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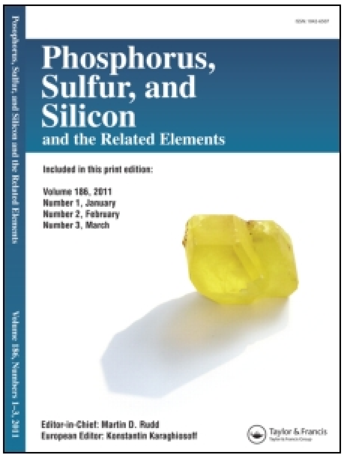

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O,O'-Dialkyl/Alkylene Dithiophosphato Bridged Heterobimetallic Complexes: Synthesis and Spectral Characterization

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O,O′-Dialkyl/Alkylene Dithiophosphato Bridged Heterobimetallic Complexes: Synthesis and Spectral Characterization

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Heterobimetallic adducts of triphenyltin (IV) O,O′-dialkyl/alkylene dithiophosphate of the formulae $[Ph_3SnS(S)P(OCH_2CH_3)_2].MA$ *and* $[Ph_3Sn\{S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2\}O}\}].MA$ $(MA = CdI_2, AgOCOCF_3, AgOCOCCl_3, AgSCN, Hg(OCOCCl_3)_2, Hg(OCOCF_3)_2, Hg(SCN)_2, HgCl_2$, *and* $FeCl_3$ *were prepared and characterized on the basis of physico-chemical and spectral (FTIR,* ^1H, ^{13}C, ^{31}P, *and* ^{119}Sn *NMR) studies. Heterobimetallic adducts were formed through the coordination of the sulfur atom of triphenyltin (IV) O,O′-dialkyl/alkylene dithiophosphate to metal acceptors.*

Keywords Dialkyl/alkylene dithiophosphate; heterobimetallic; organotin

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INTRODUCTION

In comparison to bimetallic dithiocarbamate complexes,[1–3] the tendency for a dithiophosphate ligand to act as a bridge between two metals via sulfur atoms to form hetero adducts are scarce, and few such compounds have been reported.[4,5] The interest in organotins for biological activity as a homogenous catalyst in industry[6–8] and our continuing interest in bimetallic complexes of phenylmercury alkylene dithiophosphates[5] prompted us to synthesize and characterize some related heterobimetallic adducts of triphenyltin (IV) O,O′-dialkyl/alkylene dithiophosphate derivatives with Hg (II), Cd (II), Ag (I), and Fe (III).

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RESULTS AND DISCUSSION

Triphenyltin chloride reacts readily with ammonium O,O′-dialkyl/alkylene dithiophosphates in a 1:1 molar ratio in absolute methanol and dry benzene, respectively, to afford white complexes as in Scheme 1.

$$(C_6H_5)_3SnCl + NH_4\{S(S)P(OCH_2CH_3)_2\} \rightarrow$$

$$[(C_6H_5)_3SnS(S)P(OCH_2CH_3)_2] + NH_4Cl\downarrow$$

$$(C_6H_5)_3SnCl + NH_4[S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2\}O}] \rightarrow$$

$$[Ph_3Sn\{S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2\}O}\}] + NH_4Cl\downarrow \ldots\text{eq. 1}$$

SCHEME 1

1:1 heterobimetallic adducts of triphenyltin (IV) O,O′-dialkyl/alkylene dithiophosphate with metal acceptors, such as Hg (II), Cd (II), Ag (I), and Fe (III), were obtained by stirring a mixture of the two components in absolute methanol at r.t. (Scheme 2).

$$[(C_6H_5)_3SnS(S)P(OCH_2CH_3)_2] + MA \rightarrow [(C_6H_5)_3SnS(S)P(OCH_2CH_3)_2].MA$$

$$[(C_6H_5)_3Sn\{S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2O}\}] + MA \rightarrow$$

$$[(C_6H_5)_3Sn\{S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2O}\}].\ MA \ \ldots\ldots\text{eq. 2}$$

$MA = AgOCOCF_3$, $AgOCOCCl_3$, $AgSCN$, $Hg(OCOCCl_3)_2$,

$Hg(OCOCF_3)_2$, $Hg(SCN)_2$, $HgCl_2$, CdI_2, $FeCl_3$

SCHEME 2

The analytical data of the newly synthesized triphenyltin (IV) O,O′-dialkyl/alkylene dithiophosphates are given in Table I, which indicates a 1:1 $[(C_6H_5)_3Sn{:}dtp]$ stoichiometry. The products are solid, stable at r.t., and are not affected by atmospheric oxygen and moisture. They are soluble in common organic solvents, such as $CHCl_3$, CCl_4, and C_6H_6, etc.

