DALTON

The first crystal structures of mixed chalcogen derivatives $SnR_2[(OPPh_2)(SPPh_2)N]_2$ (R = Me or Ph)

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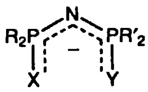
The compounds $SnR_2[(OPPh_2)(SPPh_2)N]_2$ (R = Me, Bu^n, CH_2Ph or Ph) were prepared by metathesis reactions between SnR_2Cl_2 and $K[(OPPh_2)(SPPh_2)N]$ in toluene. Reactions between SnR_3Cl (R = Me or Ph) and $K[(OPPh_2)(SPPh_2)N]$ (1 : 1 molar ratio) in boiling toluene also produced the dimethyl- and diphenyltin(IV) derivatives as redistribution products. The same reactions in chloroform at room temperature afford the corresponding triorganotin(IV) compounds. The compounds were characterized by means of IR and multinuclear NMR spectroscopy. The crystal and molecular structures of $SnR_2[(OPPh_2)(SPPh_2)N]_2$ (R = Me **1** or Ph **2**) derivatives were determined by X-ray diffractometry. Both compounds exhibit very similar spirobicyclic structures, with the tin atom as spiro atom. The ligand moieties are monometallic biconnective (bidentate) through both oxygen and sulfur atoms [Sn–S 2.758(1) in **1** and 2.680(4) in **2**, Sn–O 2.199(2) in **1** and 2.189(5) Å in **2**]. The co-ordination geometry around the central metal atom is octahedral, with C–Sn–C, O–Sn–O (*trans*) and S–Sn–S (*trans*) angles of 180°. The conformation of the six-membered $SnOSP_2N$ inorganic rings is twisted boat.

Organotin(IV) derivatives of 1,1-dithiolato ligands (dithiocarbonate, dithiocarbamate, dithiophosphate, dithiophosphinate, dithioarsinate) have been the subject of numerous structural studies[1] and the restricted S···S bite distance was often suggested to play an important role in the distortion from ideal geometry around the central tin atom.

In order to explore structural changes produced in the absence of such a restrictive factor we have decided to study organotin(IV) complexes of ligands of general formula **I**. This type of ligand contains a flexible XPNPY skeleton, and generally co-ordinates symmetrically through both chalcogen atoms. We have previously reported the synthesis and spectroscopic characterization of $SnR_n[(XPPh_2)(YPPh_2)N]_{4-n}$ (X = Y = O or S) derivatives containing symmetric ligand units.[2–5] In the $SnMe_2[(SPPh_2)_2N]_2$ and $SnBu^n{}_2[(OPPh_2)_2N]_2$ complexes the ligands exhibited a symmetrical monometallic biconnective pattern resulting in an almost perfect C_2SnX_4 octahedron.[3,5] By contrast, in the trimethyltin(IV) derivative $SnMe_3[(SPPh_2)_2N]$ the ligand is bonded to tin only through one sulfur atom (Sn–S 2.517 Å). There is a weak interaction between the second sulfur atom and the tin atom of a neighbouring molecule (Sn···S 3.627 Å), thus leading to a chain polymeric structure with the ligand acting as an asymmetric bridge.[4] Moreover, interesting structural patterns have been reported for the related di- and tri-organotin(IV) derivatives of β-diketones and monothio-β-diketones: $SnMe_2[(OCMe)_2CH]_2$ contains a *trans*-Me_2Sn group (C–Sn–C 180°),[6] in $SnMe_2[(OCR)(SCR)CH]_2$ (R = Me or Ph) the Me_2Sn moiety exhibits a strong deviation from linearity (C–Sn–C 139.4° for R = Me, 134.2° for R = Ph),[7] while $SnPh_3[(OCPh)_2CH]$ is monomeric with an asymmetric monometallic biconnective ligand.[8]



I

X, Y = O or S
R, R′ = alkyl or aryl

To establish possible changes which might be produced by asymmetric ligand units we have synthesized and characterized $SnR_n[(OPPh_2)(SPPh_2)N]_{4-n}$ derivatives both in solution and solid state. The molecular structures of $SnR_2[(OPPh_2)(SPPh_2)N]_2$ (R = Me or Ph) were established by X-ray diffractometry and are compared with those of diorganotin(IV) derivatives containing symmetric $[N(XPPh_2)_2]^-$ ligand moieties, as well as related 1,1-dithio- and monothio-phosphorus ligands, β-diketonates and monothio-β-diketonates.

