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STANNANEDITHIOCARBOXYLATES: NOVEL α-FUNCTIONAL ORGANOTIN LIGANDS *

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Summary

In spite of the high nucleophilicity of organotin anions, their addition to heteroallenes to form a stable Sn–C bond is restricted to carbon disulfide. The resulting stannanedithiocarboxylates $R_3SnCS_2^-$ have been alkylated to give the dithioesters R_3SnCS_2R' as the first α-thiocarbonyltin compounds. The synthesis of transition metal complexes such as $R_3SnCS_2M(CO)_4$ (M = Mn, Re) requires the isolation of the dioxane adducts $R_3SnCS_2M' \cdot nC_4H_8O_2$ (M′ = Li, Na, K). The thermal substitution of the chelate complexes by σ-donor ligands of Main Group V elements proceeds stereospecifically with the formation of *fac* tricarbonylmetal compounds. Photolytic activation leads to disubstitution in most cases; only with tricyclohexylphosphine is the *mer*-isomer obtained as the kinetic product. The *trans*-disubstituted dicarbonyl complexes tend to revert to the monosubstituted species, and the recombination has been followed by IR and UV spectroscopy. The controlled synthesis of monocoordinate stannanedithiocarboxylato complexes has been achieved by substitution of the CO group with bidentate donor ligands. All the stannanedithiocarboxylates show an unexpected diamagnetic shift of the tin-119 NMR signals, which span the range from δ −120 to −260 ppm (relative to Me_4Sn) and are among the highest shieldings observed for tetraorganotin compounds.

Introduction

In the late sixties, Dessy and King [1] determined the nucleophilicity of a large number of carbonylmetallate anions and related species, which found preparative application in the following years [2–5]. As strong nucleophiles, triorganotin anions should react easily with heteroallenes to form novel ligand systems which could be suitable for use in the synthesis of organometallic complexes in which a Main Group element is connected to a transition metal through a functional group. In fact, the

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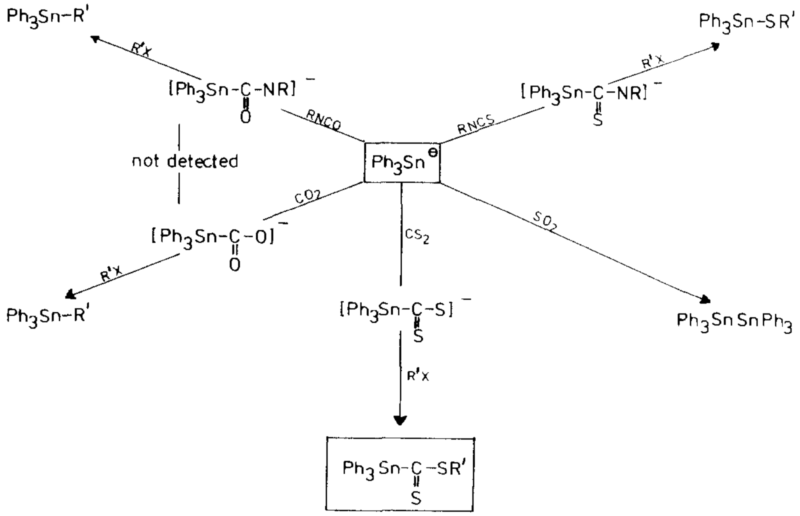
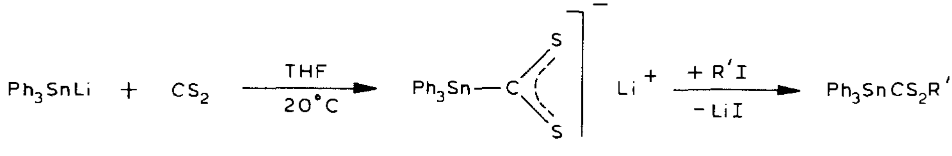


Fig. 1. Nucleophilic addition of the triphenyltin anion to heteroallenes.

range of known nucleophilic additions of IVB organoelement anions is rather narrow; only a few α-carbonyl [6,7] and α-carbamoyl compounds [8–10] have been described (cf. also ref. 10a). Organo-silicon and -germanium anions are known to react with carbon dioxide [11–15], but the analogous organo-tin and -lead compounds do not undergo addition to CO_2 or isocyanates [16–18], and subsequent alkylation yields mixed tetraorganotins (Fig. 1). Formation of distannanes by the reaction of organotin anions with CS_2 and SO_2 has been reported [2,16,18]. The addition of isothiocyanates seems to proceed through an unstable thiocarbamoyl intermediate which decomposes to a thiolate upon alkylation [19]. Unlike the known α-carbamoylstannanes [8,9], a metathetical approach employing thiocarbamoyl chloride failed.

1. Nucleophilic addition of triorganotin anions to carbon disulfide and synthesis of stannanedithioesters

Although there are reports to the contrary [2,18], triphenylstannyllithium has been found to react with carbon disulfide with formation of a Sn–C bond. The resulting stannanedithiocarboxylate was stabilized by alkylation, giving the new stannanedithioesters as the first α-thiocarbonyltin compounds [20,21]:



$(R' = CH_3,\ C_2H_5,\ i\text{-}C_3H_7,\ C_3H_5)$

The analogous tri-*o*-tolyl- and tri-*p*-tolyl-stannane dithiocarboxylates were prepared in the same way. With aryl halides like iodobenzene, *p*-bromotoluene or *p*-iodoanisole, no dithioesters were obtained, but only small amounts of bis(triphenyltin) sulfide. Attempts to achieve the nucleophilic addition of trialkyltin anions failed in most cases; only with tricyclohexylstannyllithium was the methyl ester isolated in low yield [22].

