Unlike the result reported elsewhere,[16] no trimethyldisilane was found in the products from the reaction between potassium silyl and trimethylchlorosilane. Instead, the result can be ascribed to a transmetalation and the subsequent reactions of the products as shown by

$$KSiH_3 + (CH_3)_3SiCl \rightarrow (CH_3)_3SiK + H_3SiCl$$

$$H_3SiCl + KSiH_3 \rightarrow KCl + SiH_4 + (1/n)(SiH_2)_n$$

The trimethylsilane found after acidification must clearly have come from potassium trimethylsilyl in the condensed phase.

Potassium silyl reacting with trimethylamine-chloroborane ($Et_3N{\cdot}BH_2Cl$) gave none of the silicon-boron-bonded product reported elsewhere.[17] Instead there was a good yield of triethylamine-borane, clearly a reduction product.

Carbon dioxide and potassium silyl reacted to produce silane, carbon monoxide, potassium formate, and a solid residue containing silicon, oxygen, and hydrogen, which will be referred to as hydridosilica. The stoichiometry of the reaction was approximately

$$2KSiH_3 + 4CO_2 \rightarrow 2CO + 2KO_2CH + (1-x)SiH_4 + Si_{1+x}H_{4x}O_2$$

This was completely different from the behavior of potassium germyl with carbon dioxide:[18]

$$KGeH_3 + CO_2 \rightarrow H_3GeCO_2K$$

Moreover, if carbon dioxide was added in small increments to the potassium silyl, no carbon monoxide was formed initially. Only silane was found. As more carbon dioxide was added, the amount of silane produced per increment diminished. Finally, carbon monoxide began to appear, and no silane was found.

Because the total stoichiometry of the "titration" reaction was inexact and because the reaction sequentially formed silane followed by carbon monoxide, it is believed that an unstable intermediate was formed. This intermediate, which also acted as a reducing agent toward carbon dioxide, was produced in a fast reaction between potassium silyl and carbon dioxide. Silane and potassium formate were also products of this initial reaction. The intermediate reacted more slowly with carbon dioxide than did the silyl anion, and in dilute solution it did nothing. After all the silyl anion was consumed, however, and the reducing power resided in the intermediate, it could react with carbon dioxide to produce carbon monoxide and hydridosilica. Up to the point at which the titration reaction seemed to have stopped, the overall consumption of carbon dioxide was less than in the single reaction. This may indicate an incomplete reaction by the more slowly reacting intermediate or a reaction of the intermediate not involving carbon dioxide.

The reaction of nitrous oxide with potassium silyl was similar in many respects to the reaction with carbon dioxide, but the stoichiometry was more variable from one experiment to the next. The equation for the reaction was approximately

$$2KSiH_3 + 3N_2O \rightarrow 3N_2 + H_2 + (1-x)SiH_4 + K_2Si_{1+x}H_{4x}O_3$$

Nitrogen is isoelectronic with carbon monoxide, but in part the products differ from those from carbon dioxide because there is no nitrogen analogue of formic acid.

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Registry No. $KSiH_3$, 13812-63-0; PCl_3, 7719-12-2; SiH_4, 7803-62-5; $Et_3N{\cdot}BH_2Cl$, 13240-39-6; $(CH_3)_3SiCl$, 75-77-4; $Et_3N{\cdot}BH_3$, 1722-26-5; $(CH_3)_3SiH$, 993-07-7; CO_2, 124-38-9; KO_2CH, 590-29-4; N_2O, 10024-97-2; NO, 10102-43-9; CO, 630-08-0; N_2, 7727-37-9; H_2, 1333-74-0; dimethylchlorophosphine, 811-62-1; dimethylphosphine, 676-59-5.

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Phenylarsenic(III) and Phenylantimony(III) Bis(dialkyl dithiophosphates): Synthesis and Multinuclear (^1H, ^{13}C, ^{31}P) NMR and Mass Spectral Studies. Crystal and Molecular Structures of $C_6H_5M[S_2P(O\text{-}i\text{-}Pr)_2]_2$ [M = Sb(III) and As(III)]

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Bis(dialkyl dithiophosphate) derivatives of the type $PhM[S_2P(OR)_2]_2$ [M = As(III), Sb(III); R = Et, *n*-Pr, *i*-Pr, Ph] have been prepared and characterized by elemental analyses and molecular weight determinations. IR and NMR (^1H, ^{13}C, ^{31}P) spectral data have been used to investigate plausible structures of these complexes, and their fragmentation pathway has been suggested on the basis of mass spectral data. The crystal structures of $PhM[S_2P(O\text{-}i\text{-}Pr)_2]_2$, M = Sb(III) (**1**) and As(III) (**2**), have been determined at room temperature by using single-crystal counter data. The crystals are isomorphous with the space group $P2_1/c$, $Z = 4$, and unit cell dimensions $a = 12.451$ (2) Å, $b = 26.681$ (6) Å, $c = 9.026$ (4) Å, and $\beta = 109.70$ (2)° for **1** and $a = 12.454$ (6) Å, $b = 26.693$ (9) Å, $c = 8.901$ (5) Å, and $\beta = 109.44$ (4)° for **2**. The structures were refined by using full-matrix least-squares techniques using 2785 statistically significant reflections for **1** and 878 reflections for **2**. The dithiophosphate ligands chelate the central atom with asymmetric M-S bonds (**1**, 2.5 and 3.1 Å; **2**, 2.3 and 3.1 Å) so that the overall geometry is octahedral with a nonbonded pair of electrons occupying an axial position trans to the phenyl group.