Experimental

Materials and instrumentation

The compound $Sn(CH_2Ph)_2Cl_2$ was prepared from benzyl chloride and tin powder,[9] while the other organotin chlorides were commercial products. Infrared spectra were run in the range 4000–200 cm^{-1} on a Perkin-Elmer 283B spectrometer, as KBr discs, ^1H, ^{13}C, ^{31}P and ^{119}Sn NMR spectra on a Varian VXR 300S instrument operating at 299.5, 75.4, 121.4 and 111.9 MHz, respectively. The chemical shifts (δ) in ppm are referred relative to $SiMe_4$, 85% H_3PO_4 or $SnMe_4$.

Preparations

$NH(OPPh_2)(SPPh_2)$. The compound was prepared as described previously,[10] m.p. 172–174 °C (recrystallized from ethanol), lit.,[10] 172–174 °C; IR (cm^{-1}) ν(NH) 2695m, ν(PO) 1200vs, 1190vs, $\nu_{asym}(P_2NH)$ 950vs (br), ν(PS) 630ms (br); $\delta_H(CDCl_3)$ 7.30 [8 H, m, *m*-H of P(S)Ph, P(O)Ph], 7.41 [4 H, m, *p*-H of P(S)Ph, P(O)Ph], 7.71 [4 H, dd, ^3J(PH) 12.9, ^3J(HH) 7.1, *o*-H of P(O)Ph] and 7.97 [4 H, dd, ^3J(PH) 14.4, ^3J(HH) 7.1, *o*-H of P(S)Ph]; $\delta_C(CDCl_3)$ 128.02 [d, ^3J(PC) 14.0, C_m], 128.05 [d, ^3J(PC) 13.1, C_m], 131.61 [d, ^4J(PC) 3.5, C_p], 131.88 [d, ^4J(PC) 2.6, C_p], 132.06 [d, ^2J(PC) 10.5, C_o, P(O)Ph], 132.10 [d, ^2J(PC) 12.2, C_o, P(S)Ph], 131.18 [d, ^1J(PC) 125.5, C_{ipso}, P(O)Ph] and 133.32 [d, ^1J(PC) 102.4, C_{ipso}, P(S)Ph]; $\delta_P(CDCl_3)$ 23.1 [d, ^2J(PP) 17.5, Ph_2PO] and 56.1 [d, ^2J(PP) 17.5 Hz, Ph_2PS].

K[(OPPh$_2$)(SPPh$_2$)N]. A mixture of NH(OPPh$_2$)(SPPh$_2$) (10 g, 23 mmol) and KOBu^t (2.586 g, 23 mmol) in anhydrous diethyl ether (200 cm^3) was stirred under reflux for 12 h. The potassium salt which deposited was filtered off, washed with ether and dried *in vacuo* (10.4 g, 95%), m.p. 286–288 °C; IR (cm^{-1}) ν_{asym}(P$_2$N) 1200vs (br), 1170s, ν(PO) 1130vs, 1115s, ν(PS) 593vs; δ_H(CD$_3$OD) 7.19 [12 H, m, *m*- and *p*-H of P(S)Ph, P(O)Ph], 7.75 [4 H, ddd, ^3J(PH) 12.4, ^3J(HH) 7.7, ^4J(HH) 1.7, *o*-H of P(O)Ph] and 7.90 [4 H, ddd, ^3J(PH) 13.3, ^3J(HH) 6.2, ^4J(HH) 2.3, *o*-H of P(S)Ph)]; δ_C(CD$_3$OD) 128.50 [d, ^3J(PC) 11.6, C$_m$], 128.65 [d, ^3J(PC) 11.6, C$_m$], 130.63 (s, C$_p$), 130.94 (s, C$_p$), 132.17 [d, ^2J(PC) 11.0, C$_o$, P(O)Ph], 132.69 [d, ^2J(PC) 9.8, C$_o$, P(S)Ph], 140.22 [d, ^1J(PC) 133.4, C$_{ipso}$, P(O)Ph] and 143.02 [d, ^1J(PC) 105.0 Hz, C$_{ipso}$, P(S)Ph]; δ_P(CD$_3$OD) 16.1 (s, Ph$_2$PO) and 37.9 (s br, Ph$_2$PS).