Recently, an Australian group showed that the hitherto unknown α-thiocarbamoylstannanes (or stannyl thioformamides) are easily obtained by the aminolysis of dithioesters [23], e.g.,

$$Ph_3SnCS_2R' + Me_2NH \rightarrow Ph_3SnC(S)NHMe + R'SMe$$

The resulting thioamides are stable, crystalline solids, and present another example of kinetic reaction control often encountered in organotin chemistry.

The methyl dithioester Ph_3SnCS_2Me crystallizes from petrol ether as purple, air-stable needles (m.p. 128–129°C). A surprising result of the X-ray structural analysis was that the compound adopts exactly the tetragonal crystal system of tetraphenyltin (space group $P\bar{4}2_1c$, $Z = 2$) [24]. The molecular arrangement is best described as an "orderly disordered" tetraphenyltin structure in which each fourth phenyl ring is statistically replaced by the planar methyl dithioester unit (Fig. 2). The C(1′)–S(1) and C(1′)–S(2) distances are nearly equal and considerably shorter than C(7)–S(2). The Sn–C(1′) distance of 2.14 Å is consistent with the standard value for a Sn–C single bond.

The stannanedithioesters behave as monodentate ligands and form neutral complexes by reaction with metal carbonyls [21,22]. Because of their facile dissociation in solution, analytically pure samples were isolated only of the complexes from

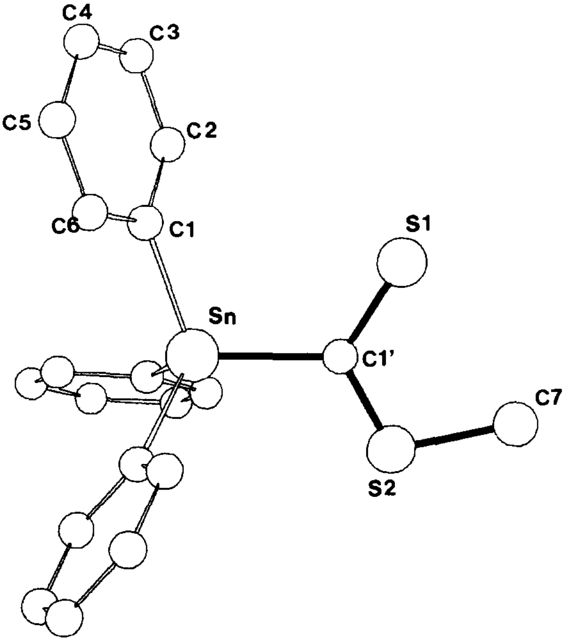
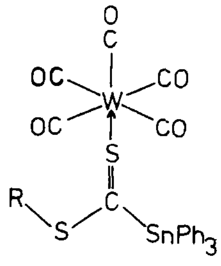
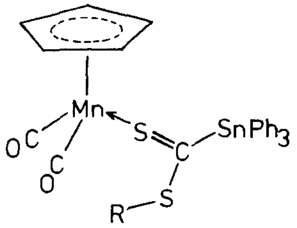
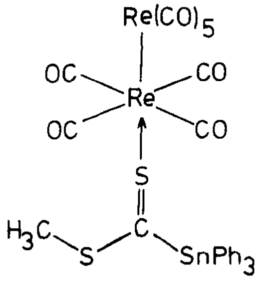


Fig. 2. Molecular structure of the methyl ester Ph_3SnCS_2Me. Important bond distances (Å) and angles (°) are: Sn–C(1′) 2.14(9), S(1)–C(1′) 1.66(2), S(2)–C(1′) 1.64(2), S(2)–C(7) 1.79(5), Sn–C(1′)–S(1) 120.8(8), Sn–C(1′)–S(2) 118.6(6), S(1)–C(1′)–S(2) 121(1), C(1′)–S(2)–C(7) 105(2) (From ref. 21).

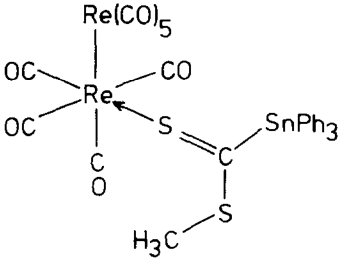
$W(CO)_6$, $CpMn(CO)_3$ and $Re_2(CO)_{10}$. The free ligands are characterized by two medium IR bands at 1050 and 810 cm^{-1} (ν(C=S) and ν(C–S–C), respectively) which are not present in the spectra of the ester complexes, and no detailed information on the coordination mode can be derived from them [25]. The same situation was encountered with the related phosphonioalkane dithiocarboxylato complexes [26]. In the dirhenium complex, the ligand probably occupies the axial position according to the IR evidence [22].







ax



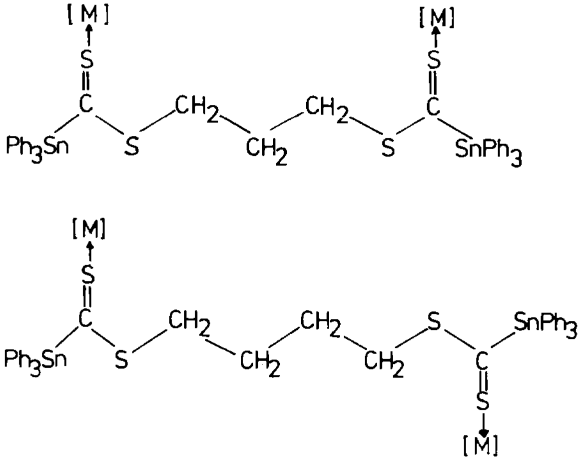
eq

Symmetrical diesters are obtained by reaction of the stannanedithiocarboxylate anion with 1,*n*-dibromoalkanes in the mol ratio of 2/1 [27]:

$$2\ Ph_3SnCS_2Li + \underset{(3 \leqslant n \leqslant 6)}{Br(CH_2)_nBr} \xrightarrow[20\,^{\circ}C]{THF} Ph_3SnCS_2(CH_2)_nS_2CSnPh_3 + 2\ LiBr$$

