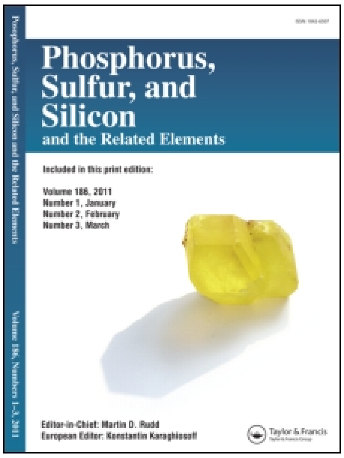

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Synthesis and Properties of Organogermanium and Organotin Dithiophosphonate Complexes; Crystal Structures of $(C_6H_5)_2$Sn(Cl)[(*p*-MeOC$_6$H$_4$)(EtO)PS$_2$-*S*, *S*′], Me$_2$Sn[(*p*-MeOC$_6$H$_4$)(MeO)PS$_2$-S]$_2$, Me$_2$Sn[(*p*-MeOC$_6$H$_4$)(<i>i</i>PrO)PS$_2$-S]$_2$, and Me$_2$Ge{[(C$_6$H$_5$)$_3$SiO](*p*-MeOC$_6$H$_4$)PS$_2$-S}$_2$

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Synthesis and Properties of Organogermanium and Organotin Dithiophosphonate Complexes; Crystal Structures of $(C_6H_5)_2Sn(Cl)[(p\text{-}MeOC_6H_4)(EtO)PS_2\text{-}S, S']$, $Me_2Sn[(p\text{-}MeOC_6H_4)(MeO)PS_2\text{-}S]_2$, $Me_2Sn[(p\text{-}MeOC_6H_4)(^iPrO)PS_2\text{-}S]_2$, and $Me_2Ge\{[(C_6H_5)_3SiO](p\text{-}MeOC_6H_4)PS_2\text{-}S\}_2$

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2,4–Bis-(4-methoxyphenyl)-1,3,2λ^5,4λ^5-dithiadiphosphetane-2,4-disulfide (Lawesson's reagent) reacts with a variety of alcohols and silanols to form dithiophosphonic acids in a facile manner. Their lithium salts react with organotin- and organogermanium chlorides to produce organometallic dithiophosphonate complexes of the type ***A*** *$R_3''M[S(S)P(R)(OR')]$ ($M = Ge, Sn; R = 4\text{-}MeOC_6H_4; R' = Me, SiPh_3, GePh_3, SnPh_3; R'' = Me, Ph$) and* ***B*** *$R_2''M[S(S)P(R)(OR')]_2$ ($M = Ge, Sn; R = 4\text{-}MeOC_6H_4; R' = Me, Et, {}^iPr, {}^tBu, SiPh_3; R'' = Me, Ph$). The ligands in the new organometallic compounds are bound in an asymmetric fashion as revealed by four X-ray structure determinations, containing one representative example of type* ***A*** *and three examples of type* ***B****. All new compounds are fully characterized by analytical and spectroscopic methods.*

Keywords Crystal structures; dithiophosphonates; germanium; organometallic compounds; tin

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INTRODUCTION

Phosphorus-1,1-dithiolates (**I–III**, Figure 1) have found widespread use in diverse technological areas ranging from antioxidant additives in oil and petroleum industry,[1], agricultural insecticide and pesticide derivatives,[2] and metal ore extraction reagents.[3] In recent years, due to potential application in electrochemistry, microelectronics, catalysis, ion exchange, photophysics and materials science, metal phosphonate chemistry has flourished.[4] More recently, research has been conducted on attempts to use these compounds to form liquid transition metal complexes, specifically of Pt, for use in the preparation of thin layers by chemical vapour deposition (CVD) or of polymer-inorganic nanocomposites.[5]

Structural investigations have revealed a great variety of coordination patterns and metal-sulphur bonding interaction modalities in dithiophosphato ($[PS(S)(OR)_2]M$) and dithiophosphinato-complexes ($[PS(S)R_2]M$), M = transition metal or heavier main group element, depending on the electronic effects in those ligands and on the steric requirements around the central atom[6] (Figure 2). Furthermore, related metal complexes play also an important role in material science,[7] crystal engineering, supramolecular networks,[8] and in tuning electronic properties leading to luminescent or electron-transferring reagents.[9]

In contrast, research utilizing the related dithiophosphonate ligand $[PS(S)(OR)R]^-$ in metal complex formation, has not been so abundant. This is exemplified by the fact that among the corresponding main group derivatives only three crystal structures have been determined by X-ray diffraction: $[Pb[S(S)P(Ar)(OR)]_2$; Ar = ferrocenyl (**i**), anisyl (**ii**, **iii**); and R = Et (**ii**), ^{i}Pr (**i**), (**iii**)$]$[9a–c], displaying monodentate and bridging (**ii**), as well as bidentate (**i**, **iii**), coordination patterns.

There are three general routes available for the preparation of the germanium and tin dithiophosphonate complexes. First, the reaction of dithiophosphonic acid or dithiophosphonic salts with

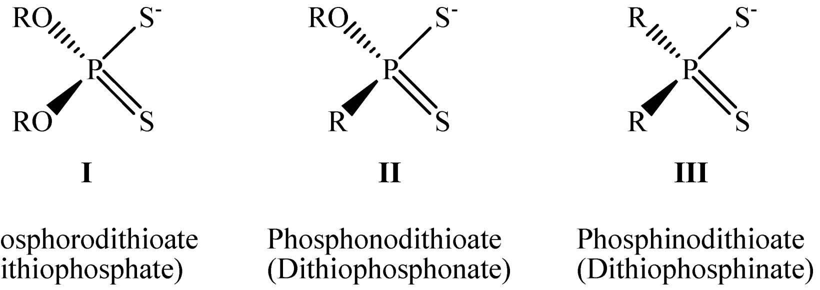


FIGURE 1 Phosphorus-1,1-dithiolates.

monodentate coordination
(a)

isobidentate coordination
(b)

anisobidentate coordination
(secondary interaction)
(c)

anisobidentate coordination
(dative bond)
(d)

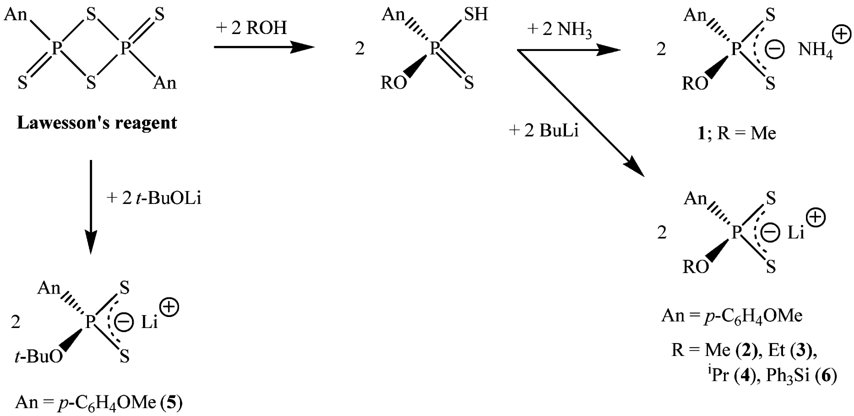
FIGURE 2 Coordination modes of dithiophosphorus ligands.

inorganic halides or organometallic derivatives leads to dithiophosphonate complexes via hydrogen halide or salt elimination process.[10] An alternative pathway comprises the fragmentation of the 1,3,2,4-dithiadiphosphetane ring of Lawesson's reagent with trialkyl(triaryl)alkoxygermanes and stannanes,[11] whereas a recently published method is based on the reactions of *O*,*S*-disilylaryldithiophosphonates and *O*-trimethylsiloxyorganyl-*S*-trimethysilylaryldithiophosphonates with *S*,*S*-diethyldithiogermanium, diphenylgermanium dichloride and diphenyltin dichloride, respectively.[12]

In the present paper, we report a novel route for the preparation of dithiophosphonate complexes containing germanium(IV) and tin(IV) via reactions of the corresponding dithiophosphonic lithium salts with organogermanium and organotin chlorides, respectively, leading to germanium(IV)- and tin(IV) dithiophosphonate complexes. Additionally, one crystal structure of a tin(IV) *mono*-dithiophosphonate and three crystal structures of germanium(IV) and tin(IV) *bis*-dithiophosphonate complexes are described.

RESULTS AND DISCUSSION

The synthesis of dithiophosphonic acids, their salts and esters is well established and numerous examples appeared in the literature. Formation of their corresponding salts comprises interaction of the acids with sodium alkoxides.[13] Alternatively, neutralization with appropriate hydroxides or anhydrous ammonia and also reaction



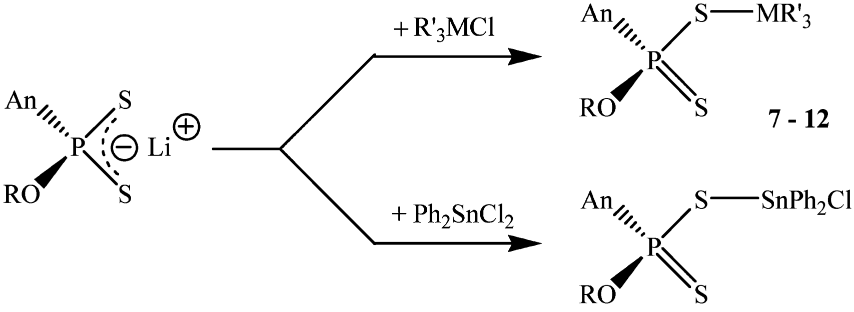
SCHEME 1 The synthesis of the dithiophosphonato salts **1** to **6**.

with triethylamine leads to the alkali or ammonium salts.[1,14] The dithiophosphonic alkali salts can also be synthesized by treating alkyl(aryl)phosphonothioic dichlorides with alcoholic solution of sodium or potassium hydrosulfide.[15]

In extension of the reported methods, we found that Lawesson's reagent readily reacts with primary or secondary alcohols to produce the dithiophosphonic acids as oily liquids. Upon treatment of the residues with gaseous ammonia or alkyllithium compounds, the corresponding salts **1–6** are formed in good to excellent yields as white high-melting solids, which can be stored under nitrogen indefinitely without decomposition (Scheme 1).

It has been well established that acid formation is only possible with primary or secondary alcohols. Reactions with tertiary alcohols lead to elimination reactions.[16] On the other hand, in this article it has been found that Lawesson's reagent reacts with lithium *tert*-butoxide to form the lithium salt of the corresponding dithiophosphonic acid with satisfactory yield. Additionally, it has been reported that Lawesson's reagent reacts with triphenylsilanol (the silicon analogue of a tertiary alcohol) without elimination side reactions to give the corresponding acid, which was converted readily to the ammonium salt.[17] Our procedure permits access to the lithium salt **5** in a straightforward manner (Scheme 1). The new salts **1** to **6** all gave satisfactory analyses and NMR spectra consistent with their structure, displaying ^{31}P NMR shifts at low-field between 95 and 110 ppm.