SnMe$_2$[(OPPh$_2$)(SPPh$_2$)N]$_2$ 1. (*i*) The compounds SnMe$_2$Cl$_2$ (0.292 g, 1.33 mmol) and K[(OPPh$_2$)(SPPh$_2$)N] (1.257 g, 2.66 mmol) in toluene (25 cm^3) were stirred for 2 h, under reflux. The resulting KCl was filtered off and the solvent partially removed from the clear filtrate. The solid product which deposited was recrystallized from toluene, leading to colourless crystals of SnMe$_2$[(OPPh$_2$)(SPPh$_2$)N]$_2$ (1.03 g, 76.5%), m.p. 251 °C (Found: C, 59.9; H, 4.80; N, 2.60. C$_{50}$H$_{46}$N$_2$O$_2$P$_4$S$_2$Sn requires C, 59.3; H, 4.55; N, 2.75%); IR (cm^{-1}) ν_{asym}(P$_2$N) 1200vs (br), 1180s, ν(PO) 1115s, 1050vs, ν(PS) 570vs, ν(SnC$_2$) 523ms; δ_H(CDCl$_3$) 1.15 [6 H, s, ^2J($^{119/117}$SnH) 101.1, SnMe], 7.29 [24 H, m, *m*- and *p*-H of P(S)Ph, P(O)Ph], 7.73 [8 H, ddd, ^3J(PH) 12.6, ^3J(HH) 8.2, ^4J(HH) 1.5, *o*-H of P(O)Ph] and 7.83 [8 H, ddd, ^3J(PH) 13.9, ^3J(HH) 8.0, ^4J(HH) 1.5, *o*-H of P(S)Ph]; δ_C(CDCl$_3$) 29.77 (s, SnMe), 127.86 [d, ^3J(PC) 12.8, C$_m$], 128.03 [d, ^3J(PC) 13.1, C$_m$], 130.28 (s, C$_p$), 130.73 [d, ^2J(PC) 10.3, C$_o$, P(O)Ph], 130.79 (s, C$_p$), 131.13 [d, ^2J(PC) 10.4, C$_o$, P(S)Ph], 136.52 [d, ^1J(PC) 137.3, C$_{ipso}$, P(O)Ph] and 139.41 [d, ^1J(PC) 110.5 Hz, C$_{ipso}$, P(S)Ph]; δ_P(CDCl$_3$) 20.0 (s, Ph$_2$PO) and 35.0 (s, Ph$_2$PS).

(*ii*) The compounds SnMe$_3$Cl (0.398 g, 2 mmol) and K[(OPPh$_2$)(SPPh$_2$)N] (0.942 g, 2 mmol) in toluene (20 cm^3) were stirred for 2 h, under reflux. The KCl was filtered off and removal of the solvent *in vacuo* resulted in a glassy product. Recrystallization from CH$_2$Cl$_2$–heptane gave a small amount of colourless crystals (0.3 g, *ca.* 29% related to the potassium reagent), identified as SnMe$_2$[(OPPh$_2$)(SPPh$_2$)N]$_2$ (m.p., IR, NMR, X-ray). Evaporation to dryness again left an oily product which was not characterized.