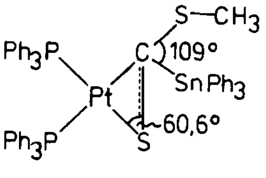
The stability of the 1,*n*-alkanediyl bis(stannanedithioesters) decreases with increasing chain length. The lower homologues ($n = 1$ and 2) were not isolable because of interfering elimination reactions. The β-elimination of ethylene-bridged compounds is well known in organometallic chemistry [28]. Similarly, the insertion of $SnBr_2$ into 1,*n*-dibromoalkanes succeeds only for $n \geqslant 3$ [29]. On the other hand, $Sn-(CH_2)_n-El$ units ($n = 1,2$) with El = Sn, S, N, P are known to be thermodynamically stable [30–33]. The easy decomposition of the methylene and ethylene bis(dithioesters) is surely of kinetic origin.

Reaction of the propylene diester with *cis*-bis(acetonitrile)tungsten tetracarbonyl and with (norbornadiene)molybdenum tetracarbonyl did not result in the expected chelate complexes. Inspection of a molecular model showed that the formation of such a 10-membered ring is not excluded [34] but is sterically fairly unfavourable. It is preferable to assume that the open-chain *n*-alkane structure is maintained in the diesters [35]. Thus, ligand-bridged, monocoordinate dimetal complexes were obtained with two mol of activated metal carbonyl.



[M] = W(CO)$_5$, CpMn(CO)$_2$

The recently described platinum complexes of stannanedithioesters [23] contain a η^2(C=S) ligand which is bound side-on, since platinum(0) prefers a square-planar geometry. This type of coordination requires a more drastic rearrangement of the bonds of the free dithioester and results in a significant difference between the C–S distances (1.82 and 1.75 Å) and a slight increase in the Sn–C distance (2.17 Å).



Sn–C = 2,17 Å

C$\equiv$S = 1,82

C—S = 1,75

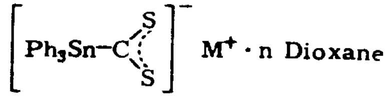
δ(Sn) = -185 ppm

triclinic, P$\bar{1}$

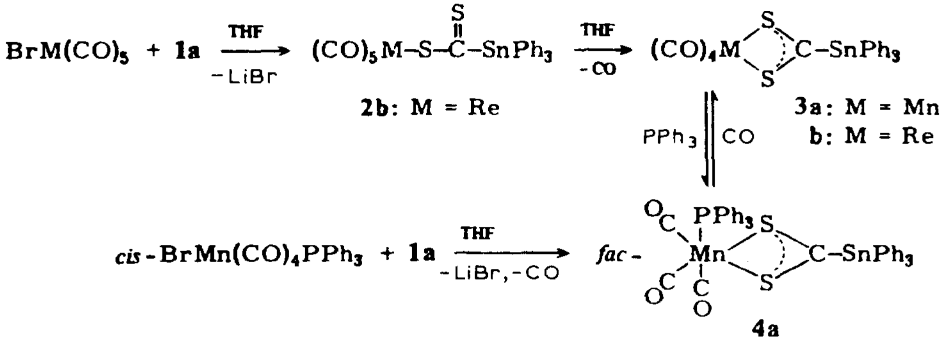
2. Isolation of alkali stannanedithiocarboxylates and synthesis of metal carbonyl complexes

The experiments discussed above showed that it was not possible in THF solution to obtain metal complexes containing the anionic stannanedithiocarboxylate ligand. Organoalkali compounds are considerably stabilized by stronger coordinating donor ligands, and this principle was successfully applied by Kramolowsky [36] in the synthesis of the related phosphinodithioformato complexes in dioxane solution. When a THF solution of triphenylstannyllithium is added to a solution of CS_2 in dioxane, the slightly soluble bis(dioxane) adduct of lithium stannanedithiocarboxylate is isolable in the form of air-sensitive, golden-yellow prisms which may be kept under a solvent atmosphere. The red solvates of the sodium and potassium salts were obtained by a similar procedure and show increased thermal stability [37,38].

The IR spectra of the alkali salts contain a characteristic band between 960 and 980 cm^{-1}, corresponding to ν(C=S) of a π-delocalized CS_2 moiety [39,40]. The ^{13}C NMR signal of the C=S group (δ 219 ppm) has a diamagnetic shift of nearly 50 ppm compared to that of the alkyl dithioesters. The intense UV absorptions between 300 and 400 nm are assigned to π–π^* transitions. The bathochromic shift of the maxima in relation to sodium dithiobenzoate [41] reflects the electronic influence of the stannyl group.



1a: M = Li, n = 2
b: M = Na, n = 1.5
c: M = K, n = 2



2b: M = Re

3a: M = Mn
b: M = Re

4a

The direct reaction of carbonylmetal halides with THF-dissolved alkali stannanedithiocarboxylates does not give the expected transition metal complexes [2,19]. In some cases, stannyl metal compounds were detected which arise from the elimination of CS_2. However, the stannanedithiocarboxylato complexes are easily obtained by use of the isolated dioxane adducts [37,38]. The complexation proceeds in two steps: halogen displacement and substitution of CO. The monocoordinate form is isolable only with rhenium. The rate of chelate formation is considerably higher when starting from the dinuclear tetracarbonylmetal halides. The *fac* tricarbonylmetal phosphine complex is obtained either by direct synthesis or by CO displacement of the tetracarbonyl complex. The chelate ring is not opened by an excess of PPh_3 or by CO under pressure.