According to the salt elimination route described by Coray et al.,[9a–c] the ammonium salt **1** and the lithium salts **2–6** have been employed in



7 - 12

13; R = Et
An = *p*-C_6H_4OMe

Compound	R	R′	M
7	Me	Me	Ge
8	$SiPh_3$	Me	Ge
9	Me	Me	Sn
10	$SiPh_3$	Me	Sn
11	Me	Ph	Sn
12	$SiPh_3$	Ph	Sn

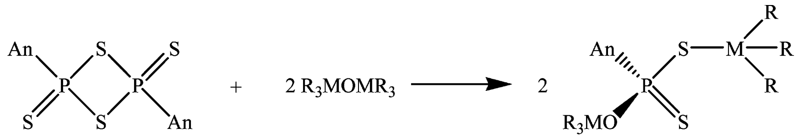
SCHEME 2 The synthesis of the *mono*-dithiophosphonato complexes **7** to **13**.

the synthesis of new *mono*-dithiophosphonato complexes of tin(IV) and germanium(IV) (Scheme 2).

All reactions were performed at ambient temperature and gave the new compounds **7–15** in good to excellent yields. The metal complexes were isolated as either white powders with melting points in the range of 100°C to 160°C or as colorless viscous liquids. All are soluble in common organic solvents (CH_2Cl_2, $CHCl_3$, THF, CS_2, acetone, toluene, etc.). An alternative pathway for synthesizing the monodithiophosphonato complexes employs the reactivity of Lawesson's reagent towards metalloxanes of the type $(Ph_3M)_2O$; M = Ge, Sn (Scheme 3).

Both reactions can be performed advantageously as one-pot syntheses, giving the complexes **14** and **15** in satisfactory yields. Selected analytical data are presented in Table I.

Compound **9** has been already obtained by Nizamov et al. by fragmentation of Lawesson's reagent with trimethyl(methoxy)stannane.[11b]



An = p-C_6H_4OMe

R = Ph, M = Sn (**14**), Ge (**15**)

SCHEME 3 The synthesis of the *mono*-dithiophosphonato complexes **14** and **15**.

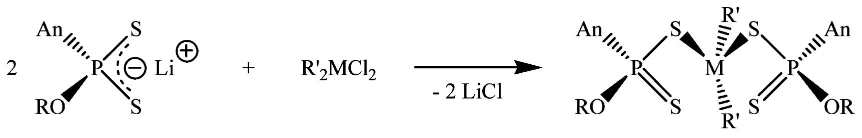
The ^1H NMR spectra of the new complexes show for the p–$MeOC_6H_4$ moiety one singlet for the OMe protons at approximately 3.8 ppm and two well-resolved multiplets in the range of 6 to 8 ppm for the phenyl group. In complexes, that contain the P-O-Me moiety, a doublet at approximately 3.6 ppm ($^3J_{PH} = 15.5$ Hz) is observed. The protons of methyl groups attached to the metal atom are found at approximately 0.5 ppm. In the case of tin, both the satellites from ^{117}Sn and ^{119}Sn are observed with coupling constants $^2J(^{117}Sn,H)$ of 55 Hz and $^2J(^{119}Sn,H)$ of 57 Hz, respectively. As expected, the $^{31}P\{^1H\}$ NMR spectra reveal a singlet peak for each compound in the range of 65 to 100 ppm. In comparison with their lithium salts, the ^{31}P resonances of the complexes are slightly shifted to high field.

So far, very few tin *bis*-dithiophosphonate complexes are known, and the reported examples are exclusively tin(II) compounds, obtained

TABLE I Selected Analytical Data for *mono*-Dithiophosphonato Complexes

Compound		Yield (%)	Mp (°C)	Elemental analysis (%)		
				C	H	S
8	$Me_3Ge[S_2P(OSiPh_3)(An)]$	76	101	56.21 (56.44)	5.15 (5.21)	10.98 (10.77)
10	$Me_3Sn[S_2P(OSiPh_3)(An)]$	78	104	52.04 (52.38)	4.71 (4.83)	10.01 (10.00)
11	$Ph_3Sn[S_2P(OMe)(An)]$	90	oil	52.96 (53.54)	4,27 (4.32)	10.35 (11.00)
12	$Ph_3Sn[S_2P(OSiPh_3)(An)]$	90	163	62.59 (62.40)	4.54 (4.51)	7.50 (7.75)
13	$Ph_2SnCl[S_2P(OEt)(An)]$	47	72	45.36 (45.39)	4.04 (3.99)	11.30 (11.54)
15	$Ph_3Ge[S_2P(OGePh_3)(An)]$	56	63	62.27 (62.52)	4.52 (4.52)	7.70 (7.76)

Calculated values in brackets. **9** and **14** did not give satisfactory elemental analyses. An = p-$MeOC_6H_4$.



16 - 24

An = p-C_6H_4OMe

Compound	R	R′	M
16	Me	Me	Ge
17	$SiPh_3$	Me	Ge
18	Me	Me	Sn
19	$SiPh_3$	Me	Sn
20	Et	Me	Sn
21	^{i}Pr	Me	Sn
22	^{t}Bu	Me	Sn
23	Me	Ph	Sn
24	$SiPh_3$	Ph	Sn

SCHEME 4 The synthesis of the *bis*-dithiophosphonato complexes **16** to **24**.

by the salt elimination route of Woollins et al. employing $SnCl_2$ and the sodium salts of dithiophosphonic acids.[9a–c] For germanium, no *bis*-dithiophosphonate compounds are described in the literature.

Again following the salt elimination route, a variety of diorganogermanium and diorganotin chlorides has been used to react with the dithiophosphonate Li-salts in a 1 : 2 molar ratio to form the corresponding organometallic complexes (Scheme 4).

The organometallic *bis*-dithiophosphonato complexes were isolated in good yields as either white-yellowish powders with melting points in the range of 55 to 128°C or as viscous liquids. They are also soluble in common organic solvents like CH_2Cl_2, $CHCl_3$, THF, CS_2, acetone and toluene. Selected analytical data are given in Table II.

It has been observed that the reactivity of diphenylgermanium- and diphenyltin dichlorides towards lithium salts is somewhat lower than that of the corresponding dimethyl derivatives. Thus, in reactions with diphenylsubstituted germanium and tin chlorides, a stepwise substitution of chlorine was observed, as revealed by ^{31}P NMR analysis. For instance, from the reactions between Li[S(S)P(An)(OR)], R = Me, $SiPh_3$,

TABLE II Selected Analytical Data of the *bis*-Dithiophosphonato Complexes 16 to 24

Compound		Yield (%)	Mp (°C)	Elemental analysis (%) C	H	S
16	$Me_2Ge[S_2P(OMe)(An)]_2$	81	55	37.77 (37.98)	4.71 (4.60)	22.96 (22.53)
17	$Me_2Ge[S_2P(OSiPh_3)(An)]_2$	51	75	58.65 (59.04)	4.92 (4.76)	12.11 (12.12)
18	$Me_2Sn[S_2P(OMe)(An)]_2$	89	110	34.98 (35.14)	4.20 (4.26)	20.76 (20.84)
20	$Me_2Sn[S_2P(OEt)(An)]_2$	63	oil	37.56 (37.34)	4.91 (4.70)	18.19 (19.93)
21	$Me_2Sn[S_2P(O^iPr)(An)]_2$	72	115	39.19 (39.36)	5.21 (5.10)	18.54 (19.10)
22	$Me_2Sn[S_2P(O^tBu)(An)]_2$	74	128	39.91 (41.21)	5.35 (5.48)	17.55 (18.33)
24	$Ph_2Sn[S_2P(OSiPh_3)(An)]_2$	69	60	60.68 (60.63)	4.61 (4.43)	11.18 (10.44)

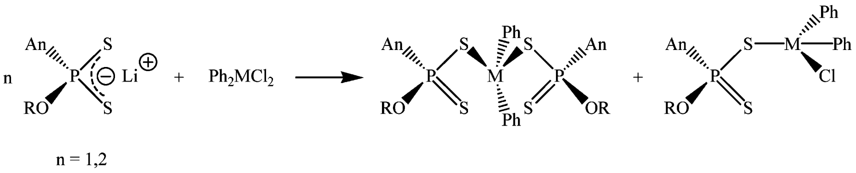
19 and **23** did not give satisfactory elemental analyses. calculated values in brackets. An = p-$MeOC_6H_4$.

and Ph_2GeCl_2 in a 1 : 1 molar ratio, as well as in a 2 : 1 molar ratio, a mixture of two different compounds was obtained (Scheme 5).

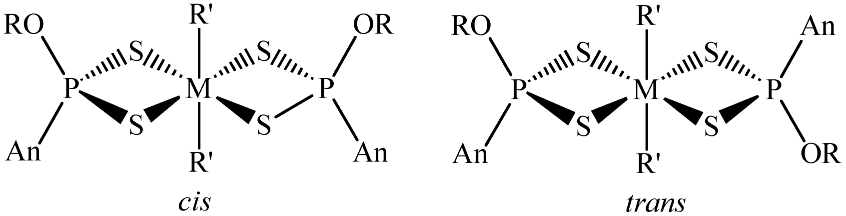
A separation of the two germanium derivatives failed. In the case of tin, however, a separation of both products in the reaction of derivative **3** with Ph_2SnCl_2 in a 1 : 1 molar ratio was successful.

The asymmetrical nature of the ligands allows for the diorganometallic dithiophosphonato compounds to form *cis* and *trans* isomers. In accordance with the solid state structures of bis-dithiophosphonato complexes available in the literature,[9a,b,e,f] we propose two possible structures for the germanium and tin bis-dithiophosphonato complexes as illustrated in Scheme 6.

Multinuclear NMR studies in solution confirm the formation of the *cis*/*trans* isomers in cases, where the resolution was good enough to



SCHEME 5 Stepwise formation of *mono*- and *bis*-dithiophosphonato complexes; An = p-$MeOC_6H_4$.



SCHEME 6 *cis/trans* isomers of *bis*-dithiophosphonates; An = *p*-MeOC$_6$H$_4$.

permit the observation of discrete signals. The ^{31}P{^{1}H} NMR spectra show a singlet peak for each of the two isomers, very close to each other, in the range of 70 to 100 ppm (Table III).

The ^{1}H and ^{13}C NMR spectra also confirm the presence of two individual isomers in solution and display distinct peaks for each isomer. As an example, the ^{1}H and ^{1}H{^{31}P} spectra of compound **16** are given in Figure 3.

In both ^{1}H and ^{1}H{^{31}P} NMR spectra, two sets of signals can be observed. In the case of the methyl groups at germanium, the signals of which are found in the range of 1–1.5 ppm, only one signal is observed for the *trans*-configured compound, whereas the *cis* isomer shows two resonances due to the different environment around the methyl protons. Variable temperature ^{1}H and ^{31}P{^{1}H} NMR experiments in the range of −90°C to +20°C (in CD$_2$Cl$_2$) and of +20°C to +90°C (in CD$_2$Cl$_2$-CDCl$_2$), respectively, were conducted for the same compound. The spectra were recorded every 10°C. Apart from a small shift to high field, the isomeric ratio is almost unchanged at low temperature. On the other hand, both

TABLE III ^{31}P{^{1}H} NMR Data and *cis-trans* Ratio of Diorganometallic Dithiophosphonato Complexes

Compound		δ [ppm]	*cis* / *trans* ratio [%]
16	Me$_2$Ge[S(S)P(OMe)(An)]$_2$	94,30 / 94,33	58/42
17	Me$_2$Ge[S(S)P(OSiPh$_3$)(An)]$_2$	79,46 / 79,50	48/52
18	Me$_2$Sn[S(S)P(OMe)(An)]$_2$	98.7	[a]
19	Me$_2$Sn[S(S)P(OSiPh$_3$)(An)]$_2$	84.5	[a]
20	Me$_2$Sn[S(S)P(OEt)(An)]$_2$	95.6	[a]
21	Me$_2$Sn[S(S)P(O^{i}Pr)(An)]$_2$	93.5	[a]
22	Me$_2$Sn[S(S)P(O^{t}Bu)(An)]$_2$	84.7	[a]
23	Ph$_2$Sn[S(S)P(OMe)(An)]$_2$	95.9/94.2	30/70
24	Ph$_2$Sn[S(S)P(OSiPh$_3$)(An)]$_2$	82.4/81.0	31/69

[a] Not Resolved; An =*p*-MeOC$_6$H$_4$.