Analytical data for the heterobimetallic adducts are given in Tables II and III. They are of a 1:1 (donor:acceptor) stoichiometry and are solid and stable at r.t. The adducts are insoluble in common organic solvents but soluble in DMSO.

TABLE I Analytical Data of Triphenyltin(IV) O,O′-Dialkyl/Alkylene Dithiophosphate

S. no.	Compounds	Color	M.P. (°C)	Yield (%)	Elemental analysis (%) found (Calcd.) Sn	S
1.	$[(C_6H_5)_3SnS(S)P(OCH_2CH_3)_2]$	White	105	70	22.04 (22.18)	11.86 (11.98)
2.	$[(C_6H_5)_3Sn\{S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2O}\}]$	White	266	84	19.52 (19.63)	10.51 (10.60)

The molar conductance data (2.97–3.46 $\Omega^{-1}cm^2mol^{-1}$) of triphenyltin (IV) O,O′-dialkyl/alkylene dithiophosphate and their heterobimetallic adducts point toward their non-electrolytic nature in DMSO.

IR SPECTRA

FTIR spectra of triphenyltin (IV) O,O′-dialkyl/alkylene dithiophosphates were recorded in the range of 4000–450 cm^{-1} in CsI. Tentative assignments have been made on the basis of earlier reports.[5,9] Bands present at 1160, 1015, and 655 cm^{-1} (dialkyl dithiophosphate[14]) and at 1011, 796, and 709 cm^{-1} (alkylene dithiophosphate) are assigned to [ν(P)—O—C], [νP—O—(C)] and ν(P=S), respectively.

TABLE II Analytical Data of $[(C_6H_5)_3SnS(S)P(OCH_2CH_3)_2]$.MA

S. no.	MA	Color	M.P. (°C)	Yield (%)	Elemental analysis (%) found (Calcd.) Sn	Cd	Hg	Ag	Fe	S
1.	$HgCl_2$ $[C_{22}H_{25}O_2S_2PSnHgCl_2]$	White	100	76	14.49 (14.71)	—	24.57 (24.86)	—	—	7.63 (7.95)
2.	CdI_2 $[C_{22}H_{25}O_2S_2PSnCdI_2]$	White	110	78	13.32 (13.17)	12.62 (12.47)	—	—	—	6.93 (7.11)
3	$Hg(OCOCF_3)_2$ $[C_{26}H_{25}O_6S_2PSnHgF_6]$	Cream	98	68	12.00 (12.20)	—	20.42 (20.62)	—	—	7.12 (6.59)
4.	$Hg(OCOCCl_3)_2$ $[C_{26}H_{25}O_6S_2PSnHgCl_6]$	White	110	73	11.00 (11.19)	—	18.70 (18.91)	—	—	6.26 (6.04)
5.	$Hg(SCN)_2$ $[C_{24}H_{25}O_2S_4PSnN_2Hg]$	White	96	64	14.10 (13.93)	—	23.72 (23.54)	—		15.32 (15.05)
6.	$AgOCOCF_3$ $[C_{24}H_{25}O_4S_2PSnAgF_3]$	Grey	140 (d)	67	15.51 (15.70)	—	—	14.42 (14.27)	—	8.28 (8.48)
7.	$AgOCOCl_3$ $[C_{24}H_{25}O_4S_2PSnAgCl_3]$	Grey	108 (d)	72	14.52 (14.74)	—	—	12.64 (12.94)	—	7.71 (7.96)
8.	$AgSCN$ $[C_{23}H_{25}O_2S_3PSnNAg]$	Grey	140	75	16.72 (16.93)	—	—	15.18 (15.38)	—	13.51 (13.72)
9.	$FeCl_3$ $[C_{22}H_{25}O_2S_2PSnFeCl_3]$	Brown	82	66	16.88 (17.02)	—	—	—	7.90 (8.01)	9.28 (9.19)