SnBu$^n{}_2$[(OPPh$_2$)(SPPh$_2$)N]$_2$. The compounds SnBu$^n{}_2$Cl$_2$ (0.304 g, 1 mmol) and K[(OPPh$_2$)(SPPh$_2$)N] (0.943 g, 2 mmol) in toluene (25 cm^3) were stirred for 2 h, under reflux. The resulting KCl was filtered off and the solvent partially removed from the clear filtrate. The solid product which deposited was recrystallized from toluene, leading to colourless crystals of SnBu$^n{}_2$[(OPPh$_2$)(SPPh$_2$)N]$_2$ (0.73 g, 69%), m.p. 206–208 °C (Found: C, 61.6; H, 5.35; N, 2.55. C$_{56}$H$_{58}$N$_2$O$_2$P$_4$S$_2$Sn requires C, 61.3; H, 5.35; N, 2.55%); IR (cm^{-1}) ν_{asym}(P$_2$N) 1261vs (br), 1178m, ν(PO) 1123s (br), 1050vs, ν(PS) 583vs; δ_H(CDCl$_3$) 0.33 [6 H, t, ^3J(HH) 7.2, Sn(CH$_2$)$_3$C*H*$_3$], 0.63 [4 H, tq, ^3J(HH) 7.2, Sn(CH$_2$)$_2$C*H*$_2$CH$_3$], 1.36 (4 H, m, SnCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.73 [4 H, m, SnC*H*$_2$(CH$_2$)$_2$CH$_3$], 7.3 [24 H, m, *m*- and *p*-H of P(S)Ph, P(O)Ph], 7.77 [8 H, ddd, ^3J(PH) 10.6, ^3J(HH) 6.9, ^4J(HH) 1.5, *o*-H of P(O)Ph] and 7.88 [8 H, ddd, ^3J(PH) 13.8, ^3J(HH) 7.5, ^4J(HH) 1.5, *o*-H of P(S)Ph]; δ_C(CDCl$_3$) 13.35 (s, C$_\delta$), 25.76 [s, ^3J($^{119/117}$SnC) 166.0, C$_\gamma$], 28.22 [s, ^2J($^{119/117}$SnC) 45.2, C$_\beta$], 41.88 [s, ^1J(^{119}SnC) 774.7, ^1J(^{117}SnC) 736.2, C$_\alpha$], 127.75 [d, ^3J(PC) 13.4, C$_m$], 127.87 [d, ^3J(PC) 12.1, C$_m$], 130.04 (s, C$_p$), 130.60 (s, C$_p$), 130.68 [d, ^2J(PC) 10.9, C$_o$, P(O)Ph], 131.17 [d, ^2J(PC) 9.8, C$_o$, P(S)Ph], 136.91 [d, ^1J(PC) 140.4, C$_{ipso}$, P(O)Ph] and 139.97 [d, ^1J(PC) 108.6 Hz, C$_{ipso}$, P(S)Ph]; δ_P(CDCl$_3$) 19.5 (s, Ph$_2$PO) and 35.4 (s, Ph$_2$PS); δ_{Sn}(CDCl$_3$) −468.6 (s).

Sn(CH$_2$Ph)$_2$[(OPPh$_2$)(SPPh$_2$)N]$_2$·C$_6$H$_5$Me. The compounds Sn(CH$_2$Ph)$_2$Cl$_2$ (0.372 g, 1 mmol) and K[(OPPh$_2$)(SPPh$_2$)N] (0.943 g, 2 mmol) in toluene (25 cm^3) were stirred for 2 h, under reflux. The resulting KCl was filtered off and the solid product which deposited on cooling was recrystallized from toluene, leading to colourless crystals of Sn(CH$_2$Ph)$_2$[(OPPh$_2$)(SPPh$_2$)N]$_2$·C$_6$H$_5$Me (0.92 g, 73%), m.p. 198–200 °C (Found: C, 65.7; H, 4.90; N, 2.20. C$_{69}$H$_{62}$N$_2$O$_2$P$_4$S$_2$Sn requires C, 65.9; H, 4.95; N, 2.25%); IR (cm^{-1}) ν_{asym}(P$_2$N) 1213vs, 1177m, ν(PO) 1122s (br), 1051s, ν(PS) 580vs; δ_H(CDCl$_3$) 2.36 (3 H, s, C*H*$_3$C$_6$H$_5$), 3.24 [4 H, s, ^2J($^{119/117}$SnH) 115.8, SnC*H*$_2$C$_6$H$_5$], 6.7 (10 H, m, SnCH$_2$C$_6$*H*$_5$), 7.3 [29 H, m, CH$_3$C$_6$*H*$_5$, *m*- and *p*-H of P(S)Ph, P(O)Ph], 7.57 [8 H, dd, ^3J(PH) 12.7, ^3J(HH) 7.1, *o*-H of P(O)Ph] and 7.80 [8 H, dd, ^3J(PH) 13.7, ^3J(HH) 7.1, *o*-H of P(S)Ph]; δ_C(CDCl$_3$) 21.41 (s, *C*H$_3$C$_6$H$_5$), 48.68 [s, ^1J($^{117/119}$SnC) 730, Sn*C*H$_2$C$_6$H$_5$], 124.31 (s, C$_p$, SnCH$_2$*C*$_6$H$_5$), 125.28 (s, C$_p$, CH$_3$*C*$_6$H$_5$), 127.33 (s, C$_m$, SnCH$_2$*C*$_6$H$_5$), 127.79 [d, ^3J(PC) 13.4, C$_m$], 127.95 [d, ^3J(PC) 9.9, C$_m$], 128.20 (s, C$_m$, CH$_3$*C*$_6$H$_5$), 129.00 (s, C$_o$, CH$_3$*C*$_6$H$_5$), 129.67 [s, ^3J(^{119}SnC) 54.5, ^3J(^{117}SnC) 43.0, C$_o$, SnCH$_2$*C*$_6$H$_5$], 130.27 (s, C$_p$, PPh), 130.51 (s, C$_p$, PPh), 130.89 [d, ^2J(PC) 10.4, C$_o$, P(O)Ph], 131.20 [d, ^2J(PC) 10.4, C$_o$, P(S)Ph], 136.62 [d, ^1J(PC) 139.2, C$_{ipso}$, P(O)Ph], 137.82 (s, C$_{ipso}$, CH$_3$*C*$_6$H$_5$), 139.01 [s, ^2J($^{117/119}$SnC) 80, C$_{ipso}$, SnCH$_2$*C*$_6$H$_5$] and 139.19 [d, ^1J(PC) 109.5 Hz, C$_{ipso}$, P(S)Ph]; δ_P(CDCl$_3$) 19.5 (s, Ph$_2$PO) and 34.1 (s, Ph$_2$PS); δ_{Sn}(CDCl$_3$) −468.6 (s).