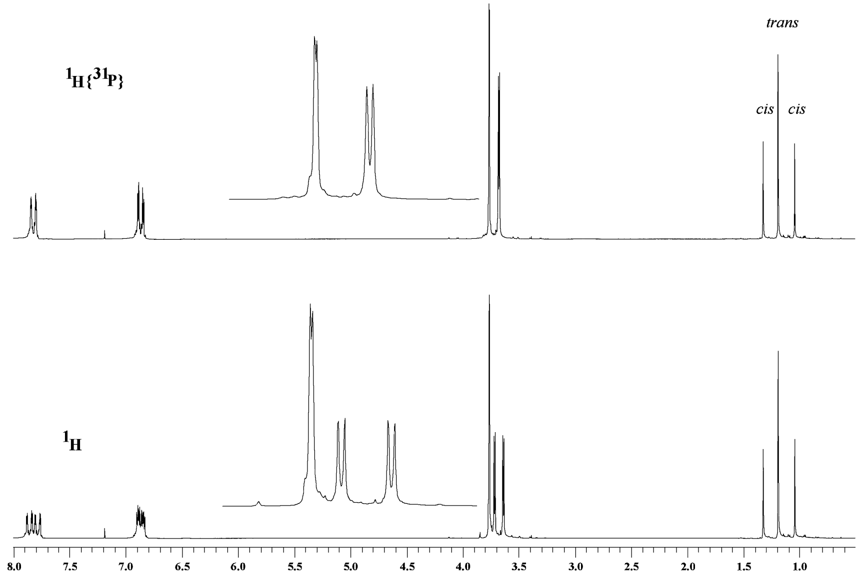


FIGURE 3 ^{1}H- and ^{1}H^{31}P NMR spectra of **16**.

^{31}P NMR and ^{1}H NMR spectra show coalescence at elevated temperature (Figures 4, 5).

X-Ray Structure Analyses

So far, there are no crystal structures of tin and germanium dithiophosphonato complexes reported, although numerous examples of dithiophosphinato and dithiophosphato complexes are described in the literature. Single crystals of $Ph_2SnCl[S(S)P(p\text{-}MeOC_6H_4)(OEt)]$ (**13**), a representative of the *mono*-dithiophosphonato complexes, were obtained from toluene and light petroleum at –20°C by slow diffusion method (Figure 6). The compound crystallizes with four molecules in the unit cell in the orthorhombic space group $P2_12_12_1$ (Table IV).

The structural data reveal a coordination of the dithiophosphonic ligand intermediate between isobidentate and anisobidentate with P—S distances P—S(1) = 2.0547(7) Å and P—S(2) = 1.9759(7) Å, showing marked delocalization in the dithiophosphonate ligand. This coordination pattern is also confirmed by different Sn-S bonds (Sn-S(1) = 2.4610(5) Å and Sn-S(2) = 2.8102(5) Å). Thus, the ligand could be regarded as a chelating ligand with non-equivalent electronic situations at the donor centers. In organometallic tin(IV)

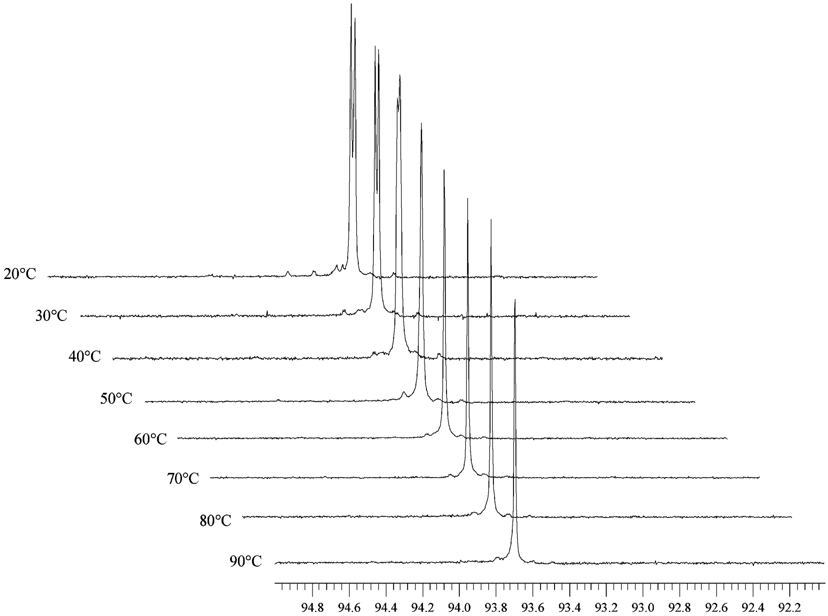


FIGURE 4 Temperature dependent ^{31}P NMR spectrum of **16** in the range of +20 to +90°C.

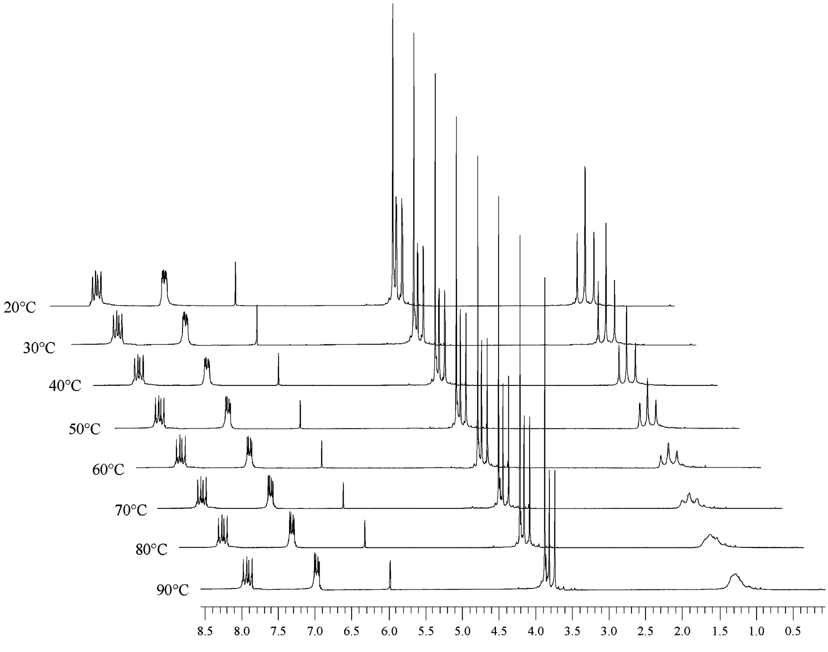


FIGURE 5 Temperature dependent ^{1}H NMR spectrum of **16** in the range of +20 to +90°C.

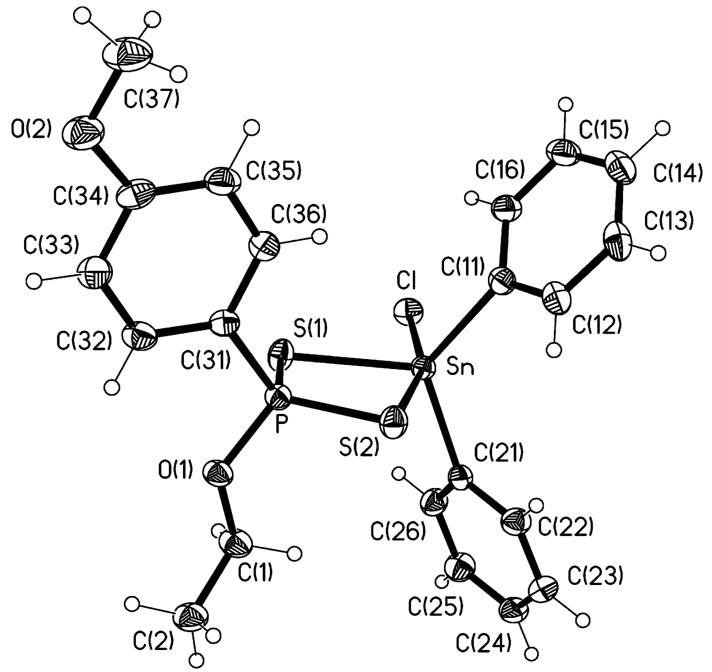


FIGURE 6 Molecular structure of $Ph_2SnCl[S(S)P(p\text{-}C_6H_4OMe)(OEt)]$ (**13**). Thermal ellipsoids with 50 % probability level. Selected bond lengths [Å] and angles [°]: Sn-C(21) 2.129(2), Sn-C(11) 2.131(2), Sn-Cl 2.4494(5), Sn-S(1) 2.4610(5), Sn-S(2) 2.8102(5), S(1)-P 2.0547(7), S(2)-P 1.9759(7), P-O(1) 1.5843(16), P-C(31) 1.7854(19), C(1)-O(1) 1.462(2), C(1)-C(2) 1.499(3), C(34)-O(2) 1.358(3), C(37)-O(2) 1.428(3); C(11)-Sn-C(21) 123.11(8), Cl-Sn-C(11) 97.35(6), Cl-Sn-C(21) 97.28(6), S(1)-Sn-C(11) 121.26(6), S(1)-Sn-C(21) 114.21(6), S(1)-Sn-Cl 86.785(17), S(2)-Sn-C(11) 88.06(6), S(2)-Sn-C(21) 93.47(5), S(2)-Sn-Cl 162.632(16), S(1)-Sn-S(2) 76.353(16), P—S(1)-Sn 91.63(2), P—S(2)-Sn 83.61(2), S(1)-P—S(2) 108.41(3), O(1)-P—S(1) 109.48(6), O(1)-P-C(31) 100.85(9), O(1)-P—S(2) 113.70(6), C(31)-P—S(1) 109.33(7), C(31)-P—S(2) 114.82(7).

mono-dithiophosphates, the bonding situation at the tin atom is somewhat different. In $Ph_3Sn[S_2P(OEt)_2]$[18] and $Ph_3Sn[S_2P(OCMe_2CMe_2O)]$[19] the PS_2-containing ligands are monodentate; although, in the latter example, a weak secondary Sn—S interaction can be found. A monodentate bonding pattern was also found in the crystal structure of the *mono*-dithiophosphinato complex $[2\text{-}(Me_2NCH_2)C_6H_4]SnPh_2[S_2PPh_2]$,[20] in which the Sn-S bond length is 2.5837(11) Å and therefore significantly longer compared to the short Sn-S bond in **13**, an interesting observation since the P—S bond lengths are comparable with those in **13**. A clear