Introduction

The preparation, characterization, and structural features of non-transition-metal complexes with the dialkyl dithiophosphate class of anions has recently been reviewed.[1] It has been noted that although the biological activity of the organometallic dithiophosphate derivatives of arsenic(III) has been reported, little is known of their chemistry and that of the corresponding antimony(III) derivatives. In each of the crystal structures reported for the series $Sb[S_2P(OR)_2]_3$, where R = Me,[2] Et,[3] and *i*-Pr,[2] the

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Table I. Synthesis and Properties[a] of Phenylarsenic and Phenylantimony Bis(dialkyl dithiophosphates)

reactants							
$PhMCl_2$		$M'S_2P(OR)_2$					
M	mmol	M′	R	mmol	wt of salt found (calcd), g	physical state (mp, °C)	mol wt found (calcd)
As	4.22	Na	Et	8.56	0.46 (0.49)	colorless liquid	518 (522)
As	4.67	Na	*n*-Pr	9.53	0.50 (0.54)	colorless liquid	
As	4.49	NH_4	*i*-Pr	9.00	0.44 (0.48)	white cryst (48–50)	580 (578)
As	4.67	Na	Ph	9.60	0.51 (0.55)	white solid (72–74)	
Sb	3.45	Na	Et	6.92	0.35 (0.40)	pale yellow cryst (78–81)	557 (569)
Sb	2.86	Na	*n*-Pr	5.89	0.30 (0.33)	white cryst (38)	
Sb	3.97	NH_4	*i*-Pr	8.14	0.39 (0.43)	white cryst (83–88)	606 (625)
Sb	3.00	Na	Ph	6.05	0.32 (0.35)	white solid (108–110)	

[a] The analytical data for the arsenic, antimony, and sulfur contents of all the derivatives were within experimental error of the corresponding calculated values.

central antimony atom is coordinated by three asymmetrically chelating dithiophosphate ligands and the overall coordination polyhedra is consistent with the presence of a stereochemically active lone pair of electrons protruding through the triangular face formed by the sulfur atoms involved in the weak Sb–S interactions. The tris(dithiophosphate) complexes of arsenic(III) are well-known;[1] however, no structure determination for these compounds has thus far been reported. In the above context, compounds of the type RML_2 (R = organic radical; M = As(III), Sb(III); L = dialkyl dithiophosphate moiety) are of special interest as the central metal atom may acquire a coordination number of three–five in addition to the lone pair present on them. In the present communication we report the synthesis and properties of a number of phenylarsenic and phenylantimony bis(dialkyl dithiophosphates).

Experimental Section

Instrumentation. Infrared spectra were recorded in the range 4000–400 cm^{-1} or 4000–200 cm^{-1} as Nujol mulls or neat films. Mass spectra were measured at 120 °C with the ionizing source operating at 70 eV. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ solution. Internal Me_4Si was used as a standard for ^1H and ^{13}C spectra, and 85% H_3PO_4 was used as external reference for ^{31}P spectra. Arsenic and antimony were determined iodometrically, and sulfur was estimated gravimetrically as barium sulfate. Molecular weights were determined ebullioscopically by using a Gallenkamp ebulliometer fitted with a thermistor sensor in benzene solution.

Preparations. Dialkyldithiophosphoric acids and their salts were prepared by the literature method.[4] Phenyldichloroarsine[5] was prepared by the reduction of phenylarsonic acid, and phenyldichlorostibine was obtained by the method of Long and Jaffe.[6] Metal complexes were prepared by the following method: a benzene solution of $PhAsCl_2$ ($PhSbCl_2$) (0.5 mol) was added dropwise to a suspension of the dialkydithiophosphoric acid (1.0 mol); in some cases an excess of the acid was used (Table I). After the reaction mixture was stirred for 4 h, it was filtered to separate the sodium/tetraethylammonium chloride formed during the reaction. The solvent was removed under vacuum, and the product, if solid, was recrystallized from petroleum ether (bp 40–60 °C). The experimental details of all the compounds have been summarized in Table I.

Crystal Structure Determinations

Data Collection. Suitable crystals for X-ray analysis for $C_6H_5Sb[S_2P(O\text{-}i\text{-}Pr)_2]_2$ (**1**) and $C_6H_5As[S_2P(O\text{-}i\text{-}Pr)_2]_2$ (**2**) were grown from the slow evaporation of dichloromethane/hexane solutions of the compounds. Intensity data were collected on an Enraf-Nonius CAD-4F diffractometer at room temperature in the $\omega{:}2\theta$ scan mode with the use of Mo Kα (graphite monochromator) radiation, λ = 1.5418 Å. Crystals of **2** were very weakly scattering, and although data were measured to a 2θ value of 50°, only those with $2\theta \leqslant 34°$ were included in the final data set. No significant variation of three strong reflections occurred during the respective data collections. The intensity data sets were corrected for Lorentz and polarization effects and for absorption. Crystal data for **1** and **2** are presented in Table II.