The yellow-orange chelate complexes are stable on air and have ν(C–S) frequencies in the range of 950–980 cm^{-1}, as do the free ligands. As expected, the IR spectra of the monocoordinate complexes reveal two ν(C–S) absorptions in the order of stannanedithioesters. The UV characteristics of the ligand and the monocoordinate and dicoordinate rhenium complexes are depicted in Fig. 3. Significant for the monodentate ligand is a weak n–π^* transition band in the visible range which is also observed in the dithioesters [20,21].

The synthesis of trialkylstannane dithiocarboxylato complexes was previously prevented by the lack of the isolable dioxane adducts of the ligand salts. However, when carbonylmetal halides were added to a THF/dioxane solution of the lithium trialkylstannane dithiocarboxylates, tetracarbonylmetal units were detected by IR spectroscopy. The more stable rhenium complexes were separated by column chromatography and purified by sublimation or recrystallisation, to give yellow, low-melting solids (10–20% yield) [42].

$$R_3SnCS_2Li + BrRe(CO)_5 \xrightarrow{THF} R_3SnCS_2Re(CO)_4 + CO + LiBr$$
$$(R = C_6H_5CH_2,\ CH_3,\ \text{cyclo-}C_6H_{11})$$

The ^1H NMR spectra of the tribenzyl- and trimethyl-tin complexes show a singlet for the CH_2 and CH_3 groups and the chemical shifts and coupling constants correspond to those of the related tribenzyl- and trimethyl-tin halides [43]. The $^{13}C{=}S$ signal is observed at δ 225 ppm, which is of the same order as that of the free ligand. The CH_2 and CH_3 signals are found at δ 20.3 and −0.6 ppm, with direct

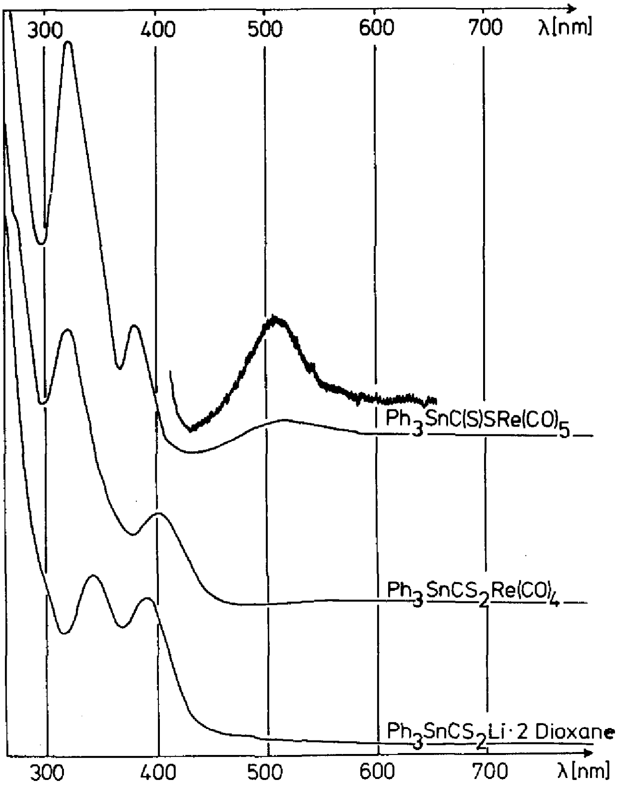
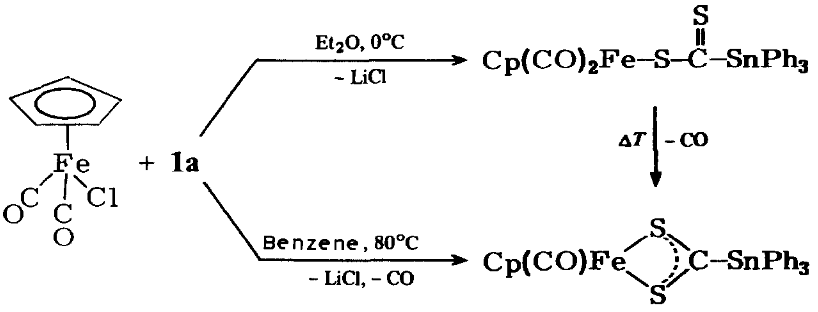


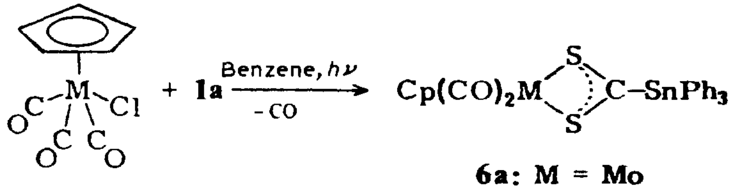
Fig. 3. UV absorption spectra of the dioxane adduct of lithium stannanedithiocarboxylate and of the mono- and di-coordinate rhenium complexes ($c \approx 10^{-4}$ M solutions in $CHCl_3$) (From ref. 38).

Sn–C coupling constants of about 280 Hz [44].