TABLE IV Crystal Data of 13, 17, 18 and 21

Compound	13	17	18	21
Formula	$C_{21}H_{22}ClO_2PS_2Sn$	$C_{52}H_{50}GeO_4P_2S_4Si_2$	$C_{18}H_{26}O_4P_2S_4Sn$	$C_{22}H_{34}O_4P_2S_4Sn$
M_r[gmol^{-1}]	555.62	1134.0	615.26	671.36
Habit	Colorless block	Colorless needle	Colorless prism	Colorless tablet
Dimensions (mm)	0.33 × 0.24 × 0.17	0.45 × 0.10 × 0.05	0.29×0.22 × 0.21	0.15 × 0.11 × 0.08
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	P-1	C2/c	C2/c
Cell constants				
a (Å)	10.1075(6)	13.1513(10)	28.4311(16)	33.867(2)
b (Å)	12.1342(8)	14.0660(12)	6.3150(4)	6.3556(4)
c (Å)	18.5827(12)	15.4404(14)	14.1992(8)	15.1491(11)
α(°)	90	86.091(3)	90	90
β(°)	90	75.771(3)	100.231(4)	113.321(1)
γ(°)	90	76.629(3)	90	90
V (Å^3)	2279.1(3)	2693.4(4)	2508.8(3)	2994.4(4)
Z	4	2	4	4
D_x (Mg m^{-3})	1.619	1.398	1.629	1.489
μ(mm^1)	1.506	0.949	1.501	1.264
F(000)	1112	1172	1240	1368
T (°C)	−140	−140	−140	−140
$2\theta_{max}$	60	57	60	57
Transmissions	0.544/0.784	0.7016/0.9541	0.6701/0.7435	0.7712/0.9112
No. of Reflections:				
Measured	48474	43046	23472	20288
Independent	6645	13281	3646	3701
R_{int}	0.0311	0.0831	0.0180	0.0777
Parameter	256	617	135	154
Restraints	0	0	0	0
wR(F^2, all Refl.)	0.0508	0.1101	0.0429	0.0558
R(F, $>4\sigma(F)$)	0.0210	0.0518	0.0161	0.0295
S	1.066	1.009	1.032	0.943
max. Δ/σ	<0.001	<0.001	<0.001	<0.001
max. $\Delta\rho$ (e Å^3)	0.87	0.62	0.42	0.45

monodentate bonding situation has also been observed in the stannocane $O(CH_2CH_2S)_2^nBuSn[S_2P(OCH_2CEt_2CH_2O)]$ bearing a cyclic dithiophosphato ligand, in which the non-bonding Sn-S distance to the P—S double bond is too long (3.710 Å) for considering a secondary interaction.[21] The central P—S-Sn-S four membered ring in **13** is nearly exactly planar with a corresponding dihedral angle of 179.50(2)°. Steric requirements lead to a distorted tetrahedral environment at phosphorus with bond angles between 100.85(9)° and 114.82(7)°. The tin is the central atom in a five-coordinate trigonal bipyramidal geometry, with the Cl-Sn-S(2) bond angle (162.63°) smaller than 180° because of the stronger P—S(2) bond. In the crystal packing, the molecules are linked via secondary non-classical hydrogen bonding employing the chlorine atoms [C(37)-H(37)—Cl^i 2.87, C(2)-H(2)—Cl^{ii} 2.86 Å; ^{i} x − 0.5, −y + 0.5, −z, ^{ii} x + 0.5, −y + 0.5, −z].

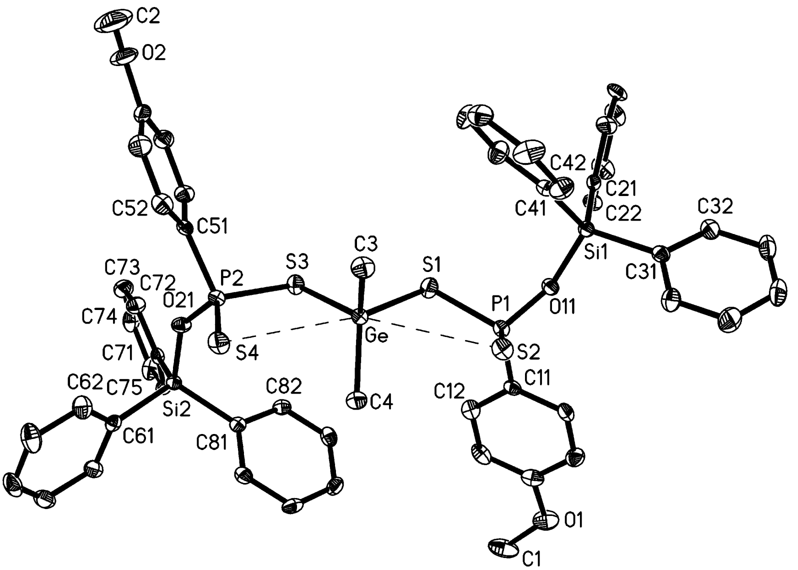


FIGURE 7 Molecular structure of $Me_2Ge[S_2P(p\text{-}C_6H_4OMe)(OSiPh_3)]_2$ **(17)**. Thermal ellipsoids with 50 % probability level. Hydrogens and CS_2 solvate omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge-C(3) 1.928(3), Ge-C(4) 1.926(3), Ge-S(1) 2.2759(9), Ge-S(3) 2.2625(9), Ge—S(2) 3.4983(9), Ge—S(4) 3.3974(9), P(1)-S(1) 2.0732(11), P(1)-S(2) 1.9407(12), P(2)-S(3) 2.0761(11), P(2)-S(4) 1.9325(11), P(1)-O(11) 1.583(2), P(1)-C(11) 1.795(4), P(2)-O(21) 1.576(2), P(2)-C(51) 1.790(3), Si(1)-O(11) 1.677(2), Si(2)-O(21) 1.667(2), C(1)-O(1) 1.428(4), C(2)-O(2) 1.412(6); C(3)-Ge-C(4) 120.21(15), S(1)-Ge-S(3) 88.75(3), S(1)-Ge-C(3) 108.72(11), S(1)-Ge-C(4) 111.70(11), S(3)-Ge-C(3) 112.35(11), S(3)-Ge-C(4) 110.69(10),Ge-S(1)-P(1) 101.38(4), Ge-S(3)-P(2) 102.21(4), P(1)-O(11)-Si(1) 137.42(15), P(2)-O(21)-Si(2) 142.36(15), C(1)-O(1)-C(14) 117.5(3), C(2)-O(2)-C(54) 117.4(3).

The molecular structure of $Me_2Ge[S_2P(p\text{-}MeOC_6H_4)(OSiPh_3)]_2$ (**17**) is shown in Figure 7. Suitable crystals were grown from a CS_2 solution by layering with hexane at room temperature. The compound crystallizes with one CS_2 solvate per formula unit in the triclinic space group P-1 (Table IV).

The coordination geometry at germanium is best described as distorted tetrahedral with the wide angle between the methyl groups [C(3)-Ge-C(4) 120.21(15)°] and a much smaller one between the sulfur atoms [S(1)-Ge-S(3) 88.75(3)°]. A similar geometry is found in the tin derivatives **18** and **21**, where these differences are of course larger. The other bond angles at germanium are very close to the ideal tetrahedral environment.

The dithiophosphonato ligands are bound in a fashion between anisobidentate and monodentate. Thus, there are clearly assignable P—S single and double bonds with P(1)-S(1) 2.0732(11), P(2)-S(3) 2.0732(11) Å, and P(1)-S(2) 1.9407(12), P(2)-S(4) 1.9325(11) Å, respectively. This is accompanied by Ge-S bond lengths of Ge-S(1) 2.2759(9) and Ge-S(3) 2.2625(9) Å. Similar values were found in the dithiophosphates $Ph_3Ge[S_2P(OMe)_2]$ and $Ph_2Ge[S_2P(OMe)_2]_2$,[22 $Me_2Ge[S_2POCMe_2CMe_2O]_2$,[23 the cyclic *mono*-dithiophosphates $Ph_3Ge[S_2POCMe_2CMe_2O]$, $Ph_3Ge[S_2POCH_2CMe_2CH_2O]$ and $Ph_3Ge[S_2POCH_2CEt_2CH_2O]{\cdot}C_6H_6$,[24 and the *mono*-dithiophosphinates $Ph_3Ge(S_2PR_2)$; R = Me, Ph,[25] whereas shorter Ge-S bonds [2.218(2) to 2.236(2) Å] are observed in the dithiophosphates $Ge[S_2P(OMe)_2]_4$ and $[(\mu\text{-}S)Ge[S_2P(OMe)_2]_2]_2$.[26 Although the SPSGe moieties in **17** are not planar, as indicated by the torsion angles S(2)-P(1)-S(1)-Ge –24.94(7)° and S(4)-P(2)-S(3)-Ge –8.41(7)°, and the angles at phosphorus are relatively large [S(1)-P—S(2) 115.52(5)°, S(3)-P(2)-S(4) 114.46(5)°], weak secondary Ge-S interactions of Ge—S(2) 3.4983(9) and Ge—S(4) 3.3974(9) Å can be observed. In comparison, the Ge(II) derivative $Ge[S_2PMe_2]_2$ shows an anisobidentate bonding fashion of the dithiophosphinato ligands.[27]

In the cell packing, the molecules of **17** are linked by non-classical hydrogen bonds of the type CH(methyl)—S and CH(phenyl)—S [C(1)-H(1)—S(3)^{i} 2.85, C(44)-H(44)—S(4)^{ii} 2.89 Å; ^{i} $-x, -y+1, -z$, ^{ii} $-x+1, -y, -z$]. The CS_2 molecules are placed in gaps and do not interact via secondary bonding.

Since the molecular structures of $Me_2Sn[S_2P(p\text{-}MeOC_6H_4)(OMe)]_2$ (**18**) (Figure 8) and $Me_2Sn[S_2P(p\text{-}MeOC_6H_4)(O^{i}Pr)]_2$ (**21**) (Figure 9) differ only slightly, they are discussed together. Suitable single crystals for X-ray analysis were obtained from a dichloromethane solution (**18**) or from a THF solution (**21**) by layering with hexane at ambient temperature using the slow diffusion method. Both compounds crystallize in the monoclinic space group C2/c with half a molecule in the asymmetric unit because of crystallographic symmetry (both Sn atoms are located on a twofold axis).