Table II. Crystal Data for $PhM[S_2P(O\text{-}i\text{-}Pr)_2]_2$ [M = Sb(III), As(III)][a]

compound	$PhSb[S_2P(O\text{-}i\text{-}Pr)_2]_2$; $PhAs[S_2P(O\text{-}i\text{-}Pr)_2]_2$
formula	$C_{18}H_{33}O_4P_2S_4Sb$; $C_{18}H_{33}O_4P_2S_4As$
fw	625.4; 578.6
space group	$P2_1/c$ (C_{2h}^5, No. 14)
a, Å	12.451 (2); 12.454 (6)
b, Å	26.681 (6); 26.693 (9)
c, Å	9.026 (4); 8.901 (5)
β, deg	109.70 (2); 109.4 (4)
vol, $Å^3$	2823; 2790
D_{expt}, Mg m^{-3}	1.46; 1.36
Z	4; 4
D_{calcd}, Mg m^{-3}	1.472; 1.378
cryst dimens,[b] mm	±(100) 0.213; ±(100) 0.175 ±(010) 0.1; ±(010) 0.05 ±(011) 0.0475; ±(001) 0.0475 ±(0$\bar{1}$1) 0.0475
temp, K	295 (2); 295 (2)
radiation, Å	Mo Kα, 0.71069
F(000)	1272; 1200
μ, mm^{-1}	1.36; 1.60
transmission factors	0.9310, 0.7988; 0.8676, 0.8169
2θ limits, deg	$2 \leqslant 2\theta \leqslant 50$; $2 \leqslant 2\theta \leqslant 34$
no. of data collcd	6026; 5027
no. of unique data	4688; 3775
no. of unique data used ($I \geqslant 2\sigma(I)$)	2785; 878
final no. of params	262; 128
R	0.044; 0.078
$k/[\sigma^2(F) + g\lvert F\rvert^2]$	$k = 1.2$, $g = 0.0005$; $k = 1.0$, $g = 0.005$
R_w	0.043; 0.079

[a] Values for As(III) follow those for Sb(III). [b] From centroid.

Solution and Refinement of Structures. The position of the antimony (arsenic) atoms was determined from a three-dimensional Patterson synthesis. All remaining non-hydrogen atoms were located from subsequent difference maps, and the structures were refined by using a full-matrix least-squares method.[7] Anisotropic thermal parameters were introduced for all non-hydrogen atoms in **1**; however, hydrogen atoms were not included in the model. At convergence R = 0.044 and R_w = 0.043. The maximum residual electron density peak in the final difference map was 0.62 e $Å^{-3}$. Due to the limited data set for **2** only the As, S, and P atoms were refined anisotropically, and all remaining non-hydrogen atoms were refined isotropically. Refinement converged with R = 0.078 and R_w = 0.079, with a maximum residual peak of 0.71 e $Å^{-3}$.

Calculations were performed by using the SHELX-76 program[7] on the University of Melbourne's CYBER 170-730 computer system. Scattering factors for neutral As and Sb were taken from ref 8, and those for the remaining atoms were those incorporated in the SHELX-76 system.

Fractional atomic coordinates for **1** and **2** are listed in Table III, and the numbering scheme used is shown in Figure 1. Interatomic distances and angles are given in Tables IV and V respectively.

Results and Discussion

The facile reactions of phenyldichloroarsine and -stibine with sodium/ammonium dialkyl dithiophosphates (M′L) at ambient

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Table III. Fractional Atomic Coordinates for $PhM[S_2P(O\text{-}i\text{-}Pr)_2]_2$ [M = As(III), Sb(III)]