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TABLE III Analytical Data of $[(C_6H_5)_3Sn(S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2O}].MA$

S. no.	MA	Color	M.P. (°C)	Yield (%)	Elemental analysis (%) found (Calcd.) Sn	Cd	Hg	Ag	Fe	S
1.	$HgCl_2$	White	106	75	13.35	—	22.67	—	—	7.16
	$[C_{27}H_{33}O_2S_2PSnHgCl_2]$				(13.57)		(22.93)			(7.34)
2.	CdI_2	White	212 (d)	72	12.06	12.20	—	—	—	6.53
	$[C_{27}H_{33}O_2S_2PSnCdI_2]$				(12.24)	(12.05)				(6.60)
3	$Hg(OCOCF_3)_2$	Green	136	67	12.72	—	21.66	—	—	6.87
	$[C_{31}H_{33}O_6S_2PSnHgF_6]$				(12.94)		(21.86)			(7.00)
4.	$Hg(OCOCCl_3)_2$	Green	142	64	12.41	—	20.58	—	—	6.59
	$[C_{31}H_{33}O_6S_2PSnHgCl_6]$				(12.27)		(20.74)			(6.65)
5.	$Hg(SCN)_2$	White	106	73	12.63	—	21.91	—		13.82
	$[C_{29}H_{33}O_2S_4PSnN_2Hg]$				(12.90)		(21.79)			(13.95)
6.	$AgOCOCF_3$	Grey	120	68	14.21	—	—	13.28	—	7.54
	$[C_{29}H_{33}O_4S_2PSnAgF_3]$				(14.38)			(13.10)		(7.78)
7.	$AgOCOCl_3$	Grey	108	78	13.81	—	—	12.66		7.22
	$[C_{29}H_{33}O_4S_2PSnAgCl_3]$				(13.58)			(12.84)	—	(7.34)
8.	$AgSCN$	Grey	105	76	15.36	—	—	14.80	—	12.73
	$[C_{28}H_{33}O_2S_3PSnNAg]$				(15.45)			(14.92)		(12.50)
9.	$FeCl_3$	Yellow	206	84	15.16	—	—	—	7.19	8.17
	$[C_{27}H_{33}O_2S_2PSnFeCl_3]$				(15.33)				(7.27)	(8.34)

The band of medium intensity at 540 cm^{-1} (dialkyl dithiophosphate[14]) and 534 cm^{-1} (alkylene dithiophosphate) may be attributed to the ν(P—S) vibration and invariably indicates the presence of the unidentate O,O′-dialkyl/alkylene dithiophosphate group attached to the triphenyltin moiety. The ν(Sn—S) stretching mode of vibration could not be identified because they lie beyond the recorded range of the spectra. A weak band at 460 ± 2 cm^{-1} may be assigned to the out-of-plane bending vibration mode of the phenyl ring attached to the tin atom.[10]

In the IR spectra of the heterobimetallic complexes of triphenyltin (IV) O,O′-dialkyl/alkylene dithiophosphate. The MA (MA referred to in Eq. (2)), absorption due to ν(P=S) is shifted to a lower frequency and appears at 640 ± 6 cm^{-1} (dialkyl dithiophosphate) and 675 ± 3 cm^{-1} (alkylene dithiophosphate). The absorption due to ν(P—S) remains almost unaffected, indicating the presence of the unidentate O,O′-dialkyl/alkylene dithiophosphate group.

The considerable lowering of the ν(P=S) frequency indicates a coordination of sulfur atoms of the ligand to the tin and other metal acceptors. There is a shift of electron density from oxygen and carbon through phosphorus and sulfur to the other metal atom.