5a

5b



6a: M = Mo
b: M = W

We have investigated further the complexation of Group VIa and VIII metals [38]. The cyclopentadienyl complexes obtained are generally less stable than the manganese and rhenium compounds described above. The monocoordinate dicarbonyliron complex from $CpFe(CO)_2Cl$ is isolated at 0 °C and is converted to the chelate complex upon warming. Chelate formation proceeds quantitatively on refluxing in benzene solution. The thermal CO substitution of the $CpM(CO)_3Cl$ (M = Mo, W) compounds is hindered by partial decomposition and CS_2 extrusion, and photochemical activation is preferred. As in the neutral stannanedithioester complexes [22,27], no significant ν(C–S) absorptions are present in the IR spectra. Attempts to synthesize stannanedithiocarboxylato complexes of d^3 and d^8 metals have so far been unsuccessful [45]. Mainly decomposition occurred both with vanadocene and nickelocene.

3. Substitution reactions of stannanedithiocarboxylato complexes with σ-donor ligands of Main Group V

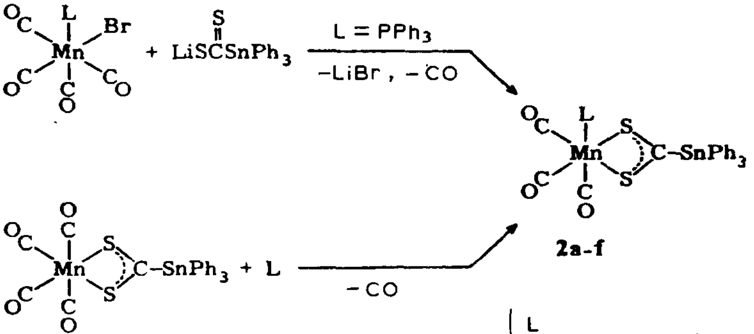
Tricarbonyl chelate complexes of transition metals of Group VII are obtained either by direct reaction of the ligand anion with the pre-substituted carbonylmetal halide, *cis*-$(CO)_4M(L)X$ (M = Mn, Re) [46], or by CO displacement in the tetracarbonyl complex [47]. In an extended study of the related diethyldithiophosphinato complex $Et_2PS_2Re(CO)_4$, Lindner and Berke [48] found partial or complete replacement of the chelate ligand by substituents without π-acceptor properties. Monodentate weak π-acceptors replace exclusively one of the *trans* CO groups. Substitution with bidentate ligands leads to opening of the chelate ring.

For further elucidation of the complex chemical properties of the new stannanedithiocarboxylate ligands, we have studied the thermal and photochemical substitution of the tetracarbonylmanganese chelate complex by donor ligands containing Main Group V elements. Principally, the following mechanisms may be involved [49]:

(a) Direct attack by the nucleophile L, via a seven-coordinate transition state (S_N2 reaction).

(b) Dissociative S_N1 reaction with elimination of CO.

(c) Dissociation of a metal–chelate bond, with subsequent attack of the ligand L on the five-coordinate intermediate.

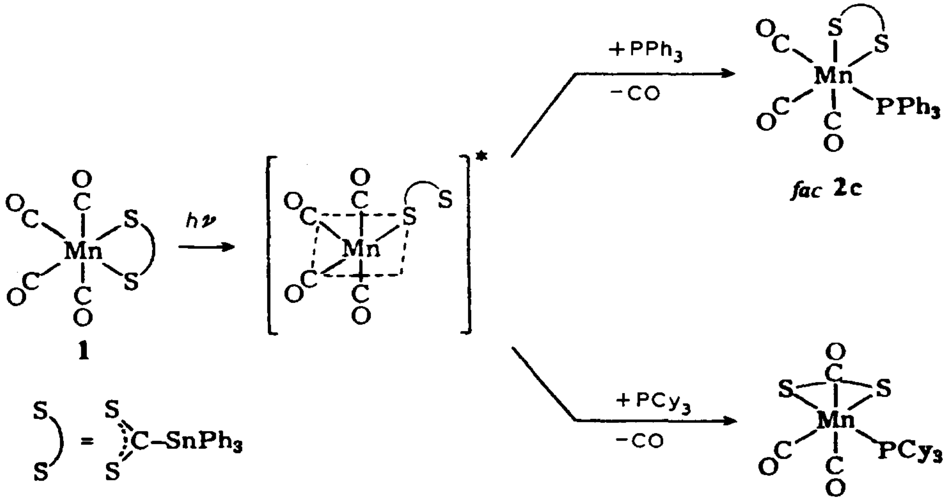


1

2a-f

	L		L
a	$P(OPh)_3$	d	$AsPh_3$
b	$P(OMe)_3$	e	$SbPh_3$
c	PPh_3	f	$P(c\text{-}C_6H_{11})_3$

By reaction at 50 °C in THF or on short refluxing in toluene, the manganese chelate complex is completely converted into the monosubstituted tricarbonylmetal complex. The thermal substitution proceeds stereoselectively to give the *fac* isomer and is compatible with a dissociative S_N1 mechanism. The stannanedithiocarboxylato ligand can be classified as a weak π-acceptor which exerts no labilizing effect on the equatorial CO groups.