	M = As(III)			M = Sb(III)		
atom	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
M	0.2858 (2)	0.0983 (1)	0.1623 (4)	0.26912 (5)	0.09103 (2)	0.16984 (6)
S(1)	0.1716 (6)	0.1509 (4)	−0.0315 (9)	0.1492 (2)	0.1524 (1)	−0.0293 (3)
S(2)	0.0325 (6)	0.0694 (4)	0.1139 (9)	0.0180 (2)	0.0698 (1)	0.1191 (3)
P(1)	0.0140 (6)	0.1238 (3)	−0.0293 (9)	−0.0036 (2)	0.1255 (1)	−0.0274 (3)
O(1)	−0.0545 (14)	0.1724 (7)	−0.0053 (20)	−0.0758 (5)	0.1708 (2)	−0.0008 (7)
C(1)	−0.0294 (26)	0.1945 (13)	0.1601 (37)	−0.0504 (9)	0.1923 (4)	0.1572 (11)
C(2)	−0.0028 (30)	0.2498 (14)	0.1447 (42)	−0.0262 (11)	0.2487 (4)	0.1436 (14)
C(3)	−0.1442 (27)	0.1833 (14)	0.1934 (39)	−0.1570 (10)	0.1809 (5)	0.2013 (14)
O(2)	−0.0579 (15)	0.1149 (7)	−0.2129 (22)	−0.0798 (5)	0.1140 (2)	−0.2031 (7)
C(4)	−0.0327 (24)	0.0722 (12)	−0.2996 (36)	−0.0513 (9)	0.0729 (4)	−0.2915 (13)
C(5)	−0.1381 (29)	0.0399 (15)	−0.3471 (40)	−0.1573 (10)	0.0382 (4)	−0.3381 (14)
C(6)	−0.0112 (35)	0.0975 (18)	−0.4494 (52)	−0.0329 (14)	0.0994 (6)	−0.4325 (16)
S(3)	0.4322 (6)	0.1385 (4)	0.1043 (9)	0.4238 (2)	0.1398 (1)	0.1100 (3)
S(4)	0.5204 (7)	0.0500 (4)	0.3782 (10)	0.5022 (2)	0.0518 (1)	0.3800 (3)
P(2)	0.5689 (6)	0.1033 (3)	0.2744 (10)	0.5565 (2)	0.1059 (1)	0.2800 (3)
O(3)	0.6410 (14)	0.1472 (8)	0.3820 (21)	0.6286 (4)	0.1468 (2)	0.3918 (7)
C(7)	0.5969 (22)	0.1771 (12)	0.4809 (32)	0.5782 (7)	0.1764 (4)	0.4913 (10)
C(8)	0.6771 (30)	0.1684 (15)	0.6572 (45)	0.6607 (10)	0.1694 (5)	0.6601 (11)
C(9)	0.5093 (31)	0.2288 (16)	0.4322 (44)	0.5723 (10)	0.2312 (4)	0.4368 (13)
O(4)	0.6554 (15)	0.0890 (7)	0.1858 (22)	0.6477 (5)	0.0902 (2)	0.2039 (7)
C(10)	0.6343 (26)	0.0459 (14)	0.0829 (39)	0.6277 (9)	0.0470 (4)	0.0973 (12)
C(11)	0.7272 (33)	0.0076 (16)	0.1555 (47)	0.7179 (12)	0.0078 (5)	0.1725 (15)
C(12)	0.6488 (28)	0.0639 (15)	−0.0730 (43)	0.6387 (11)	0.0671 (5)	−0.0587 (13)
C(13)	0.2900	0.1359	0.3536	0.2733 (6)	0.1336 (3)	0.3742 (9)
C(14)	0.2986	0.1066	0.4869	0.2892 (8)	0.1057 (3)	0.5119 (11)
C(15)	0.3060	0.1294	0.6309	0.2974 (10)	0.1317 (5)	0.6506 (11)
C(16)	0.3046	0.1816	0.6417	0.2905 (9)	0.1841 (5)	0.6517 (12)
C(17)	0.2960	0.2109	0.5084	0.2757 (9)	0.2106 (4)	0.5138 (13)
C(18)	0.2887	0.1880	0.3643	0.2671 (8)	0.1852 (3)	0.3737 (11)

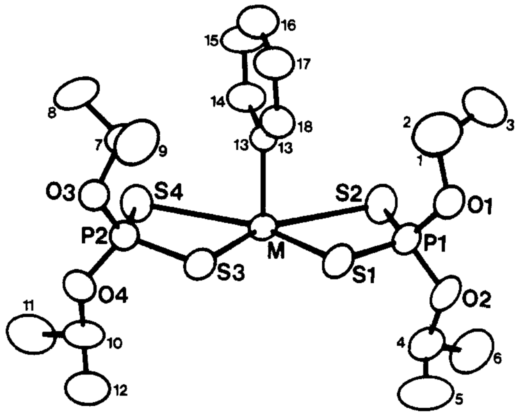

Figure 1. Numbering scheme used for $PhM[S_2P(O\text{-}i\text{-}Pr)_2]_2$ [M = As(III), Sb(III)]. The four sulfur atoms define an approximate square plane, and the lone pair of electrons is postulated to occupy a position trans to the phenyl substituent. Atoms otherwise not indicated are carbons.