SnPh$_2$[(OPPh$_2$)(SPPh$_2$)N]$_2$ 2. (*i*) The compounds SnPh$_2$Cl$_2$ (0.343 g, 1 mmol) and K[(OPPh$_2$)(SPPh$_2$)N] (0.942 g, 2 mmol) in toluene (20 cm^3) were stirred for 2 h, under reflux. The hot reaction mixture was filtered, and the white solid product was extracted several times with acetonitrile, in a Soxhlet apparatus. The compound SnPh$_2$[(OPPh$_2$)(SPPh$_2$)N]$_2$ was isolated as a white powder, of low solubility in organic solvents (0.33 g, 29%), m.p. 257–259 °C (Found: C, 62.9; H, 4.35; N, 2.55. C$_{60}$H$_{50}$N$_2$O$_2$P$_4$S$_2$Sn requires C, 63.3; H, 4.45; N, 2.45%); IR (cm^{-1}) ν_{asym}(P$_2$N) 1240vs (br), 1178m, ν(PO) 1120ms, 1045vs, ν(PS) 570vs; δ_P(CDCl$_3$) 20.3 (s, Ph$_2$PO) and 33.2 (s, Ph$_2$PS).

(*ii*) The compounds SnPh$_3$Cl (0.770 g, 2 mmol) and K[(OPPh$_2$)(SPPh$_2$)N] (0.942 g, 2 mmol) in toluene (25 cm^3) were stirred for 2 h, under reflux. The KCl was filtered off and partial removal of the solvent afforded the deposition of colourless crystals, which were separated. Evaporation of the solvent to dryness *in vacuo* resulted in a glassy product which was not further investigated. Recrystallization of the crystalline product from CH$_2$Cl$_2$–heptane led to a small amount of colourless crystals (0.26 g, *ca.* 23% related to the potassium reagent), identified as SnPh$_2$[(OPPh$_2$)(SPPh$_2$)N]$_2$ (m.p., IR, ^{31}P NMR, X-ray).

SnMe$_3$[(OPPh$_2$)(SPPh$_2$)N]. The compounds SnMe$_3$Cl (0.2 g, 1 mmol) and K[(OPPh$_2$)(SPPh$_2$)N] (0.471 g, 1 mmol) in chloroform (25 cm^3) were stirred for 2 h at room temperature. The resulting KCl was filtered off and the solvent removed to dryness *in vacuo*. A white solid product was obtained, which was recrystallized from CHCl$_3$–hexane leading to colourless crystals of SnMe$_3$[(OPPh$_2$)(SPPh$_2$)N] (0.5 g, 84%), m.p. 58–60 °C (Found: C, 54.0; H, 4.80; N, 2.20. C$_{27}$H$_{29}$NOP$_2$SSn requires C, 54.4; H, 4.90; N, 2.35%); IR (cm^{-1}) ν_{asym}(P$_2$N) 1230vs (br), 1177m, ν(PO) 1124vs, 1065m, ν(PS) 587m; δ_H(CDCl$_3$) 0.42 [9 H, s, ^2J(^{119}SnH) 60.6, ^2J(^{117}SnH) 58.2, SnMe], 7.23 [12 H, m, *m*- and *p*-H of P(S)Ph, P(O)Ph], 7.61 [4 H, dd, ^3J(PH) 12.9, ^3J(HH) 6.9, *o*-H of P(O)Ph] and 7.82 [4 H, dd, ^3J(PH) 13.8, ^3J(HH) 7.5, *o*-H of P(S)Ph]; δ_C(CDCl$_3$) 0.18 [s, ^1J(^{119}SnC) 408.3, ^1J(^{117}SnC) 390.7, SnMe], 127.58 [d, ^3J(PC) 12.8, C$_m$], 127.92 [d, ^3J(PC) 12.8, C$_m$], 129.77 (s, C$_p$), 130.79 (s, C$_p$), 130.87 [d, ^2J(PC) 11.6, C$_o$, P(O)Ph], 131.34 [d, ^2J(PC) 10.4, C$_o$, P(S)Ph], 135.58 [d, ^1J(PC) 142.7, C$_{ipso}$, P(O)Ph] and 140.15 [d, ^1J(PC) 111.3 Hz, C$_{ipso}$, P(S)Ph];