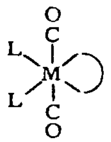
1

fac **2c**

mer **3f**

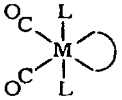
Cy = Cyclohexyl

Phosphite ligands, when in excess, form disubstituted products, which are also obtained by photochemical activation in the presence of PPh_3, $AsPh_3$ and $SbPh_3$. However, in contrast to the thermal substitution, tricyclohexylphosphine gives the *mer* tricarbonylmetal complex after irradiation of the tetracarbonyl compound. The *mer* form gradually rearranges to the thermodynamically stable *fac* isomer, which is identical to the thermal product. The difference in the behaviour of triphenyl- and tri-cyclohexylphosphine may be explained by assuming that dissociation of a metal–chelate bond occurs as a result of the photochemical excitation, and that the activated five-coordinate complex reacts with the entering ligand with reformation of the chelate ring and elimination of the CO group: the direction of formation of the ring depending on the size and electronic properties of the introduced ligand. As Schenk and Müller [50] have found in the series of Group VIa metal olefin complexes, $(dppe)M(ol)(CO)_3$ (M = Cr, Mo, W), the *mer* isomer is clearly favoured by increasing π-acceptor ability of the olefin ligand. The *fac* and *mer* isomers of tricarbonylmetal complexes are easily differentiated by the different intensities of the ν(CO) absorption bands [51]. Since the site symmetry is reduced to C_s, three IR-active CO absorptions are observed in both cases.



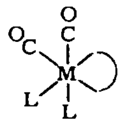
I

trans(CO)-*cis*(L)



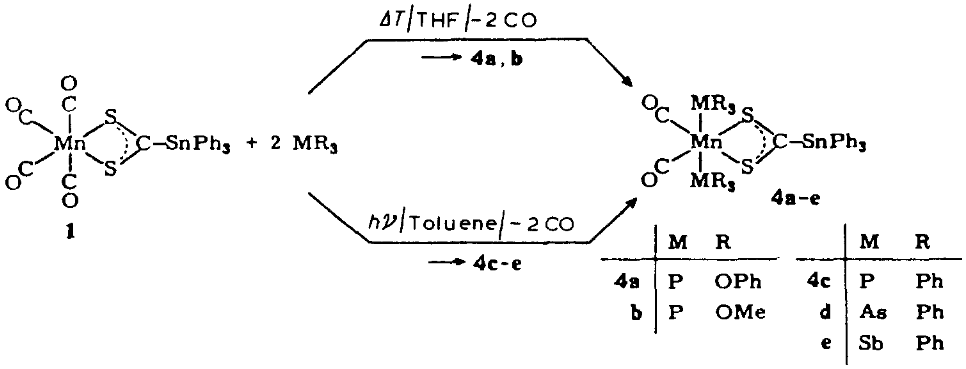
II

cis(CO)-*trans*(L)



III

cis(CO)-*cis*(L)



	M	R		M	R
4a	P	OPh	**4c**	P	Ph
b	P	OMe	**d**	As	Ph
			e	Sb	Ph

The disubstitution of tetracarbonylmetal complexes needs a higher activation energy and so requires photolytic excitation with weaker π-acceptors. Of the three possible isomers, the *trans* L form (II) is formed as the first substituent exerts a stronger *trans*-effect than the chelate ligand [52,53].

The *trans*-bis(phosphite) complexes are obtained by extended thermal reaction (10–60 h at 50 °C). The ^1H NMR spectrum of the bis(trimethylphosphite) complex shows a pseudo-triplet, centred at δ 3.68 ppm, which is assigned to an $AA'X_9X_9'$ spin system of magnetically non-equivalent ligands [54]. The number and intensity of the spectral lines depend on the ratio of the coupling constants. Within certain limits, the values for $|N| = |J(AX) + J(AX')|$, $|L| = |J(AX) - J(AX')|$ and $|J(AA')|$ can be derived. But if $|J(AA')| \gg |L|$, a "deceptively simple" spectrum is observed from which $|N|$ is determined as the distance between the outer peaks. A computer simulation with $|J(AA')| = 50$ Hz, $|J(AX)| = |J(A'X')| = 7.55$ Hz, and $|J(AX')| = |J(A'X)| = 3.49$ Hz is in good agreement with the experimental spectrum.

The lower thermal stability of the dicarbonyl complexes is shown in the significant tendency to reform the tricarbonyl species. The recombination of the bis(arsine) complex was followed quantitatively by UV spectroscopy. The UV spectra show a characteristic shift of the π–π^* transition from 491 to 422 nm. The reaction proceeds stoichiometrically in the mol ratio of 3/2. The plot of the absorbance curves reveals two isosbestic points at 420 and 362 nm. Following the method of absorbance diagrams developed by Mauser [55], the time-dependent concentrations of all components can be determined during the course of the reaction. The absorbances at various wavelengths (which need not be maxima) are plotted vs. the absorbance of an arbitrarily chosen reference wavelength. Uniform reactions give linear relations for all wavelengths. For a reaction $\nu_A A \rightarrow \nu_B B$, by applying a first-order equation, we obtain:

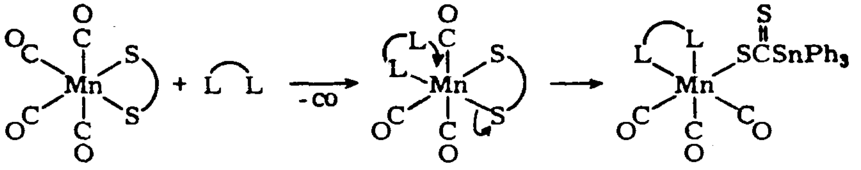
$$\ln c_A = \ln\left[c(A_0) - \frac{\nu_A}{\nu_B} c(B)\right] = \ln c(A_0) - kt \qquad \text{(a) or}$$

$$\ln[c(B_\infty) - c(B)] = \ln c(B_\infty) - kt \qquad \text{(b) and}$$

$$k = (1.14 \pm 0.01) \times 10^{-4}\ \mathrm{s}^{-1}\ (T = 25\,^\circ\mathrm{C}).$$

The rate constant k is calculated from the slope of the plots of the linear functions (a) and (b) using the known parameters ν_A, ν_B, $c(A_0)$ and $c(B_\infty)$. The results obtained from eq. a and b differ by less than 1%.