Table IV. Interatomic Distances (Å) for $PhM[S_2P(O\text{-}i\text{-}Pr)_2]_2$

	dist			dist	
atoms	M = Sb	M = As	atoms	M = Sb	M = As
M–S(1)	2.516 (3)	2.310 (9)	P(2)–O(3)	1.551 (6)	1.59 (2)
M–S(2)	3.056 (2)	3.135 (8)	O(3)–C(7)	1.49 (1)	1.43 (3)
S(1)–P(1)	2.039 (3)	2.10 (1)	C(7)–C(8)	1.53 (1)	1.57 (5)
S(2)–P(1)	1.947 (4)	1.90 (1)	C(7)–C(9)	1.54 (2)	1.44 (5)
P(1)–O(1)	1.572 (6)	1.61 (2)	P(2)–O(4)	1.569 (6)	1.58 (2)
O(1)–C(1)	1.47 (1)	1.52 (4)	O(4)–C(10)	1.47 (1)	1.44 (4)
C(1)–C(2)	1.55 (2)	1.53 (5)	C(10)–C(11)	1.52 (2)	1.52 (5)
C(1)–C(3)	1.54 (2)	1.58 (4)	C(10)–C(12)	1.56 (2)	1.54 (4)
P(1)–O(2)	1.580 (6)	1.60 (2)	M–C(13)	2.152 (8)	1.962 (3)
O(2)–C(4)	1.47 (1)	1.47 (4)	C(13)–C(14)	1.40 (1)	*a*
C(4)–C(5)	1.55 (2)	1.51 (5)	C(14)–C(15)	1.41 (1)	*a*
C(4)–C(6)	1.54 (2)	1.60 (5)	C(15)–C(16)	1.40 (2)	*a*
M–S(3)	2.529 (3)	2.317 (8)	C(16)–C(17)	1.39 (2)	*a*
M–S(4)	3.067 (3)	3.187 (9)	C(17)–C(18)	1.41 (1)	*a*
S(3)–P(2)	2.048 (4)	2.09 (1)	C(18)–C(13)	1.38 (1)	*a*
S(4)–P(2)	1.941 (4)	1.90 (1)			

[a] C–C distance constrained to 1.394 Å.

temperatures in a 1:2 molar ratio in benzene yield quantitative yields of the derivatives, $PhML_2$, with the simultaneous precipitation of M′Cl:

$$PhMCl_2 + 2M'S_2P(OR)_2 \rightarrow PhM[S_2P(OR)_2]_2 + 2M'Cl$$

$$M = As(III), Sb(III) \qquad M' = Na, NH_4$$

$$R = Et,\ n\text{-}Pr,\ i\text{-}Pr,\ Ph$$

These products were found to be crystalline solids or colorless liquids, soluble in common organic solvents, monomeric in refluxing benzene, and nonvolatile under reduced pressure.

Infrared Spectra. In the IR spectra of $PhM[S_2P(OR)_2]_2$, the (P)O–C and P–O(C) stretching modes have been observed in the region 1020–970 and 850–790 cm^{-1}, respectively.[9,10] However, for the complexes where R = Ph, the aforementioned and absorbance bands shift toward higher wavenumbers and appear around 1180 and 1025 cm^{-1}, respectively. The strong bands due to $\nu(P{=\!=}S)$ vibrations present in the region 680–620 cm^{-1} in the spectra of the ligands shift to lower frequencies by approximately 30 cm^{-1} in the corresponding spectra of the phenylantimony complexes while no appreciable shift was observed in the spectra of the related phenylarsenic derivatives. The observation in IR absorbances may indicate a degree of chelation in the antimony complexes and monodentate coordination in the arsenic complex. Bands present in the 590–515 cm^{-1} region may be assigned to ν(P–S) asymmetric and symmetric vibrations. Medium-intensity ν(M–C) bands[11,12] are observed around 470 ± 15 cm^{-1}, whereas the ν(M–S) bands[13] (for the spectra recorded below 400 cm^{-1}) have been observed at approximately 375 cm^{-1}.

Mass Spectra. The mass spectra of two typical compounds of the series, i.e. $PhAs[S_2P(O\text{-}i\text{-}Pr)_2]_2$ and $PhSb[S_2P(O\text{-}n\text{-}Pr)_2]_2$,

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Table V. Bond Angles (deg) for $PhM[S_2P(O\text{-}i\text{-}Pr)_2]_2$