The crystal structures show that the dithiophosphonate ligands are bound in an anisobidentate manner. This is supported by the P—S bond lengths of P—S(1) 2.0584(4) Å and P—S(2) 1.9580(4) Å in **18** [P—S(1) 2.0605(8) Å and P—S(2) 1.9562(8) Å in **21**], indicating localized P—S single and double bonds. As a consequence, the Sn-S bond lengths differ markedly. Apparently, the molecules of **18** and **21** contain strong Sn-S single bonds [Sn-S(1) 2.5059(3) Å (**18**); 2.5031(6) Å (**21**)] and show secondary interactions [Sn-S(2) 3.1090(3) Å (**18**); 3.1529(6) Å (**21**)],

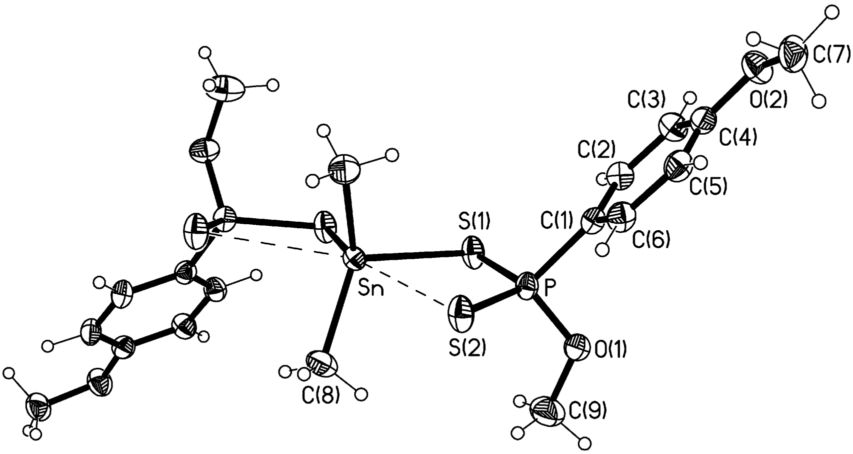


FIGURE 8 Molecular structure of $Me_2Sn[S_2P(p\text{-}C_6H_4OMe)(OMe)]_2$ (**18**). Thermal ellipsoids with 50 % probability level. Selected bond lengths [Å] and angles [°]: Sn-C(8) 2.1183(12), Sn-S(1) 2.5059(3), Sn-S(2) 3.1090(3), P—S(1) 2.0584(4), P—S(2) 1.9580(4), P-C(1) 1.7894(12), P-O(1) 1.5971(9), O(1)-C(9) 1.4403(16), O(2)-C(4) 1.3604(15), O(2)-C(7) 1.4331(17); C(8)-Sn-C(8)^{i} 131.04(8), C(8)-Sn-S(1) 110.84(4), C(8)-Sn-S(1)^{i} 105.39(4), S(1)-Sn-S(1)^{i} 82.914(14), Sn-S(1)-P 96.012(14), S(1)-P—S(2) 111.311(18), S(1)-P-O(1) 106.56(4), S(1)-P-C(1) 109.81(4), O(1)-P-C(1) 99.56(5), C(1)-P—S(2) 114.16(4), O(1)-P—S(2) 114.65(4), P-O(1)-C(9) 120.01(9). Symmetry operator i: $-x + 1, y, -z + 3/2$

leading to a distorted geometry at the tin atom. The coordination geometry could be regarded as distorted octahedral (considering secondary bonds) or as distorted tetrahedral (ignoring the secondary bonds) with C-Sn-C bond angles of 131.04(8)° (**18**) and 129.69(13)° (**21**) much larger than the ideal one. As expected, the geometry around the phosphorus atoms is distorted tetrahedral with bond angles between 99.3(2) and 115.3(2)° (**18**) [98.67(9) to 115.79(6)° (**21**)]. The S-P—S-Sn four-membered rings are almost planar as indicated by a corresponding torsion angle S(2)-P—S(1)-Sn of 4.15(2)° (**18**) and 0.38(4)° (**21**), respectively. Comparable bonding situations are found in the *bis*-dithiophosphinato derivatives $[Me_2Sn(S_2PR_2)_2]$; R = Me,[28] Et[29] and the *bis*-dithiophosphato compound $Ph_2Sn[S_2P(OEt)_2]_2$,[30] where the ligands are bound asymmetrically in an anisobidentate fashion. In the case of tin, one unique example for an isobidentate bound *bis*-dithiophosphato ligand was found in $Ph_2Sn[S_2P(OPr^i)_2]_2$, in which the Sn-S bonds are virtually identical (2.678, 2.689 Å), but much longer than in **13** and **18**.[31]

The molecules of **18** are linked by non-classical hydrogen bonds of the type CH(methyl)—S and CH(phenyl)—O [C(7)-H(7)—S(2)^{i} 3.00,

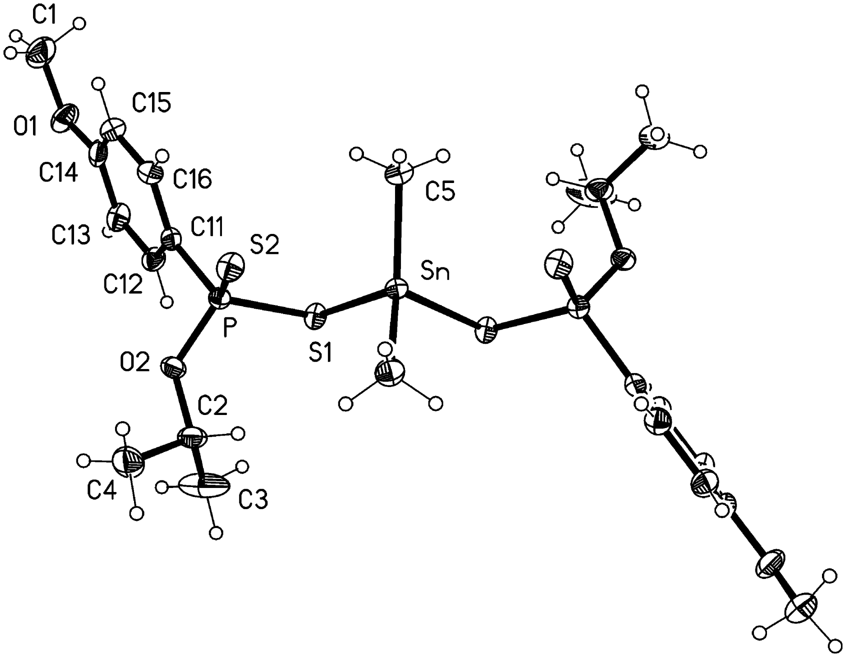


FIGURE 9 Molecular structure of $Me_2Sn[S_2P(p\text{-}C_6H_4OMe)(O^iPr)]_2$**(21)**. Thermal ellipsoids with 50 % probability level. Selected bond lengths [Å] and angles [°]: Sn-C(5) 2.118(2), Sn-S(1) 2.5031(6), Sn-S(2) 3.1529(6), P—S(1) 2.0605(8), P—S(2) 1.9562(8), P-C(11) 1.795(2), P-O(2) 1.5935(15), O(1)-C(1) 1.427(3), O(2)-C(2) 1.467(3), O(1)-C(14) 1.363(3); C(5)-Sn-C(5)^i 129.69(13), C(5)-Sn-S(1) 106.65(7), C(5)-Sn-S(1)^i 110.65(6), S(1)-Sn-S(1)^i 82.51(3), Sn-S(1)-P 97.33(3), S(1)-P—S(2) 111.09(4), S(1)-P-O(2) 106.52(6), S(1)-P-C(11) 109.25(7), O(2)-P-C(11) 98.67(9), C(11)-P—S(2) 114.61(8), O(2)-P—S(2) 115.79(6), C(2)-O(2)-P 121.11(14). Symmetry operator i: −x, y, −z + 1/2

C(3)-H(3)—O(2)^{ii} 2.55 Å; ^{i} −x + 1/2, y + 1/2, −z + 1/2,^{ii} −x + 1/2, −y + 3/2, −z + 1]. In the packing diagram of **21**, there are only non-classical hydrogen bonds of the type CH(phenyl)—S with C(12)-H(12)—S(2)^{iii} 2.90 Å; ^{iii} x, y − 1, z.

As a conclusion, it seems that the coordination pattern in dithiophosphinato complexes is not predictable so far. Steric requirements should play a role, but even in cases where these are not too big (as in **13**), the ligand is often not bound symmetrically. Therefore, it is likely that apart from the often observed unsymmetrical bridging in transition metal chelates, where the bridging mode is strongly influenced by the electronic structure of the metal atom, the coordination mode is mostly dependent on a mixture of electronic and crystal lattice effects (delocalization in the PS_2 moiety, non-classical hydrogen bonding and secondary interactions of the type M—S). Further X-ray and electronical studies are necessary to investigate these influences.

EXPERIMENTAL

General Remarks

All reactions were performed under dry nitrogen atmosphere using standard Schlenk techniques. Toluene, *n*-hexane and petroleum benzene were freshly distilled under nitrogen from sodium/benzophenone ketyl. Dichloromethane was freshly distilled under nitrogen from P_4O_{10}. Alcohols were refluxed over $CaSO_4$ or CaO and then distilled. Dried solvents were stored over molecular sieves and under nitrogen. Lawesson's reagent, butyllithium (1,6 M in hexane), triphenylsilanol, organogermanium, and organotin chlorides were purchased from Aldrich. Hexaphenyldigermoxane and hexaphenyldistannoxane were prepared according to literature methods.[32,33]

^1H, ^{13}C, and ^{31}P NMR spectra were recorded in chloroform-d_1, aceton-d_6 or water-d_2 solutions, using a Bruker DRX-400, a Bruker DPX-200, or a Bruker AC-200 spectrometer operating at 400(200) MHz for ^1H, 100(50) MHz for ^{13}C and 162(81) MHz for ^{31}P. Chemical shifts are given in ppm relative to TMS (internal standard) or to residual protons of the deuterated solvents $CDCl_3$ ($\delta = 7.24$), $(CD)_3CO(CD)_3$ ($\delta = 2.04$), and D_2O ($\delta = 4.67$) for ^1H, $CDCl_3$ ($\delta = 77.0$) and $(CD)_3CO(CD)_3$ ($\delta = 29.8$) for ^{13}C and to H_3PO_4 85% (external standard) for ^{31}P. Coupling constants (*J*) are given in Hz. All heteronuclear measurements were recorded under ^1H decoupling, if not otherwise stated.

IR spectra were recorded on a Bio-Rad FTS 165 spectrometer as KBr pellets from 300 to 4000 cm^{-1} using 1 mg of substance in 150 mg of KBr per pellet.

Crystal Structure Analyses

The crystal structures for **13, 17, 18**, and **21** were performed on a Bruker SMART 1000CCD area detector (graphite-monochromated Mo-K_α radiation, $\lambda = 71.073$ pm) at $-140°C$ in the ω- and ϕ-scan mode. Empirical absorption corrections were applied using the internal program SADABS. The structures were solved by direct methods using SHELXS-86/97,[34] and subjected to full-matrix least-squares refinement on F^2 using SHELXL-93/97,[35] with anisotropic displacement parameters for non-H atoms. Methyl groups were treated as rigid groups, all other hydrogen atoms were included using a riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 268965 **(13),** CCDC 600136 **(17),** CCDC 268996 **(18)** and CCDC 600137(**21**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code +(44)1223/336033; E-mail: deposit@ccdc.cam.ac.uk).

Syntheses

Ammonium 4-Methoxyphenyl–O–methyl–dithiophosphonate, $NH_4[S_2P$(p-$MeOC_6H_4)(OMe)]$ (1)

A 250 mL three-necked round bottom flask was charged with 10 g (24.72 mmol) of Lawesson's reagent (LR) in 150 mL of benzene. To this suspension was added dropwise 10 mL of methanol. The mixture was refluxed for 2 hs. Then, anhydrous gaseous ammonia was bubbled slowly through the solution at 0°C via a glass syringe, which immediately yielded a white precipitate. The solid was filtered off, washed with benzene and dried in vacuum. Yield: 97%, mp. 180°C.