Only a few monocoordinate dithiocarboxylato complexes have been reported [25]. In our previous studies on stannanedithiocarboxylates, we observed monocoordination with rhenium and iron, and a more general synthetic route was found by the use of bidentate co-ligands [49].



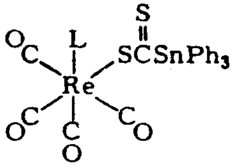
1

5c: L L = dppe

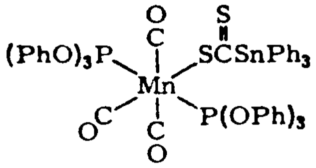
d: L L = dipy

5a': L = CO

b': L = PPh$_3$



5a', b'



5e

With 1,2-bis(diphenylphosphino)ethane and 2,2′-dipyridine, a *mer* tricarbonyl complex is obtained in the first step, and this rearranges to the *fac* isomer by replacement of one metal–sulfur bond. In this case, the kinetic preference of the *mer* isomer is certainly due to steric reasons. A monocoordinate dithiocarboxylato complex is also derived from the *trans,mer*-bis(triphenylphosphite) complex $[P(OPh)_3]_2$-$Mn(CO)_3Br$.

The rather low thermal stability of the monocoordinate stannanedithiocarboxylato complexes is shown in the mass spectra, where the molecular peak is detected only for dppe and dipy compounds. The ^1H and ^{31}P NMR spectra of the dppe complex show equivalence of the phosphorus atoms and of the methylene groups, as expected for *fac* geometry [50]. As the indirect coupling is not resolved, a doublet is observed for the CH_2 groups, with $|^3J(PH)|$ 15.1 Hz.

4. Tin-119 NMR characteristics of stannanedithiocarboxylates

The chemical shift of an NMR-active nucleus can be described as the sum of a diamagnetic, a paramagnetic and a special term (which includes indirect interaction, mesomeric and anisotropic effects):

$$\sigma = \sigma^{\mathrm{d}} + \sigma^{\mathrm{p}} + \sigma'$$

σ^{d} and σ^{p} have opposite signs where σ^{p} corresponds to a deshielding (low-field shift). For heavy atoms, the paramagnetic contribution σ^{p} is dominant, and for this Jameson and Gutowky [56,57] have developed the simplified expression:

$$\sigma^{\mathrm{p}} = \frac{2e^2h^2}{3m^2c^2\Delta E}\left(\langle r^{-3}\rangle_{np} Q_{np} + \langle r^{-3}\rangle_{nd} Q_{nd}\right) \qquad (\mathrm{Sn}: n = 5)$$

where ΔE is the average excitation energy, $\langle r^{-3}\rangle_{np'nd}$ are the average reciprocal cubes of the p,d valence electron-nucleus distances, and Q_{np},Q_{nd} are the effective nuclear charges (the amount of the asymmetric charge distribution of the p,d valence orbitals).

The ^{119}Sn NMR spectra of a series of triarylstannane dithiocarboxylates were recorded in order to get a comprehensive picture of this new class of organotin compounds. The data were collected with a Bruker multinuclear spectrometer WP80DS with a pulse programmer [58]. The recording time was considerably reduced by application of the DEPT (Distortionless Enhancement by Polarisation Transfer) pulse sequence using the $^3J(SnH)$ coupling with the *ortho* protons of triaryltin compounds as indicator [59,60].

Recent NMR studies of triphenyltin compounds indicate a range of −40 to −120 ppm for four-coordinate and −180 to −260 ppm for five-coordinate tin (relative to tetramethyltin) [61]. Surprisingly, nearly all of the chemical shifts of the stannanedithiocarboxylates recorded by us fall within the five-coordinate tin range (Fig. 4). The $Ph_3SnCS_2^-$ anion (δ −261 ppm) marks the high-field limit because of its negative charge, and it has a value comparable to that of $[Ph_3SnCl_2]^-$ (δ −257.2 ppm). The structural analogy of the dithioester Ph_3SnCS_2Me with tetraphenyltin [21] suggests a similar point-charge model. The additional shielding compared with that in tetraphenyltin (δ −128.1 ppm) could be explained by a stronger $(d\text{–}p)\pi$ interaction between tin and the dithiocarboxylate unit, but the molecule structure reveals no shortening of the Sn–C single bond distance. Also, no intermolecular association or "through-space" interaction between tin and the sulfur atoms has been detected. The direct coupling constant $|^1J(\mathrm{SnC})|$ of ca. 550 Hz is unambiguously of the order expected of four-coordinate tin compounds [61–63]. The anisotropic effect of the dithiocarboxylic group would be expected to induce a deshielding of the ^{119}Sn signal, as the tin atom lies outside of the anisotropy cone. Regardless of any theoretical explanation, it is obvious that the CS_2 group attached to tin causes a high diamagnetic increment. This is clearly seen by a comparison with the recently described stannyl thioformamides, which show tin-chemical shifts in the range expected of four-coordinate tin ($\delta \approx -50$ ppm) [23].

Complexing of the dithioesters leads to an increase in the asymmetry of the charge distribution at the tin nucleus (increase of Q_{5p}), and the ^{119}Sn resonance shifts to lower field due to the greater σ^{P} share. In the fairly stable tungsten complexes $LW(CO)_5$, the coordination shift is constant within a narrow range, whereas the cyclopentadienyl complexes $CpM(CO)_2L$ (M = Mn, Re) show much larger differences.