	angle			angle	
atoms	M = Sb	M = As	atoms	M = Sb	M = As
S(1)–M–S(2)	71.51 (8)	72.9 (3)	O(1)–P(1)–O(2)	97.0 (3)	97 (1)
S(1)–M–S(3)	79.86 (8)	83.5 (3)	M–S(3)–P(2)	95.3 (1)	98.2 (4)
S(1)–M–S(4)	150.91 (8)	155.4 (3)	M–S(4)–P(2)	82.2 (1)	77.3 (4)
S(2)–M–S(3)	151.36 (8)	156.0 (3)	S(3)–P(2)–S(4)	110.9 (2)	112.0 (5)
S(2)–M–S(4)	137.43 (7)	131.5 (3)	S(3)–P(2)–O(3)	108.7 (3)	105.4 (9)
S(3)–M–S(4)	71.20 (8)	72.0 (3)	S(4)–P(2)–O(3)	115.9 (3)	117.8 (9)
S(1)–M–C(13)	96.1 (2)	99.7 (2)	P(2)–O(3)–C(7)	119.9 (5)	122 (2)
S(2)–M–C(13)	87.4 (2)	88.9 (2)	O(3)–C(7)–C(8)	104.9 (7)	107 (3)
S(3)–M–C(13)	96.4 (2)	99.3 (2)	O(3)–C(7)–C(9)	107.3 (7)	110 (3)
S(4)–M–C(13)	84.6 (2)	86.0 (2)	C(8)–C(7)–C(9)	112.2 (9)	113 (3)
M–S(1)–P(1)	95.5 (1)	97.4 (4)	S(3)–P(2)–O(4)	108.1 (3)	105.9 (8)
M–S(2)–P(1)	82.0 (1)	78.2 (3)	S(4)–P(2)–O(4)	115.0 (3)	116.2 (9)
S(1)–P(1)–S(2)	111.0 (2)	111.5 (5)	P(2)–O(4)–C(10)	120.6 (6)	120 (2)
S(1)–P(1)–O(1)	108.3 (3)	105.2 (8)	O(4)–C(10)–C(11)	108.2 (8)	108 (3)
S(2)–P(1)–O(1)	116.0 (3)	118.7 (8)	O(4)–C(10)–C(12)	106.0 (8)	106 (3)
P(1)–O(1)–C(1)	120.1 (6)	120 (2)	C(11)–C(10)–C(12)	111 (1)	107 (3)
O(1)–C(1)–C(2)	106.7 (8)	106 (2)	O(3)–P(2)–O(4)	97.3 (3)	98 (1)
O(1)–C(1)–C(3)	104.6 (8)	102 (2)	M–C(13)–C(14)	115.7 (6)	115.06 (8)
C(2)–C(1)–C(3)	115 (1)	116 (3)	M–C(13)–C(18)	122.6 (6)	124.88 (8)
S(1)–P(1)–O(2)	107.8 (3)	104.4 (8)	C(13)–C(14)–C(15)	118.2 (8)	*a*
S(2)–P(1)–O(2)	115.6 (3)	118.4 (9)	C(14)–C(15)–C(16)	120.9 (9)	*a*
P(1)–O(2)–C(4)	121.2 (6)	121 (2)	C(15)–C(16)–C(17)	120 (1)	*a*
O(2)–C(4)–C(5)	104.7 (8)	106 (2)	C(16)–C(17)–C(18)	120 (1)	*a*
O(2)–C(4)–C(6)	103.7 (9)	104 (3)	C(17)–C(18)–C(13)	119.4 (8)	*a*
C(5)–C(4)–C(6)	114 (1)	112 (3)	C(18)–C(13)–C(14)	121.5 (8)	*a*

[a] Angles constrained to 120°.

Table VI. ^1H NMR Spectral Data[a] of $PhM[S_2P(OR)_2]_2$ Complexes

	^1H NMR, δ			
complex	CH_3–	–CH_2–	–CH	aromatic
$PhAs[S_2P(OEt)_2]_2$	1.2–1.5 (dt, 4 peaks)	3.6–4.5 (m, more than 8 peaks)		7.2–8.0 (m)
$PhAs[S_2P(O\text{-}n\text{-}Pr)_2]_2$	0.7–1.1 (dt, 4 peaks)	1.3–1.9 (h), 3.6–4.2 (m, more than 6 peaks)		7.2–7.8 (m)
$PhAs[S_2P(O\text{-}i\text{-}Pr)_2]_2$	1.2–1.5 (dd)		4.2–5.2 (m, 13 peaks)	7.2–8.1 (m)
$PhSb[S_2P(OEt)_2]_2$	1.1–1.3 (t)	3.7–4.1 (dq, 5 peaks)		7.2–8.2 (m)
$PhSb[S_2P(O\text{-}n\text{-}Pr)_2]_2$	0.7–0.9	1.3–1.7 (h), 3.5–3.8 (dt, 4 peaks)		7.2–8.1 (m)
$PhSb[S_2P(O\text{-}i\text{-}Pr)_2]_2$	1.2–1.3 (d)		4.1–4.6 (m)	7.2–8.1 (m)

[a] (d) = doublet; (t) = triplet; (h) = hextet; (m) = multiplet; (dd) = doublet of doublets; (dt) = doublet of triplets.

Table VII. ^{13}C NMR Spectral Data of $PhM[S_2P(OR)_2]_2$ Complexes[a]

	type of carbon atom			aromatic			
complex	C–CH_3	C–CH_2–CH_3	O–C	C(o)	C(m)	C(p)	δ′
$PhAs[S_2P(O\text{-}n\text{-}Pr)_2]_2$	10.01	23.69 (d) $^3J_{PC} \simeq 8.1$ Hz	69.36 (dd) $^2J_{PC} \simeq 5.4$ Hz	132.92	130.15	128.45	−1.70
$PhAs[S_2P(O\text{-}i\text{-}Pr)_2]_2$	23.41 (d) $^3J_{PC} \simeq 2.7$ Hz		73.30 (dd) $^2J_{PC} \simeq 5.4$ Hz	133.01	129.88	128.18	−1.70
$PhSb[S_2P(O\text{-}i\text{-}Pr)_2]_2$	23.33 (d) $^3J_{PC} \simeq 5.4$ Hz		72.89 (d) $^2J_{PC} \simeq 6.7$ Hz	135.96	128.81	128.00	−0.81
$PhSb[S_2P(OEt)_2]_2$	15.59 (d) $^3J_{PC} \simeq 8.1$ Hz		63.55 (d) $^2J_{PC} \simeq 5.4$ Hz	136.05	128.98	128.09	−0.89

[a] (d) = doublet; (dd) = doublet of doublets; C(o), C(m), and C(p) are the chemical shift values of the ortho, meta, and para carbon atoms of the phenyl ring. All chemical shifts in δ.

could be obtained. The peaks observed in the two spectra have been tentatively assigned to the species indicated in brackets after each mass number.