^{1}H NMR (D_2O): $\delta = 3.80$ (s, 3H, CH_3-O-C), 3.54 (d, $^3J_{PH} = 14.8$ Hz, 3H, CH_3-O-P), 6.98 (m, 4H, C-C_6H_4-O); ^{31}P NMR (D_2O): $\delta = 108.9$; IR: 1598(s), 1569(w), 1498(s), 1429(m), 1404(s), 1302(m), 1287(m), 1180(m), 1175(m), 1105(s), 1019(vs), 827(m), 808(w, sh), 801(m), 739(s), 719(m), 680(vs), 649(m), 627(m), 555(s), 550(m, sh), 525(w), 388(m).

Lithium 4-Methoxyphenyl–O-methyl–dithiophosphonate, $Li[S_2P$(p-$MeOC_6H_4)(OMe)]$ (2)

Methanol, 5 mL, was added with stirring to a suspension of 2.022 g (5 mmol) of Lawesson's reagent in 100 mL toluene. The mixture was heated under reflux for 2 h, giving a clear solution. Toluene and excess of methanol were removed under reduced pressure and an oily product was obtained. The product was redissolved in 70 mL of toluene, cooled to −20°C and treated with 6 mL (8.54 mmol) *n*-BuLi, 1,6 M in hexane. Instantaneously, a white precipitate was formed. The reaction mixture was stirred at ambient temperature for 1 h. Then the white solid was filtered off, washed with toluene and hexane and dried in vacuum. Yield: 57%, mp. 475–480°C.

^{1}H NMR (CD_3OCD_3): $\delta = 3.80$ (s, 3H, CH_3-O-C), 3.42 (d, $^3J_{PH} = 14.6$ Hz, 3H, CH_3-O-P), 6.82–8.14 (m, 4H, C-C_6H_4-O); ^{31}P NMR (CD_3OCD_3): $\delta = 109.7$.

Lithium 4-Methoxyphenyl-O-ethyl–dithiophosphonate, $Li[S_2P$(p-$MeOC_6H_4)(OEt)]$ (3)

Similarly, from 2.022 g (5 mmol) of Lawesson's reagent and 5 mL of ethanol in 100 mL of toluene followed by addition of 5.5 mL (8.05 mmol) of *n*-BuLi (1.6 M in hexane) at −20°C, **3** was obtained. Yield: 52%, m.p. > 250°C.

^{1}H NMR (CD_3OCD_3): $\delta = 1.11$ (t, $^3J_{HH} = 7.1$ Hz, 3H, CH_3-CH$_2$-O), 3.80 (s, 3H, CH_3-O-C), 3.84–3.92 (m, 2H, CH$_3$-CH_2-O), 6.82–8.13 (m, 4H, C-C_6H_4-O); ^{31}P NMR (CD_3OCD_3): $\delta = 106.7$.

Lithium 4-Methoxyphenyl–O-isopropyl-dithiophosphonate, Li[S$_2$P(p-MeOC$_6$H$_4$)(O^{i}Pr)] (4)

Similarly, the reaction of 3.20 g (7.42 mmol) of Lawesson's reagent and 8 mL of *iso*-propanol in 90 mL of toluene followed by addition of 8 mL (14.83 mmol) *n*-BuLi (1.6 M in hexane) at –20°C, afforded **4**. Yield: 83%, m.p. > 250°C.

^{1}H NMR (CD_3OCD_3): $\delta = 1.14$ (d, $^3J_{HH} = 6.2$ Hz, 6H, CH_3-CH-CH_3), 3.80 (s, 3H, CH_3—O—C), 5.00–5.20 (m, H, CH$_3$—CH—CH$_3$), 6.90–7.94 (m, 4H, C—C_6H_4-O); ^{31}P NMR (CD_3OCD_3): $\delta = 104.8$; IR: 1595 (m), 1498 (m), 1372 (w), 1301 (w, sh), 1292 (w), 1246 (s), 1192 (w, sh), 1182 (m), 1110 (m, sh), 1101 (s), 1026(m), 942 (s), 869 (m), 823 (m), 802 (m), 736 (s), 685 (m), 650 (m), 630 (m), 557 (s).

Lithium 4-Methoxyphenyl–O-tert-butyl–dithiophosphonate, Li[S$_2$P(p-MeOC$_6$H$_4$)(O^{t}Bu)] (5)

To a solution of 1 mL (10 mmol) of *t*-BuOH in 30 mL of toluene 6.24 mL (10 mmol) of *n*-BuLi (1.6 M in hexane) was added dropwise at 0°C. After 1 h of stirring, the resulting solution was added to the suspension of 2.022 g (5 mmol) of Lawesson's reagent in 50 mL of toluene. The reaction mixture was stirred at ambient temperature for 24 hrs. The white solid formed was filtered off, washed with toluene and hexane and dried in vacuum. Yield: 68%, m.p. >250°C.

^{1}H NMR (CD_3OCD_3): $\delta = 1.54$ (s, 3H, CH_3—C—), 3.81 (s, 3H, CH_3—O—C), 6.82–8.05 (m, 4H, C—C_6H_4—O); ^{31}P NMR (CD_3OCD_3): $\delta = 96.3$; IR: 1596 (s), 1571 (w), 1499 (s), 1467 (w), 1368 (w), 1292 (m), 1253 (s), 1178 (m), 1106 (s), 1028 (m), 956 (m, br), 908 (w, br), 829 (w), 801 (m), 666 (m), 650 (m), 624 (m), 551 (m).

Lithium 4-Methoxyphenyl–O-triphenylsilyl–dithiophosphonate, Li[S$_2$P(p-MeOC$_6$H$_4$)(OSiPh$_3$)] (6)

A solution of 3.42 g (12.37 mmol) of triphenylsilanol in 100 mL of toluene was added dropwise to a suspension of 2.50 g (6.18 mmol) of Lawesson's reagent in 70 mL of toluene. The mixture was stirred at 80°C for 3 h. The resulting clear solution was cooled to −25°C and treated with 9 mL of *n*-BuLi (1.6 M in hexane, 14.4 mmol), yielding a white precipitate. After complete addition the mixture was stirred at ambient temperature for 1 h. The white solid was filtered off, washed with toluene and hexane and dried in vacuum. Yield: 91%, m.p. >250°C.

^{1}H NMR (CD_3OCD_3): $\delta = 3.72$ (s, 3H, CH_3-O-C), 6.66–7.98 (m, 4H, C-C_6H_4-O, 15H, C_6H_5-SiO); ^{31}P NMR (CD_3OCD_3): $\delta = 96.5$; IR: 1590 (s), 1499 (s), 1463 (w), 1429 (s), 1304 (m, sh), 1290 (m), 1255 (s), 1184 (m), 1119 (s), 1107 (s, sh), 1030 (s, sh), 1010 (s), 1004 (s), 989 (s), 831 (w), 800 (m), 744 (w), 715 (s), 700 (s, sh), 668 (m), 650 (m, sh), 626 (m), 539 (s), 515 (s), 506 (s), 488 (m), 376 (m).

Trimethylgermanium(IV)-4-Methoxyphenyl-O-methyl-dithiophosphonate, $Me_3Ge[S_2P(p\text{-}MeOC_6H_4)(OMe)]$ (7)

A 250 mL three-necked round bottom flask was charged with 1 g (3.96 mmol) of **2** in 70 mL of toluene. Then 0.5 mL (3.96 mmol) of Me_3GeCl was added at ambient temperature and the mixture was stirred for 3 h. The precipitated lithium chloride was removed by filtration over dry Cellite. An oily product was obtained after evaporation of the solvent under reduced pressure, which could not be crystallized.

^{1}H NMR ($CDCl_3$): $\delta = 0.58$ (s, 9H, CH_3-Ge), 3.66 (d, $^3J_{PH} = 15.4$ Hz, 3H, CH_3-O-P), 3.75 (s, 3H, CH_3-O-C), 6.89–8.00 (m, 4H, C-C_6H_4-O); ^{31}P NMR ($CDCl_3$): $\delta = 96.5$.

Trimethylgermanium(IV)-4-Methoxyphenyl-O-triphenylsilyl-dithiophosphonate, $Me_3Ge[S_2P(p\text{-}MeOC_6H_4)(OSiPh_3)]$ (8)

Similarly, compound **8** was obtained from 1 g (2.06 mmol) of **6** and 0.26 mL (2.06 mmol) of Me_3GeCl as an oil, which was crystallized from CH_2Cl_2 and hexane. Yield: 76%, m.p. 100–103°C.

^{1}H NMR ($CDCl_3$): $\delta = 0.55$ (s, 9H, CH_3-Ge); 3.81 (s, 3H, CH_3-O-C); 6.77–7.93 (m, 4H, C-C_6H_4-O, 15H, C_6H_5-Si); ^{13}C NMR ($CDCl_3$): $\delta = 3.3$ (d, $^3J_{PC} = 3.3$ Hz, Ge-CH_3); 55.3 (OCH_3); 161.9 (d, $^4J_{PC} = 3.3$ Hz, C_p of $-C_6H_4$-); 132.0 (d, $^3J_{PC} = 14.7$ Hz, C_m of $-C_6H_4$-); 113.2 (d, $^2J_{PC} = 16.4$ Hz, C_o of $-C_6H_4$-); C_i of $-C_6H_4$- not resolved; 132.7 (d, $^4J_{PC} = 1.4$ Hz, C_i of C_6H_5); 135.7 (C_o, C_6H_5); 127.7 (C_m of C_6H_5); 130.3 (C_p, C_6H_5); ^{31}P NMR ($CDCl_3$): $\delta = 81.7$; IR: 1654 (w), 1598 (m), 1500 (m), 1430 (m), 1258 (m), 1179 (w), 1120 (s), 1108 (s), 1035 (s), 1024 (s), 996 (m), 826 (m), 802 (w), 724 (w, sh), 714 (s), 697 (m), 669 (w), 607 (m), 526 (m, sh), 517 (s), 508 (s), 481 (w), 378 (w).

Trimethyltin(IV)-4-methoxyphenyl-O-methyl-dithiophosphonate, $Me_3Sn[S_2P(p\text{-}MeOC_6H_4)(OMe)]$ (9)

Similarly, compound **9** was prepared from 1 g (3.96 mmol) of **1** and 0.79 g (3.96 mmol) of Me_3SnCl as an oil, which could not be crystallized.

^{1}H NMR ($CDCl_3$): $\delta = 0.54$ (s, $^2J^{119}_{SnH} = 57.3$ Hz, $^2J^{117}_{SnH} = 55$ Hz, 9H, CH_3-Sn), 3.62 (d, $^3J_{PH} = 15.5$ Hz, 3H, CH_3-O-P), 3.73 (s, 3H, CH_3-O-C), 6.83–7.88 (m, 4H, C-C_6H_4-O); ^{31}P NMR ($CDCl_3$): $\delta = 99.0$.

Trimethyltin(IV)-4-methoxyphenyl-O-triphenylsilyldithiophosphonate, $Me_3Sn[S_2P(p\text{-}MeOC_6H_4)(OSiPh_3)]$ (10)

Compound **10** was obtained similarly from 1 g (2.06 mmol) of **6** and 0.41 g (2.06 mmol) of Me_3SnCl as a white solid. Yield: 78%, m.p. 103–105°C.