Coordination to the anionic stannanedithiocarboxylate ligand causes a downfield shift of about 40–70 ppm in the manganese chelate complexes. The largest coordination shift is observed for the unsubstituted complex. Substitution of the CO by Group VB element ligands induces an increase of σ charge density at the transition metal, which leads to smaller coordination shifts. Notable substituent effects are also shown in the relatively large $|^4J(\mathrm{SnP})|$ coupling constants of the phosphine and phosphite complexes.

The rhenium complexes show larger coordination shifts than the equivalent manganese compounds and smaller $|^4J(\mathrm{SnP})|$ coupling constants. Apparently, the greater atomic radius of rhenium allows a more extended charge transfer and contributes to a deshielding of $\delta(^{119}\mathrm{Sn})$, reaching a maximum in the tribenzyltin complex $Bz_3SnCS_2Re(CO)_4$ (δ −73.3 ppm). Monocoordinate rhenium complexes

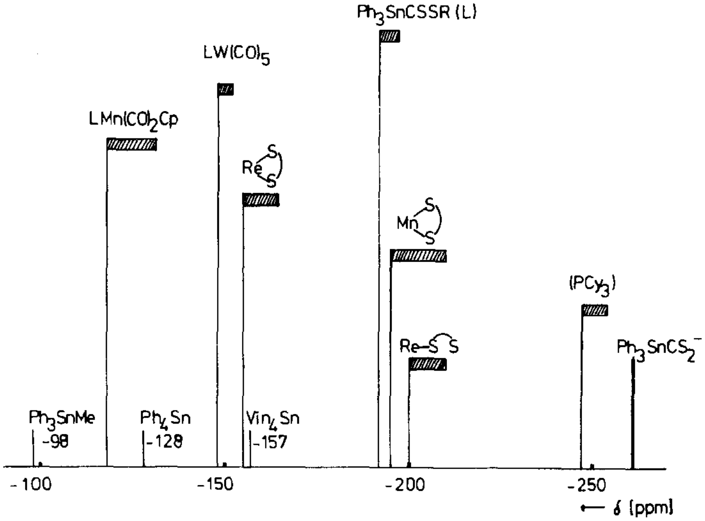


Fig. 4. Range of δ values from the ^{119}Sn NMR spectra of stannanedithiocarboxylates. The values for triphenylmethyltin, tetraphenyltin and tetravinyltin are included for comparison.

show a larger shielding of the tin NMR signal than the chelate complexes because of incomplete charge transfer. Only poorly resolved spectra were recorded for monocoordinate manganese complexes [45].

The results show that all of the recorded tin-chemical shifts of triarylstannane dithiocarboxylates lie between δ -118 and -261 ppm, and are among the highest tin-119 shifts known for SnC_4 compounds. In stannanedithiocarboxylato complexes, $\delta(^{119}Sn)$ operates as a sensitive probe for the σ donor ability of the co-ligands and is closely related to coordination, substituent influence and complex stability.

Outlook

Let us finally draw a comparison between transition metal and organotin dithiocarboxylates: the nucleophilic addition of carbonylmetallates to carbon disulfide, the alkylation to metallodithioesters and the (mono- and bi-dentate) coordination of metallodithiocarboxylates proceed by exactly the same route [2] (Fig. 5). There is no hint for a principally different stability of equivalent Main Group and transition metal species. It has been emphasized several times that the previous failures to prepare stannanedithiocarboxylates are certainly kinetic in origin. Busetto's fine results have opened the way from metallodithiocarboxylato to (cationic) metallodithiocarbene complexes which are stabilized by electron-rich transition metals [64,65]. The analogous Main Group metal complexes are unknown since the stabilization of carbene complexes requires occupied *d*-orbitals. Nevertheless, it seems a fascinating challenge to consider the possible synthesis of a "stanniodithiocarbene" complex to fill the last gap in the set of analogous transition and Main Group metallodithiocarboxylates. Work on this is in progress.

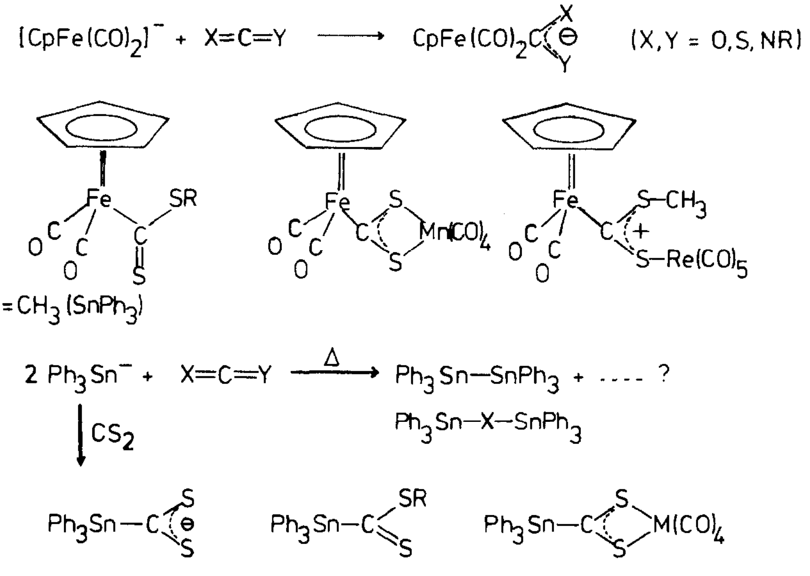


Fig. 5. Analogies between ferrio- and stannanedithiocarboxylates.

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