$PhAs[S_2P(O\text{-}i\text{-}Pr)_2]_2$: 549 $[(i\text{-}PrO)_2PS_2As(Ph)S_2P(OCH_2)(O\text{-}i\text{-}Pr)]$; 501 $[As\{S_2P(O\text{-}i\text{-}Pr)_2\}_2]$; 442 $[(i\text{-}PrO)_2S_2PAsS_2P(O\text{-}i\text{-}Pr)]$; 400 $[(i\text{-}PrO)_2S_2PAsS_2POH]$; 365 $[PhAsS_2P(O\text{-}i\text{-}Pr)_2$; 336 $[PhAsS_2P(OCH_2)(O\text{-}i\text{-}Pr)]$; 323 $[PhAsS_2P(OH)(O\text{-}i\text{-}Pr)]$; 316 $[(OH)_2PS_2AsS_2P(OH)]$; 281 $[PhAsS_2P(OH)_2$ and $As(S_2P)_2O]$; 261 $[SAsS_2P(O\text{-}i\text{-}Pr)]$; 229 $[As(S_2PO\text{-}i\text{-}Pr)]$; 216 $[PhAsS_2]$; 214 $[HS_2P(O\text{-}i\text{-}Pr)_2]$; 204 $[AsS_2P(OH)_2]$; 186 $[AsS_2PO]$; 184 [PhAsS]; 172 $[HS_2P(OH)(O\text{-}i\text{-}Pr)]$; 155 $[HS_2PO\text{-}i\text{-}Pr]$; 152 [PhAs]; 139 $[AsS_2]$; 130 $[HS_2P(OH)_2]$; 112 $[S_2P(OH)]$; 107 [AsS]; 75 [As].

$PhSb[S_2P(O\text{-}n\text{-}Pr)_2]_2$: 624 $[PhSb\{S_2P(O\text{-}n\text{-}Pr)_2\}_2]$; 547 $[Sb(S_2P(O\text{-}n\text{-}Pr)_2)_2]$; 488 $[(n\text{-}PrO)_2PS_2SbS_2P(O\text{-}n\text{-}Pr)]$; 411 $[PhSbS_2P(O\text{-}n\text{-}Pr)_2]$; 369 $[PhSbS_2P(OH)(O\text{-}n\text{-}Pr)]$; 344 $[SbS_2P(O\text{-}n\text{-}Pr)_2]$; 327 $[PhSbS_2P(OH)_2]$; 307 $[SSbS_2P(O\text{-}n\text{-}Pr)]$; 291 $[SbS_2PO(O\text{-}n\text{-}Pr)]$; 275 $[SbS_2P(O\text{-}n\text{-}Pr)]$; 262 $[PhSbS_2]$; 250 $[SbS_2P(OH)_2]$; 232 $[SbS_2PO)$; 230 [PhSbS]; 214 $[HS_2P(O\text{-}n\text{-}Pr)_2]$; 198 [PhSb]; 172 $[HS_2P(OH)(O\text{-}n\text{-}Pr)]$; 155 $[HS_2P(O\text{-}n\text{-}Pr)]$; 153 [SbS]; 130 $[HS_2P(OH)_2]$; 123, 121 [Sb]; 112 $[S_2P(O\text{-}H)]$.

The fragmentation patterns of the two compounds exhibit some obvious similarities. The appearance of high-intensity peaks due to sulfides and also the presence of peaks corresponding to the fragments of the ligands (m/e = 214, 172, 155, 130, 112, etc.) suggest a pyrolytic decomposition of these complexes. A comparison of the two mass spectra reveals that fragments containing Ph–As are more abundant than Ph–Sb moieties, which is in accordance with the fact that As–C bonds are stronger than Sb–C bonds.

NMR Spectra. The ^1H NMR spectra of these complexes (Table VI) show the characteristic resonances due to the alkoxy and aromatic protons. The protons attached to the carbon atom of

Table VIII. Proton-Coupled ^{31}P NMR Spectral Data of $PhM[S_2P(OR)_2]_2$ Complexes

complexes	^{31}P chem shifts, δ	multiplicity	J_{POCH}, Hz
$PhAs[S_2P(OEt)_2]_2$	89.04	5	10.0
$PhAs[S_2P(O\text{-}n\text{-}Pr)_2]_2$	89.70	5	9.3
$PhAs[S_2P(O\text{-}i\text{-}Pr)_2]_2$	86.27	3	12.7
$PhSb[S_2P(OEt)_2]_2$	92.07	5	10.0
$PhSb[S_2P(O\text{-}n\text{-}Pr)_2]_2$	92.50	5	9.4
$PhSb[S_2P(O\text{-}i\text{-}Pr)_2]_2$	88.46	3	13.4

the P–O–C group show additional coupling with the ^{31}P nuclei; interestingly, the terminal methyl protons of the alkoxy groups also exhibit splitting in the phenylarsenic complexes while no such splitting is observed in the spectra of the corresponding antimony complexes.