Two absorptions associated with [ν(P)—O—C] and [νP—O—(C)] appear at 1174 ± 3 cm^{-1}, 1020 ± 2 cm^{-1} (dialkyl dithiophosphate), and at 1019 ± 2 cm^{-1}, and 807 ± 3 cm^{-1} (alkylene dithiophosphate) in the heterobimetallic adducts suggested unidentate mode of coordination. It is evident that on coordination from the sulfur to the metal acceptor, a considerable shift of electron density increases the bond order of the C—O and P—O bonds. The ν(Sn—Ph) stretching mode of vibration remains almost unaffected and appear at 462 ± 2 cm^{-1}. The ν(Sn—S) stretching mode of vibration could not be identified because they lie beyond the recorded range of spectra.

The trichloroacetate group is unidentately coordinated[11,12] as ν_{asy} (OCO) and ν_{sym} (OCO) are located at 1685 ± 5 cm^{-1} and 1338 ± 8 cm^{-1} respectively, with $-\Delta\nu = 347 \pm 13$ cm^{-1}. The trifluoroacetate group is unidentate[11] since ν_{asy} (OCO) and ν_{sym} (OCO) appear at 1636 ± 2 cm^{-1} and 1380 ± 3 cm^{-1}, respectively, with $-\Delta\nu = 256 \pm 8$ cm^{-1}. The thiocyanate group is S-bonded since ν(SCN), ν(C═S), and δ(SCN), appear at ~2096 ± 2, 718 ± 2, and 468 cm^{-1}, respectively.[13]

The absorption due to Hg—Cl, Cd—I, and Fe—Cl stretching modes could not be identified because they lie beyond the recorded range of spectra.

It is concluded that one of the sulfur atoms of the dithiophosphate group in triphenyltin (IV) O,O′-dialkyl/alkylene dithiophosphate is coordinated to another metal atom, giving rise to dithiophosphato bridged heterobimetallic adducts.

^{1}H, ^{13}C, ^{31}P and ^{119}Sn NMR Spectra

In ^{1}H NMR spectra of $[(C_6H_5)_3SnS(S)P(OCH_2CH_3)_2].Hg(OCOCF_3)_2$, there is low-field shift in C_6H_5-Sn (~0.1 ppm), OCH_2 (~0.4 ppm), and CH_3 (~0.36 ppm) signals.

In the ^{1}H NMR of $[(C_6H_5)_3Sn\{S(S)\underline{POCH_2C(C_2H_5)\ (C_4H_9)CH_2O}\}].FeCl_3$ and $[(C_6H_5)_3Sn\{S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2O}\}].Hg(SCN)_2$, a low-field shift in C_6H_5-Sn (~0.1 ppm), OCH_2 (~0.3 ppm), and $CH_2 + CH_3$ (~0. 2 ppm) signals appear. The low-field shift in an aryl as well as an alkyl/alkylene proton indicates a considerable shift of electron density from the dithiophosphates moiety to the metal atom through sulfur. In heterobimetallic adducts, a higher deshielding of alkyl/alkylene protons favor the presence of bridging ligands,[15,16] which support results obtained from infrared spectral data.

In the ^{31}P NMR (proton decoupled) spectra of $[(C_6H_5)_3SnS(S)P(OCH_2CH_3)_2]$ and $[(C_6H_5)_3Sn\{S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2O}\}]$, a single peak is observed at δ 92.09 and δ 108.67 ppm, respectively, which is in agreement with the earlier report for a four-coordinated tin atom in dithiophosphate derivatives.[17] However, ^{31}P NMR spectra of $[(C_6H_5)_3SnS(S)P(OCH_2CH_3)_2].CdI_2$ and $[(C_6H_5)_3Sn\{S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2O}\}]$. AgSCN show a deshielding of the

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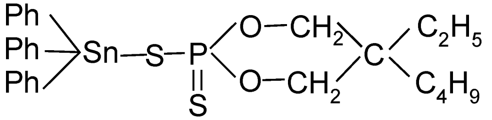

FIGURE 1 The structure of the triphenyltin (IV) O,O′-2-butyl-2-ethyl-1,3-propane dithiophosphate.

phosphorus atom to an extent of about δ 3–17 ppm from the parent triphenyltin (IV) O,O′-dialkyl/alkylene dithiophosphate. The deshielding of the phosphorus atom in heterobimetallic adducts supports findings of IR and ^1H NMR spectra.