$\delta_P(CDCl_3)$ 10.3 (s, Ph_2PO) and 39.7 (s br, Ph_2PS); $\delta_{Sn}(CDCl_3)$ 146.2 (br).

$SnPh_3[(OPPh_2)(SPPh_2)N]$. The compounds $SnPh_3Cl$ (0.513 g, 1.5 mmol) and $K[(OPPh_2)(SPPh_2)N]$ (0.628 g, 1 mmol) in chloroform (25 cm^3) were stirred for 2 h at room temperature. The resulting KCl was filtered off and the solvent removed to dryness *in vacuo*. The compound $SnPh_3[(OPPh_2)(SPPh_2)N]$ was isolated as a glassy product (0.89 g, 86%), m.p. 115–125 °C (Found: C, 62.2; H, 4.30; N, 1.70. $C_{42}H_{35}NOP_2SSn$ requires C, 64.5; H, 4.50; N, 1.80%); IR (cm^{-1}) $\nu_{asym}(P_2N)$ 1255vs, ν(PO) 1140s, 1070s, ν(PS) 565s; $\delta_H(CDCl_3)$ 7.11 (9 H, m, *m*- and *p*-H of SnPh), 7.30 [12 H, m, *m*- and *p*-H of P(S)Ph, P(O)Ph], 7.45 [4 H, dd, ^3J(PH) 13.3, ^3J(HH) 7.8, *o*-H of P(O)Ph], 7.53 [6 H, d, ^3J(HH) 7.0, *o*-H of SnPh] and 7.64 [4 H, dd, ^3J(PH) 13.7, ^3J(HH) 7.4, *o*-H of P(S)Ph]; $\delta_C(CDCl_3)$ 127.55 [d, ^3J(PC) 12.7, C_m, PPh], 127.67 [d, ^3J(PC) 13.3, C_m, PPh], 128.78 [s, $^3J(^{117/119}SnC)$ 64.3, C_m, SnPh], 129.72 (s, C_p, PPh), 129.90 (s, C_p, SnPh), 130.68 (s, C_p, PPh), 131.08 [d, ^2J(PC) 11.3, C_o, P(O)Ph], 131.82 [d, ^2J(PC) 11.2, C_o, P(S)Ph], 134.80 [d, ^1J(PC) 135.3, C_{ipso}, P(O)Ph], 135.30 [C_{ipso}, P(S)Ph; only the downfield peak of the corresponding doublet was observed, the other being overlapped by the stronger upfield C_o of SnPh], 136.64 [s, $^2J(^{117/119}SnC)$ 47.4 Hz, C_o, SnPh] and 137.30 (s, C_{ipso}, SnPh); $\delta_P(CDCl_3)$ 20.5 (s, Ph_2PO) and 38.7 (s br, Ph_2PS).

Crystal structure determinations

White block crystals of $SnMe_2[(OPPh_2)(SPPh_2)N]_2$ **1** and $SnPh_2[(OPPh_2)(SPPh_2)N]_2$ **2** were mounted on glass fibres and sealed with epoxy glue. Data were collected on a Rigaku AFC6S diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å), operating at 50 kV and 35 mA. Cell constants and an orientation matrix for data collection, obtained from 21 carefully centred reflections in the range $8.3 < 2\theta < 13.8°$, corresponded to monoclinic cells with dimensions as given in Table 4. The systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) were observed for both **1** and **2**. Based on packing considerations, statistical analyses of intensity distributions and the successful solution and refinement of the structure, the space group was determined to $P2_1/c$ (no. 14).