^{1}H NMR ($CDCl_3$): $\delta = 0.50$ (s, 9H, CH_3-Sn); 3.81 (s, 3H, CH_3-O-C); 6.78–7.93 (m, 4H, C-C_6H_4-O, 15H, C_6H_5-Si); ^{13}C NMR ($CDCl_3$): $\delta = -1.8$ (CH_3-Sn); 55.3 (CH_3-O-C); 161.7 (d, $^4J_{PC} = 3.3$ Hz, C_p of $-C_6H_4$-); 131.6 (d, $^3J_{PC} = 14.7$ Hz, C_m of $-C_6H_4$-); 113.2 (d, $^2J_{PC} = 16.4$ Hz, C_o of $-C_6H_4$-); 133.5 (C_i, d, $^1J_{PC} = 125.6$ Hz, C-P); 132.8 (C_i, C-Si); 135.7 (C_o, C_6H_5); 127.7 (C_m, C_6H_5); 130.3 (C_p, C_6H_5); ^{31}P NMR ($CDCl_3$): $\delta = 83.9$; IR: 1597 (m), 1499 (m), 1430 (m), 1296 (w), 1256 (m), 1177 (w), 1120 (s), 1107 (s), 1033 (s), 1020 (s), 996 (m), 827 (w), 801 (w), 724 (w, sh), 714 (s), 698 (s), 682 (m), 669 (m), 609 (m), 527 (m), 509 (s), 480 (m), 436 (m).

Triphenyltin(IV)-4-methoxyphenyl-O-methyldithiophosphonate, $Ph_3Sn[S_2P(p\text{-}MeOC_6H_4)(OMe)]$ (11)

Compound **11** was synthesized similarly employing 1.19 g (4.95 mmol) of **2** and 1.91 g (4.95 mmol) of Ph_3SnCl. An oily product was obtained, which could not be crystallized. Yield: 90%.

^{1}H NMR ($CDCl_3$): $\delta = 3.65$ (d, $^3J_{PH} = 15.5$ Hz, 3H, CH_3-O-P), 3.83 (s, 3H, CH_3-O-C), 6.86–7.93 (m, 4H, C-C_6H_4-O, 15H C_6H_5-Sn); ^{31}P NMR ($CDCl_3$): $\delta = 96.0$.

Triphenyltin(IV)-4-methoxyphenyl-O-triphenylsilyldithiophosphonate, $Ph_3Sn[S_2P(p\text{-}MeOC_6H_4)(OSiPh_3)]$ (12)

Treatment of compound **6** (2.84 g, 4.94 mmol) with Ph_3SnCl (1.9 g, 4.93 mmol) afforded compound **12** as a white solid. Yield: 90%, m.p. 162–163°C.

^{1}H NMR ($CDCl_3$): $\delta = 3.8$ (s, 3H, CH_3-O-C); 6.62–7.71 (m, 4H, C-C_6H_4-O, 15H, C_6H_5-Si, 15H C_6H_5-Sn); ^{31}P NMR ($CDCl_3$): $\delta = 81.5$.

Diphenyltin(IV)-Chloro-4-methoxyphenyl-O-ethyldithiophosphonate, **$Ph_2SnCl[S_2P(p\text{-}MeOC_6H_4)(OEt)]$ (13)**

Similarly, compound **13** was obtained from 1.26 g (4.95 mmol) of **3** and 1.7 g (4.95 mmol) of Ph_2SnCl_2 as an oil, which was crystallized from CH_2Cl_2 and hexane. Yield 47%, m.p. 71–72°C.

^{1}H NMR ($CDCl_3$): $\delta = 1.32$ (t, $^3J_{HH} = 7.1$ Hz, 3H, CH_3-CH_2-O); 3.83 (s, 3H, CH_3-O-C); 4.10–4.22 (m, 2H, CH_3-CH_2-O); 6.91–8.15 (m, 4H, P-C_6H_4-O, 10H, C_6H_5-Sn); ^{31}P NMR ($CDCl_3$): $\delta = 90.0$.

Triphenyltin(IV)-4-methoxyphenyl-O-triphenylstannyl-dithiophosphonate, $Ph_3Sn[S_2P(p\text{-}MeOC_6H_4)(OSnPh_3)]$ (14)

A 250 mL three-necked round-bottom flask was charged with 0.14 g (0.35 mmol) of Lawesson's reagent and 0.5 g (0.7 mmol) of $(Ph_3Sn)_2O$ in 60 mL of toluene. The reaction mixture was stirred at ambient temperature for 17 h, giving a clear solution. Removal of the solvent afforded an oil, which was crystallized from CH_2Cl_2 and hexane. Yield: 75%, m.p. 172°C.

^{1}H NMR ($CDCl_3$): $\delta = 3.82$ (s, 3H, CH_3-O-C); 7.28–7.73 (m, 4H, C-C_6H_4-O, 30H, C_6H_5-Sn); ^{31}P NMR ($CDCl_3$): $\delta = 68.3$; IR: 1597 (s), 1501 (s), 1482 (m), 1432 (s), 1301 (m), 1261 (s), 1179 (m), 1121 (s), 1075 (s), 1021 (s), 995 (s), 829 (w), 804 (w), 731 (vs), 696 (vs), 668 (m), 531 (w), 454 (m, sh), 444 (m), 374 (w), 330 (w).

Triphenylgermanium(IV)-4-methoxyphenyl-O-triphenylgermyl-dithiophosphonate, $Ph_3Ge[S_2P(p\text{-}MeOC_6H_4)(OGePh_3)]$ (15)

Similarly, **15** was prepared from 0.16 g (0.4 mmol) of Lawesson's reagent and 0.5 g (0.8 mmol) of $(Ph_3Ge)_2O$ in 60 mL of toluene. Yield: 56%, mp.63°C.

^{1}H NMR ($CDCl_3$): $\delta = 3.80$ (s, 3H, CH_3-O-C); 6.62–7.76 (m, 4H, C-C_6H_4-O, 30H, C_6H_5-Ge); ^{31}P NMR ($CDCl_3$): $\delta = 83.6$; IR: 1596 (s), 1499 (m), 1432 (s), 1306 (w), 1253 (s), 1183 (m), 1106 (m), 1029 (m), 956 (s, br), 802 (w), 735 (s), 696 (m), 625 (m), 548 (s), 459 (m), 327 (m).

The following bis(dithiophosphonato) complexes have been prepared according to the procedure for the synthesis of **7**.

Dimethylgermanium(IV)-Bis(-4-methoxyphenyl-O-methyl-dithiophosphonate), $Me_2Ge[S_2P(p\text{-}MeOC_6H_4)(OMe)_2$ (16)

Compound **16** was obtained from 1.86 g (7.37 mmol) of **1** and 4.42 mL (3.69 mmol) of Me_2GeCl_2 as a white solid. Yield: 81%, m.p. 55°C.

cis-**16**. ^{1}H NMR ($CDCl_3$): $\delta = 1.04$ (3H, CH_3-Ge); 1.32 (3H, CH_3-Ge); 3.67 (d, $^3J_{PH} = 15.6$ Hz, 6H, CH_3-O-P); 3.76 (6H, CH_3-O-C); 6.83–7.88 (m, 8H, P-C_6H_4-O); ^{13}C NMR ($CDCl_3$): $\delta = 8.9$ (CH_3-Ge); 10.7 (CH_3-Ge); 51.9 (d, $^2J_{PC} = 7{,}1$ Hz, CH_3-O-P); 55.4 (CH_3-O-C); 162.7 (d, $^4J_{PC} = 3.5$ Hz, C_p); 132.7 (d, $^3J_{PC} = 14.2$ Hz, C_m);113.7 (d, $^2J_{PC} = 16.4$ Hz, C_o); 128.8 (d, $^1J_{PC} = 127.3$ Hz, C_i); ^{31}P NMR ($CDCl_3$): $\delta = 94.30$.

trans-**16**. ^{1}H NMR (CDCl$_3$): $\delta = 1.19$ (6H, CH_3-Ge); 3.68 (d, $^3J_{\mathrm{PH}} = 15.6$ Hz, 6H, CH_3-O-P); 3.77 (6H, CH_3-O-C); 6.83–7.88 (m, 8H, P-C_6H_4-O); ^{13}C NMR (CDCl$_3$): $\delta = 9.8$ (CH_3-Ge); 51.9 (d, $^2J_{\mathrm{PC}} = 7.1$ Hz, CH_3-O-P); 55.4 (CH_3-O-C); ^{31}P NMR (CDCl$_3$): $\delta = 94.33$.

IR. 1597 (s), 1502 (s), 1456 (w), 1407 (w), 1300 (s), 1265 (s), 1181 (s), 1114 (s), 1024 (vs), 836 (w), 802 (m, sh), 785 (m), 682 (s), 669 (m), 642 (m), 614 (s), 527 (s), 513 (s), 479 (m), 386 (m).

Dimethylgermanium(IV)-Bis(4-methoxyphenyl-O-triphenylsilyl-dithiophosphonate, $Me_2Ge[S_2P(p\text{-}MeOC_6H_4)(OSiPh_3)_2$ (17)

Complex **17** was prepared from 2 g (4.13 mmol) of **6** and 0.24 mL (2.07 mmol) of Me$_2$GeCl$_2$. A white solid was obtained. Yield: 51%, m.p. 70°C.

cis-**17**. ^{1}H NMR (CDCl$_3$): $\delta = 1.00$ (3H, CH_3-Ge); 1.07 (3H, CH_3-Ge); 3.80 (6H, CH_3-O-C); 6.75–8.07 (m, 8H, P-C_6H_4-O, 30H, C_6H_5-Si); ^{13}C NMR (CDCl$_3$): $\delta = 8.5$ (CH_3-Ge); 10.7 (CH_3-Ge); 55.3 (CH_3-O-C); 162.1 (C$_p$ of—C_6H_4-); 131.6 (d, $^3J_{\mathrm{PC}} = 15.2$ Hz, C$_{\mathrm{m}}$ of—C_6H_4-); 113.4 (d, $^2J_{\mathrm{PC}} = 17.0$ Hz, C$_{\mathrm{o}}$ of—C_6H_4-); 132.3 (d, $^1J_{\mathrm{PC}} = 124.3$ Hz, C$_{\mathrm{i}}$ of—C_6H_4-) 132.4 (C$_{\mathrm{i}}$, C_6H_5-); 135.6 (C$_{\mathrm{o}}$, C_6H_5-); 127.8 (C$_{\mathrm{m}}$, C_6H_5-); 130.5 (C$_p$, C_6H_5-); ^{31}P NMR (CDCl$_3$): $\delta = 79.46$.

trans-**17**. ^{1}H NMR (CDCl$_3$): $\delta = 1.03$ (6H, CH_3-Ge); 3.82 (6H, CH_3-O-C); 6.75–8.07 (m, 8H, P-C_6H_4-O, 30H, C_6H_5-SiO); ^{13}C NMR (CDCl$_3$): $\delta = 9.5$ (CH_3-Ge); 55.3 (CH_3-O-C); 162.1 (C$_p$ of—C_6H_4-); 131.6 (d, $^3J_{\mathrm{PC}} = 15.2$ Hz, C$_{\mathrm{m}}$ of—C_6H_4-); 113.4 (d, $^2J_{\mathrm{PC}} = 17.0$ Hz, C$_{\mathrm{o}}$ of—C_6H_4-); 132.3 (d, $^1J_{\mathrm{PC}} = 124.3$ Hz, C$_{\mathrm{i}}$ of—C_6H_4-) 132.4 (C$_{\mathrm{i}}$, C_6H_5-); 135.6 (C$_{\mathrm{o}}$, C_6H_5-); 127.8 (C$_{\mathrm{m}}$, C_6H_5-); 130.5 (C$_p$, C_6H_5-); ^{31}P NMR (CDCl$_3$): $\delta = 79.50$.