In the ^{13}C NMR spectra (Table VII) the ^{13}C–^{31}P NMR coupling has been observed up to three bond lengths. In phenylarsenic complexes, the α-carbon atom attached to the P–O linkage first couples with phosphorus and then is further split, giving a double doublet, which suggests the presence of nonequivalent alkyl groups in the phenylarsenic complexes. It is interesting to note that no such splitting was observed in the spectra for β- and γ-carbon atoms. The ^{13}C NMR spectra of the phenylantimony derivatives are as expected. The corrected chemical shift values δ', where $\delta' = \delta(Cp) - \delta(Cm)$ [where $\delta(Cp)$ and $\delta(Cm)$ are the chemical shift values of para and meta carbon atoms of the phenyl ring], are negative for these complexes, which illustrates the net inductive effect of the phenyl group. The more negative value found for δ' for the arsenic complexes (Table VII) is in accordance with the greater donor ability of the arsenic atom relative to that of antimony.

The ^{31}P NMR (proton-coupled) chemical shift values for these complexes (Table VIII) occur in the range expected for bidentate ligands.[14] The upfield appearance of the ^{31}P NMR signals in the arsenic complexes compared to that in the corresponding antimony complexes may be attributed to more intense π-back-donation in the arsenic complexes.

Description of Structures

Crystals of $PhSb[S_2P(O\text{-}i\text{-}Pr)_2]_2$ (**1**) and $PhAs[S_2P(O\text{-}i\text{-}Pr)_2]_2$ (**2**) are isomorphous and consist of discrete molecules separated at distances commensurate with those expected from van der Waals radii. Interatomic distances and angles are given in Tables III and IV, respectively. The two dithiophosphate ligands form an approximate basal plane, and the phenyl group occupies an axial position in the central atom's square-pyramidal environment (Figure 1). The overall geometry of the central metal atoms in **1** and **2** is consistent with the presence of a stereochemically active lone pair of electrons occupying an axial position, trans to the phenyl group, in the octahedral distribution of six electron pairs.

Of interest is the mode of coordination of the dithiophosphate ligands. The ligands chelate the central metal atom with unequal M–S bonds (Table III), and it is interesting to note that the difference between the short and long M–S bonds in **1** of approximately 0.54 Å is significantly less than the difference of approximately 0.8 Å found in **2**. These results confirm the infrared observations, which suggest a tendency toward monodentate coordination of the ligands in these complexes, in particular for the arsenic derivatives. In this context it is worth noting that the degree of asymmetry observed for **1** is comparable to that reported for the tris(dithiophosphates) $Sb[S_2P(OR)_2]_3$ (R = Me,[2] Et,[3] and *i*-Pr[2]). The geometry of the dithiophosphate ligands in **1** and **2** are similar, as expected, as can be seen from a comparison of the chemically equivalent M–S–P and S–P–S angles; see Table IV. Therefore, the greater asymmetry found in **2** most probably reflects the smaller size of the arsenic atom compared to the antimony atom.

The anomalous splitting found in the NMR spectra may be explained in terms of these solid-state observations. In **2** the terminal isopropyl groups lying on the same side of the basal plane, defined by the two dithiophosphate moieties, as the phenyl group (Figure 1) would be significantly closer to the phenyl group than in **1** as a result of the smaller size of the central arsenic atom, and hence an interaction, albeit weak, is postulated between these organo substituents. In **2** the methine atoms are inequivalent as a result of the intramolecular interaction suggested above, and hence two distinct α-carbon resonances would be expected. In **1** no such interaction is apparent, as the isopropyl groups are further away from the phenyl substituent, and hence all methine carbon atoms are equivalent on the NMR time scale.

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Registry No. $PhAs[S_2P(OEt)_2]_2$, 97336-97-5; $PhAs[S_2P(O\text{-}n\text{-}Pr)_2]_2$, 97336-98-6; $PhAs[S_2P(O\text{-}i\text{-}Pr)_2]_2$, 97336-99-7; $PhAs[S_2P(OPh)_2]_2$, 97337-00-3; $PhSb[S_2P(OEt)_2]_2$, 97337-01-4; $PhSb[S_2P(O\text{-}n\text{-}Pr)_2]_2$, 97337-02-5; $PhSb[S_2P(O\text{-}i\text{-}Pr)_2]_2$, 97337-03-6; $PhSb[S_2P(OPh)_2]_2$, 97337-04-7; $PhAsCl_2$, 696-28-6; $PhSbCl_2$, 5035-52-9; $NaS_2P(OEt)_2$, 3338-24-7; $NaS_2P(O\text{-}n\text{-}Pr)_2$, 42401-77-4; $NaS_2P(O\text{-}i\text{-}Pr)_2$, 1071-06-3; $NaS_2P(OPh)_2$, 36408-60-3.

Supplementary Material Available: Listings of anisotropic thermal parameters and structure factors for **1** and **2** (18 pages). Ordering information is given on any masthead page.

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[14] Glidewell, C. *Inorg. Chim. Acta* **1977**, *25*, 159.