sn–Cl bond in the infrared and Raman spectra, and the structural parameters is observed for the stannylene complexes $Cl_3Sn.M$, in which there is an Sn–M σ-bond. In conformity with the increase of *IS*, the Cl–Sn–Cl valence angle decreases and the Sn–Cl bond length increases in these complexes within the range of limiting values from 109.5° and 2.31 Å for the tetrahedral sp^3 configuration of $SnCl_4$ [418] to 95° ± 2° and 2.42 Å for the sp^2 configuration of free $SnCl_2$ in the vapour phase or in the argon matrix[50,53]. Similarly the shift of the absorption bands of the Sn–Cl bond from the region of lower frequencies characteristic of free $[SnCl_3]^-$ ions in solution[419] to higher frequencies indicates the approach of the SnX_3 configuration in the complexes to the tetrahedral configuration, which is possible with participation of the $5s^2$ orbitals of tin(II) in the formation of a σ-bond with the metal.

The majority of investigators believe that the tin atom in these complexes is in a bivalent state of oxidation; the observed low *IS* values can be explained (as in the complexes $X_2Sn.M$ unstabilised by a base) by the occurrence, apart from the relatively weak Sn → M σ-interaction, of a strong M → Sn $(d–d)\pi$-interaction (Fig. 10*b*). The overlapping of the *d* orbitals of the tin atom and the *d* orbitals of the transition metal leads to additional π-bonding and hence to a decrease of the Sn–M bond length (see Table).

Generalising the results of numerous investigations, one can probably conclude that the *s* character of the sp^x-hybridised orbitals of the tin atom in stannylenes and their complexes, both stabilised and unstabilised by a base, decreases in the sequence

$$sp^2\text{-Sn(II)} > sp^3\text{-Sn(II)} > sp^3d\text{-Sn(II)} > sp^3\text{-Sn(IV)} .$$

The Mössbauer isomer shift *IS* decreases and other spectroscopic and structural characteristics vary in the same sequence.

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During the preparation of the manuscript for the press, numerous studies on the topic of this review were published. In the first place mention should be made of publications describing new sources of diorganostannylenes. This dimethylstannylene was obtained from $(Me_3Sn)_2S$ at 150° to 160 °C in the presence of copper[423].

Certain new monomeric organic compounds of tin(II) and organotin(II) compounds have been obtained and investigated. Free phenylstannylenes, stabilised by *ortho*- or 2,6-substitution (by CF_3, OMe, and t-Bu groups), have been obtained from $SnCl_2$ and the corresponding phenyl-lithium derivative[424]. A cyclic organostannylene has been obtained by the reaction of 1,1-dichloro-3,3,5,5-tetramethyl-1-stanna-3,5-disila-4-oxacyclohexane with magnesium or lithium in THF.[425,426] A series of organic compounds of tin(II), such as $Sn(OAr)_2$ (Ar = 2,6-t-Bu_2-4-MeC_6H_2 or 2,4,6-t-$Bu_2C_6H_2$), [427] $Sn[NCMe_2(CH_2)_3CMe_2]_2$,[428] $(CO)_5WP[P(O)(OEt)_2]_2SnCl$,[429] and $Sn[Al(OPr\text{-iso})_4]_2$ [430] have also been synthesised. Stannylenes forming part of the composition of various polycyclic systems have been obtained from cyclic diazastannylene[431–433].

The study of the synthetic possibilities of stannylenes has been continued. The insertion of $SnCl_2$ in the C–Br bond of allyl bromide under various conditions[434] and also the insertion of a cyclic organostannylene in the C–Cl bonds of alkyl and aryl chlorides and allyl chloride[425] have been described. The insertion of dihalogenostannylenes in the C–I bond of perfluoroalkyl iodides takes place extremely readily (in DMF at 20 °C).[435]

New examples of the insertion of stannylenes in the Hg–X and Hg–C bonds[436], of $SnCl_2$ in the Tl–Cl bonds of compounds of the type R_2TlCl (R = C_6F_5, C_6F_4H, or $C_6F_3H_2$),[437] of $(MeCp)_2Sn$: in the W–H bond of the complex $HW(CO)_3Cp$–Me,[438] of Me_2Sn: in the S–S bond of the complex [μ-dithio)-bis(tricarbonyl iron),[439] of $SnCl_2$ in the N–Cl bonds of the compounds *p*-$RC_6H_4SO_2NCl_2$ (R = Cl, H, or Me),[440] and of $[(Me_3Si)_2N]_2Sn$: in the N–Br bond of the compound $(Me_3Si)_2$.NBr [441] have been discovered.

As before, the reaction in which the dihalogenostannylenes are inserted in M–X bonds involving transition metals has continued to attract most attention. The interaction of SnX_2 with cobalt and iron complexes containing two M–X bonds has been studied[442]. It was established that the ligand SnX_2, formed when SnX_3 is inserted in the Co–X or Fe–X bond, deactivates the second M–X bond. The employment of modern research techniques makes it possible to solve in such cases the problem of the nature of the product of the reaction of the M–X bond with SnX_2. In some cases insertion products containing a quadrivalent tin atom are formed[443], while in the others the products are complexes with electron-donating ligands $:SnX_3^-$, in which the tin atom is bivalent[444–446]. The reaction in which $[Re(CO)_5]_2Sn$: [447] and a cyclic organostannylene[426] are inserted in the M–M bonds of bis-(metal pentacarbonyl) derivatives of transition metals proved to be extremely effective in the synthesis of mixed polynuclear metal carbonyls.

Numerous studies, in which stannylenes behaved as electron-donating ligands in complexes, have been published. Thus the complexes $Sn(NR_2)_2.nBF_3$ (*n* = 1, 2, or 3; R = Me or Et) have been described[448]. Stable complexes of SnX_2 with BF_3 have been obtained by stabilising them with electron-donating molecules of the type Me_3N, DMSO, tetramethylethylenediamine, etc. The high Mössbauer *IS* values confirm the bivalent state of the tin atoms in the complexes $F_3B \leftarrow :SnX_2 \leftarrow :Solv$ obtained[449].

A number of investigators have continued to study transition metal complexes of stannylenes both unstabilised[450] and stabilised[451,452] by a base B.

New examples of the substitution of chlorine atoms in dichlorostannylene complexes of transition metals $M(CO)_5$.$SnCl_2$.B, stabilised by a base B, have been reported[453,454].

Finally, it has been reported that organic compounds of tin(II) with benzil give rise to products of the formal 1,4-cycloaddition involving both carbonyl groups of benzil[455]. It has been shown that compounds of this type, 2,2-dialkyl-1,3,2-dioxastannols, are capable of forming dialkylstannylenes on thermolysis[456]. Analogous formal 1,4-cycloaddition reactions involving the carbonyl groups of *o*-benzoquinone are known for cyclohexadiene carbenes[457].

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