In $^{13}C\{^1H\}$ NMR spectra, the significant deshielding of the alkyl carbon in heterobimetallic complexes supports the results obtained from IR, ^1H, and ^{31}P NMR spectra.

The observed ^{119}Sn chemical shift of δ −81.24 ppm $[(C_6H_5)_3Sn\{S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2O}\}]$ may be interpreted in terms of four coordinated tin atoms.[17] However, a tin atom in $[(C_6H_5)_3Sn\{S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2O}\}].AgSCN$ is found to be shielded than parent triphenyltin (IV) O,O′-2-butyl-2-ethyl-1,3-propane dithiophosphate, and a peak at δ −114.92 ppm is observed. It is concluded that on coordination from the sulfur to metal acceptors, the shift of electron density from the phenyl group shielded the tin atom.

On the basis of analytical and spectral (IR, ^1H, ^{31}P, ^{13}C, and ^{119}Sn) evidences, a tetrahedral structure has been assigned to triphenyltin (IV) O,O′-2-butyl-2-ethyl-1,3-propane dithiophosphate (Figure 1). A similar structure has been assigned to $[(C_6H_5)_3SnS(S)P(OCH_2CH_3)_2]$.[14]

In the case of heterobimetallic complexes, it may be concluded that two molecules of metal acceptors are bound to two different sulfur atoms. The dithiophosphate group thus acts as a bridge between triphenyltin and an other metal. The structures in Figure 2 may be proposed for triphenyltin (IV) O,O′-dialkyl/alkylene dithiophosphate MA.

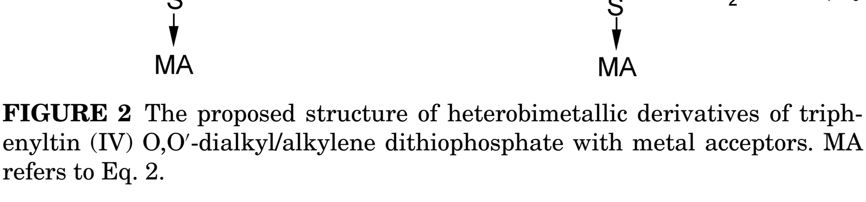

FIGURE 2 The proposed structure of heterobimetallic derivatives of triphenyltin (IV) O,O′-dialkyl/alkylene dithiophosphate with metal acceptors. MA refers to Eq. 2.

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In these heterobimetallic adducts, Hg(II) and Cd(II) are tricoordinated,[18–20] while Ag(I) and Fe(III) possess a coordination number of 2 and 4, respectively.[5,21]

EXPERIMENTAL

Triphenyltin chloride (E. Merck) was used as such. Solvents were dried and purified by standard procedures.[22] O,O′-dialkyl/alkylene dithiophosphoric acids, their ammonium salts, and triphenyltin O,O′-diethyl dithiophosphate were prepared according to an established procedure.[14,23] The molar conductance of the compounds were measured using a dip-type conductivity cell on a decible conductivity meter model DC 610 in anhydrous DMSO. Metal contents and sulfur were determined by a reported procedure.[24]

FTIR spectra were recorded on a Bruker IFS 66V (CsI, 4000–450 cm^{-1}).^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 300 MHz, 75.47 MHz, and 121.5 MHz on a Bruker DRX 300 FT NMR spectrophotometer using TMS (as an internal standard) and H_3PO_4 (as an external standard), respectively, in $CDCl_3$ and DMSO (d_6). ^{119}Sn NMR spectra were recorded at 11.7 Tesla on a Bruker Avance 500 FT NMR spectrophotometer using Me_4Sn (as external standard) in CH_3OH (d_4).