The data were collected at 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ of 50.0°. The ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.29° for compound **1** and 0.37° for **2** with a take-off angle of 6.0°. Scans of $(1.63 + 0.30 \tan \theta)°$ for **1** and $(0.84 + 0.30 \tan \theta)°$ for **2** were made at speeds of 32.0 and 16.0° min^{-1} (in ω), respectively. The weak reflections [$I < 10.0\sigma(I)$] were rescanned (maximum of four rescans) and the counts accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflections. The ratio of the peak counting time to the background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm, and the crystal-to-detector distance was 284.0 mm.

Of the 4581 reflections for compound **1** and 5243 for **2** which were collected, 4341 and 4937 were unique (R_{int} = 0.063 and 0.156). The intensities of three representative reflections measured every 150 remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied).

An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.84 to 1.00 for compound **1** and 0.79 to 1.00 for **2**. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = $2.332\,89 \times 10^{-7}$) to **1**.

The structures were solved by direct methods.[11] The tin atoms in both molecules are located in special positions. All of the non-hydrogen atoms were refined anisotropically for **1** but there were insufficient data to do so for **2** so the non-hydrogen atoms, other than the carbon atoms of the phenyl groups on phosphorus, were refined anisotropically. Hydrogen atoms were included in their idealized positions with C–H set at 0.95 Å and with isotropic thermal parameters 1.2 times that of the carbon atom to which they were attached. The final cycle of full-matrix least-squares refinement {function minimized: $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/(L_p)^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, L_p = Lorentz-polarization factor, and p = p factor} was based on 2911 observed reflections for **1** and 2294 for **2** [$I > 3.00\sigma(I)$] and 277 variable parameters for **1** and 202 for **2** and converged (largest parameter shift 0.001 times its e.s.d.) with unweighted and weighted agreement factors of $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ = 0.0328 for **1** and 0.0547 for **2** and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$ = 0.0244 and 0.0448.

The standard deviations of an observation of unit weight [$\Sigma w(|F_o| - |F_c|)^2/(N_o - N_c)^{\frac{1}{2}}$, where N_o = number of observations and N_c = number of variables] were 1.98 and 1.92 for compounds **1** and **2**, respectively. The weighting scheme was based on counting statistics and included a factor (p = 0.002 for **1** and 0.003 for **2**) to downweight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, $(\sin \theta)/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final Fourier-difference map corresponded to 0.37 and −0.44 for **1** and 0.54 and −0.51 e $Å^{-3}$ for **2**.

Neutral-atom scattering factors were taken from Cromer and Waber.[12] Anomalous dispersion effects were included in F_c;[13] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[14] All calculations were performed using the TEXSAN[15] crystallographic software package. The final atomic coordinates of the non-hydrogen atoms are given in Tables 5 and 6.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Structure-factor tables are available from the authors.

Results and Discussion

The compounds were prepared by treating $K[(OPPh_2)(SPPh_2)N]$ with the appropriate organotin chloride, in toluene or chloroform, according to equation (1) (n = 2, R = Me, Bu^n, CH_2Ph or Ph; n = 3, R = Me or Ph). The dimethyl- and diphenyl-tin derivatives were also isolated in low yields from SnR_3Cl (R = Me or Ph) and $K[(OPPh_2)(SPPh_2)N]$ (1:1 molar ratio) in boiling toluene. This result might be due to a redistribution process (2) suffered by the expected triorganotin product. No attempts were made to obtain any chemical or spectroscopic proof of the formation of SnR_4, but a similar rearrangement process has been previously reported for the (β-diketonato)triorganotin(IV) analogues.[8] However, it should be noted that authentic $SnR_3[(OPPh_2)(SPPh_2)N]$ (R = Me or Ph) can be prepared in chloroform at room temperature and for R = Me a $CHCl_3$ solution showed no sign of decomposition after 2 weeks.

$$SnR_nCl_{4-n} + (4-n)\,K[(OPPh_2)(SPPh_2)N] \longrightarrow SnR_n[(OPPh_2)(SPPh_2)N]_{4-n} + (4-n)\,KCl \quad (1)$$

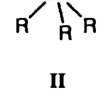
$$2SnR_3[(OPPh_2)(SPPh_2)N] \longrightarrow SnR_2[(OPPh_2)(SPPh_2)N]_2 + SnR_4 \quad (2)$$