IR: 1595 (s), 1500 (s), 1430 (s), 1297 (w), 1255 (m), 1179 (m), 1119 (s), 1015 (m), 983 (s), 830 (w), 727 (m), 7148 (s), 697 (s), 669 (m), 607 (w), 506 (s), 476 (w), 375 (w).

Dimethyltin(IV)-Bis(-4-methoxyphenyl-O-methyl-dithiophosphonate), $Me_2Sn[S_2P(p\text{-}MeOC_6H_4)(OMe)_2$ (18)

Compound **18** was prepared from 1 g (3.96 mmol) of **1** and 0.44 g (2 mmol) of Me$_2$SnCl$_2$. A white solid was obtained. Yield: 89%, m.p. 109–111°C.

^{1}H NMR (CDCl$_3$): $\delta = 1.54$ (s, $^2J^{119}_{\mathrm{SnH}} = 79.1$ Hz, $^2J^{117}_{\mathrm{SnH}} = 76.0$ Hz, 6H, CH_3-Sn); 3.74 (s, 6H, CH_3-O-C); 3.77 (d, $^3J_{\mathrm{PH}} = 15.7$ Hz, 6H, CH_3-O-P), 6.96–7.95 (m, 8H, P-C_6H_4-O); ^{13}C NMR (CDCl$_3$): $\delta = 17.5$ (CH_3-Sn); 52.9 (d, $^2J_{\mathrm{PC}} = 7.1$ Hz, CH_3-O-P); 56.6 (CH_3—O-C), 163.7 (d, $^4J_{\mathrm{PC}} = 3.3$ Hz, C$_p$ of —C_6H_4-); 133.1 (d, $^3J_{\mathrm{PC}} = 14.3$ Hz, C$_{\mathrm{m}}$ of —C_6H_4-); 114.9 (d, $^2J_{\mathrm{PC}} = 16.4$ Hz, C$_{\mathrm{o}}$ of—C_6H_4-); 130.3 (d, $^1J_{\mathrm{PC}} = 127.3$ Hz, C-P); ^{31}P NMR

($CDCl_3$): $\delta = 98.7$; IR: 1596 (s), 1567 (w), 1504 (s), 1455 (w), 1444 (w), 1409 (w), 1309 (w, sh), 1300 (s), 1266 (s), 1183 (s), 1116 (s), 1027 (vs), 836 (s), 817 (m), 820 (m), 777 (s), 669 (m), 646 (s), 643 (s), 618 (s), 613 (s), 530 (s), 520 (s), 483 (m), 435 (w), 375 (w).

Dimethyltin(IV)-Bis(4-methoxyphenyl-O-triphenylsilyl-dithiophosphonate), $Me_2Sn[S_2P(p\text{-}MeOC_6H_4)(OSiPh_3)_2$ (19)

Compound **19** was obtained from 1 g (2.06 mmol) of **6** and 0.23 g (1.03 mmol) of Me_2SnCl_2, as a white solid. Yield: 70%, m.p. 145°C.

^{1}H NMR ($CDCl_3$): $\delta = 1.16$ ($^2J^{119}_{SnH} = 77.4$ Hz, $^2J^{117}_{SnH} = 64.5$ Hz, 6H, CH_3-Sn); 3.80 (6H, CH_3-O-C); 6.77–6.83 (m, 4H, P-C_6H_4-O); 7.24–7.65 (m, 30H, C_6H_5-Si); 7.71–7.83 (m, 4H, P-C_6H_4-O); ^{13}C NMR ($CDCl_3$):$\delta =$ 15.7 (SnCH_3); 55.4 (O-CH_3); 161.9 (C_p of —C_6H_4-); 131.4 (d, $^3J_{PC} = 15.8$ Hz, C_m of —C_6H_4-); 113.5 (d, $^2J_{PC} = 17.7$ Hz, C_o of —C_6H_4-); C_i of —C_6H_4- not resolved; 132.5 (C_i, C_6H_5-); 135.7 (C_o, C_6H_5-); 127.9 (C_m, C_6H_5-); 130.6 (C_p, C_6H_5-); ^{31}P NMR ($CDCl_3$): $\delta = 84.3$.

IR: 1596 (s), 1570 (w), 1500 (s), 1462 (w), 1429 (s), 1306 (m, sh), 1297 (m), 1256 (s), 1179 (m), 1119 (vs), 1032 (s, sh), 1015 (s), 1005 (s, sh), 988 (s), 830 (m), 801 (m), 743 (w), 716 (vs), 697 (s), 679 (m), 633 (w), 621 (w), 611 (m), 529 (s), 513 (s), 481 (m), 397 (w), 376 (w).

Dimethyltin(IV)-Bis(-4-methoxyphenyl-O-ethyl-dithiophosphonate), $Me_2Sn[S_2P(p\text{-}MeOC_6H_4)(OEt)_2$(20)

Derivative **20** was prepared from 0.64 g (2.5 mmol) of **3** and 0.28 g (1.3 mmol) of Me_2SnCl_2. An oil was obtained, which could not be crystallized.

^{1}H NMR ($CDCl_3$): $\delta = 1.52$ (s, 6H, CH_3-Sn); 1.27 (t, $^3J_{HH} = 7.1$ Hz, 6H, CH_3-CH_2-O); 3.75 (s, 6H, CH_3-O-C); 4.07 (qd, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 9.4$ Hz, 4H, CH_3-CH_2-O); 6.84–7.88 (m, 8H, P-C_6H_4-O); ^{13}C NMR ($CDCl_3$): $\delta = 16.4$ (CH_3-Sn); 61.7 (d, $^2J_{PC} = 7.0$ Hz, O-CH_2-CH_3); 16.0 (d, $^3J_{PC} = 9.1$ Hz, O-CH_2-CH_3); 55.4 (O-CH_3); 162.5 (d, $^4J_{PC} = 3.3$ Hz, C_p); 131.9 (d, $^3J_{PC} = 14.3$ Hz, C_m); 113.7 (d, $^2J_{PC} = 16.3$ Hz, C_o); 129.8 (d, $^1J_{PC} = 126.5$ Hz, C_i); ^{31}P NMR ($CDCl_3$): $\delta = 95.6$.

Dimethyltin(IV)-Bis(-4-methoxyphenyl-O-isopropyl-dithiophosphonate), $Me_2Sn[S_2P(p\text{-}MeOC_6H_4)(O^iPr)_2$(21)

Compound **21** was prepared from 1.34 g (5 mmol) of **4** and 0.55 g (2.5 mmol) of Me_2SnCl_2. A white solid was obtained. Yield: 72%, m.p. 115°C.

^{1}H NMR ($CDCl_3$): $\delta = 1.51$ (s, 6H,CH_3-Sn); 1.28 (d, $^3J_{HH} = 6.2$ Hz, 12H, CH_3-CH-CH_3) 3.76 (s, 6H, CH_3-O-C); 4.54–4.87 (m, 2H, CH_3-CH-CH_3), 6.48–8.28 (m, 8H, P-C_6H_4-O); ^{13}C NMR ($CDCl_3$): $\delta = 16.4$ (CH_3-Sn); 71.4 (CH_3-CH-CH_3); 24.0 (d, $^3J_{PC} = 4.2$ Hz, CH_3-CH-CH_3); 55.4

(O-CH_3); 162.3 (C_p); 131.9 (d, $^3J_{PC}$ = 14.5 Hz, C_m); 113.7 (d, $^2J_{CP}$ = 16.6 Hz, C_o); 129.3 (C_i); ^{31}P NMR ($CDCl_3$): δ = 93.5; IR: 1600 (s), 1572 (m), 1502 (s), 1407 (w), 1372 (w), 1309 (w), 1302 (m), 1257 (s), 1178 (s), 1117 (s), 1105 (m, sh), 1029 (m), 974 (vs), 891 (w), 831 (m), 803 (m), 761 (s), 669 (m), 642 (s), 619 (m), 532 (s), 512 (s).

Dimethyltin(IV)-Bis(-4-methoxyphenyl-O-tert-butyl-dithiophosphonate), $Me_2Sn[S_2P(p\text{-}MeOC_6H_4)(O^tBu)_2$ (22)

Derivative **22** has been synthesized from 0.7 g (2.48 mmol) of **5** and 0.27 g (1.23 mmol) of Me_2SnCl_2. A white solid was obtained. Yield: 74%, m.p. 128°C.

^{1}H NMR ($CDCl_3$): δ = 1.51 (s, 6H,CH_3-Sn, 18H, $(CH_3)_3$-C); 3.74 (s, 6H, CH_3-O-C); 6.41–8.27 (m, 8H, P-C_6H_4-O); ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3-Sn); $(CH_3)_3-C$ not resolved; 30.5 (d, $^3J_{PC}$ = 4.6 Hz, $(CH_3)_3$-C); 55.3 (O-CH_3); 161.8 (C_p); 131.3 (d, $^3J_{PC}$ = 14.5 Hz, C_m); 113.4 (d, $^2J_{PC}$ = 16.6 Hz, C_o); C_i not resolved; ^{31}P NMR ($CDCl_3$): δ = 84.7.

Diphenyltin(IV)-Bis(-4-methoxyphenyl-O-methyl-dithiophosphonate), $Ph_2Sn[S_2P(p\text{-}MeOC_6H_4)(OMe)_2$ (23)

Compound **23** has been obtained from 0.5 g (1.98 mmol) of **1** and 0.34 g (0.99 mmol) of Ph_2SnCl_2, as a yellow oil, which could not be crystallized.

^{1}H NMR ($CDCl_3$): δ = 3.51 (d, $^3J_{PH}$ = 15.6 Hz, 6H, CH_3-O-P); 3.75 (s, 6H, CH_3-O-C); 3.77 (s, 6H, CH_3-O-C); 6.81–8.08 (m, 8H, C-C_6H_4-O, 10H, C_6H_5-Sn); ^{31}P NMR ($CDCl_3$): δ = 94.2; 95.9.

Diphenyltin(IV)-bis(-4-methoxyphenyl-O-triphenylsilyl-dithiophosphonate), $Ph_2Sn[S_2P(p\text{-}MeOC_6H_4)(OSiPh_3)_2$ (24)

Compound **24** was obtained from 1 g (2.06 mmol) of **6** and 0.35 g (1.02 mmol) of Ph_2SnCl_2, as a yellow solid. Yield: 69%, m.p. 60°C.

^{1}H NMR ($CDCl_3$): δ = 3.78 (s, 6H, CH_3-O-C); 3.80 (s, 6H, CH_3-O-C); 6.61–7.85 (m, 8H, C-C_6H_4-O; 10H, C_6H_5-Sn; 30H, C_6H_5-Si); ^{31}P NMR ($CDCl_3$): δ = 81.0; 82.4; IR: 1595 (s), 1499 (s), 1430 (s), 1294 (m), 1256 (s), 1181 (m), 1118 (vs), 1032 (s, sh), 1017 (s, br), 993 (s), 829 (w), 803 (w), 713 (vs), 697 (s), 607 (w), 529 (s), 512 (vs), 479 (w).

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