The Reaction of $(C_6H_5)_3SnCl$ and $NH_4[S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2O}]$

Triphenyltin chloride (3.85 g, 0.01 mol) and ammonium salt of O,O′-butyl-2-ethyl-1, 3-propane dithiophosphoric acid (2.71 g, 0.01 mol) in

TABLE IV ^1H NMR Spectral Data of Representative Compounds

S. no.	Compounds	Aryl protons (δ, ppm)	Alkyl/Alkylene protons (δ, ppm)
1.	$[(C_6H_5)_3SnS(S)P(OCH_2CH_3)_2]$	7.28–7.80 (m, 15H, C_6H_5-Sn)	3.91–3.97 (dq, 4H, OCH_2) 1.09 (t, 6H, CH_3)
2.	$[(C_6H_5)_3SnS(S)P(OCH_2CH_3)_2]\cdot Hg(OCOCF_3)_2$	7.30–7.86 (m, 15H, C_6H_5-Sn)	4.25–4.35 (m, 4H, OCH_2) 1.40-1.44 (t, 6H, CH_3)
3.	$[(C_6H_5)_3Sn\{S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2O}\}]$	7.31–7.80 (m, 15H, C_6H_5-Sn)	3.88–3.87 (d, 4H, OCH_2) 0.70–1.32 (m, 14H, all CH_2 and CH_3)
4.	$[(C_6H_5)_3Sn\{S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2O}\}]\cdot FeCl_3$	7.40–7.88 (m, 15H, C_6H_5-Sn)	4.12–4.18 (d, 4H, OCH_2) 0.84–1.58 (m, 14H, all CH_2 and CH_3)
5.	$[(C_6H_5)_3Sn\{S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2O}\}]\cdot Hg(SCN)_2$	7.38–7.84 (m, 15H, C_6H_5-Sn)	4.11 (d, 4H, OCH_2) 0.84–1.56 (m, 14H, all CH_2 and CH_3)

TABLE V ^{13}C, ^{31}P, and ^{119}Sn NMR Spectral Data of Representative Compounds

S. no.	Compounds	^{13}C (δ, ppm)	^{31}P (δ, ppm)	^{119}Sn (δ, ppm)
1.	$[(C_6H_5)_3SnS(S)P(OCH_2CH_3)_2]$	137.9 (Ar-C, linked to Sn) 136.8[Ar-C, o to Sn, $^2J(^{13}C\text{-}^{119}Sn) = 90$ Hz] 128.8[Ar-C, m to Sn, $^3J(^{13}C\text{-}^{119}Sn) = 120$ Hz] 130 (Ar-C, p to Sn) 63.7(O—CH$_2$) 15.5(CH$_3$)	92.09	—
2.	$[(C_6H_5)_3SnS(S)P(OCH_2CH_3)_2].CdI_2$	136.2 (Ar-C, o to Sn) 129.5 (Ar-C, m to Sn) 129.4 (Ar-C, p to Sn) 65.0(O—CH$_2$) 16.0(CH$_3$)	109.46	—
3.	$[(C_6H_5)_3Sn\{S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2O}\}]$	—	108.67	−81.24
4.	$[(C_6H_5)_3Sn\{S(S)\underline{POCH_2C(C_2H_5)(C_4H_9)CH_2O}\}]\cdot AgSCN$	—	111.03	−114.92

absolute methanol was stirred at r.t. for 3–4 h, after which ammonium chloride was removed by filtration, and the product was isolated by stripping off the solvent from the filtrate. The compound was crystallized from a benzene-petroleum ether (40–60°C) mixture. The product was recrystallized with chloroform and dried over P_2O_5 in vacuo.

The Reaction of Triphenyltin (IV) O,O′-Dialkyl/Alkylene Dithiophosphates and Metal Acceptors

In a representative experiment, to a solution of triphenyltin (IV) O,O′-diethyl dithiophosphate (0.535 g, 0.001 mol) in absolute methanol and $Hg(OCOCCl_3)_2$ (0.436 g, 0.001 mol) in the same solvent, were stirred together at r.t. for about 4 h. The precipitated product was filtered and washed several times with methanol and finally with diethyl ether. The product was dried over P_2O_5 under vacuo.

Similar heterobimetallic products were prepared using $Hg(SCN)_2$, $HgCl_2$, $Hg(OCOCF_3)_2$, CdI_2, AgSCN, $AgOCOCCl_3$, $AgOCOCF_3$, and $FeCl_3$ as acceptors with both triphenyltin (IV) O,O′-dialkyl/alkylene dithiophosphate.

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