The strong infrared absorptions observed for all the organotin complexes in the regions 1260–1170, 1130–1040 and

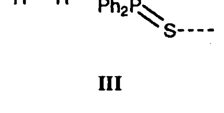
590–570 cm^{-1} were assigned to $\nu_{asym}(P_2N)$, $\nu(PO)$ and $\nu(PS)$ stretching vibrations, respectively, by comparison with the spectra of the free acid and its potassium salt, thus suggesting bidentate co-ordination of the ligand through both oxygen and sulfur to tin. The band at 523 cm^{-1} in the spectrum of $SnMe_2[(OPPh_2)(SPPh_2)N]_2$ was assigned to the SnC_2 vibration and indicates a linear arrangement of the C–Sn–C fragment, as confirmed by the X-ray diffraction study (see below). For $SnMe_3[(OPPh_2)(SPPh_2)N]$ the SnC_3 stretching vibrations could not be assigned, being obscured by strong bands of the phenyl rings.

All the organotin(IV) derivatives, as well as the free acid and its potassium salt, were investigated by solution NMR spectroscopy. The ^{31}P NMR spectrum of $NH(OPPh_2)(SPPh_2)$ exhibits two resonances at δ 23.1 ($Ph_2P{=}O$) and 56.1 ($Ph_2P{=}S$), each split into two components due to phosphorus–phosphorus coupling [^2J(PP) 17.5 Hz]. The loss of the acidic proton is reflected in a significant shift to higher field (*ca.* 20 ppm) of the resonance assigned to Ph_2PS. For the potassium salt and the organotin complexes no phosphorus–phosphorus coupling was observed at room temperature. The ^{31}P chemical shifts of $SnR_2[(OPPh_2)(SPPh_2)N]_2$ are close to those observed for organotin(IV) complexes containing symmetric ligand units, *i.e.* δ *ca.* 36 for $SnR_3[(SPPh_2)_2N]$[2] and δ *ca.* 20 for $SnR_2[(OPPh_2)_2N]_2$,[5] which is consistent with participation of both chalcogen atoms of the ligand unit in the co-ordination to tin. For the trimethyltin(IV) derivative, $SnMe_3[(OPPh_2)(SPPh_2)N]$, the ^{31}P resonance assigned to Ph_2PO (δ 10.3) is also shifted significantly (*ca.* 13 ppm) to higher field compared to the free acid, while that for Ph_2PS (δ 39.7) is broadened. This behaviour might suggest primary co-ordination of the ligand through the oxygen atom, with the sulfur being involved only in weak secondary intra- (**II**) or inter-molecular (**III**) interactions. A non-cyclic, associated structure of type **III** can be tentatively assigned in the solid state, similar to the structure of the $SnMe_3[(SPPh_2)_2N]$ analogue, which also showed only a broad ^{31}P resonance at δ 36,[2] while in the solid state a polymeric association through weak Sn $\cdots$ S intermolecular interactions was established by X-ray diffraction.[4]

The low solubility of $SnPh_2[(OPPh_2)(SPPh_2)N]_2$ precluded its investigation by multinuclear NMR spectroscopy (only the ^{31}P NMR spectrum could be obtained). By contrast, the other organotin compounds displayed good solubility in $CDCl_3$ and their ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded. Both the ^1H and ^{13}C spectra showed two groups of signals in the aromatic region (with the expected doublet pattern due to phosphorus–proton and –carbon couplings, respectively), corresponding to the phenyl groups attached to different phosphorus atoms. The resonances of *o*-protons and carbon atoms were assigned using a heteronuclear correlation (HETCOR) spectrum for the free acid, while for the *ipso*-carbons the assignment was based on the magnitude of the ^1J(PC) coupling constants. The spectra also contain characteristic resonances for the organic groups bonded to tin. The ^{119}Sn resonances for the diorganotin(IV) complexes appear as sharp signals and their chemical shifts fall in the expected range for six-co-ordinated tin.[16,17] For $SnMe_3[(OPPh_2)(SPPh_2)N]$ a broad ^{119}Sn resonance centred at δ 146.2 was recorded and its magnitude lies in the range reported for other four-co-ordinated triorganotin derivatives {*e.g.* δ 117.8 for $SnMe_3[(SPPh_2)_2N]$[2] or 114 for $SnMe_3[S_2P(OEt)_2]$[18]}. This underlines the weakness of Sn $\cdots$ S interactions, if present in solution.



II



III

The co-ordination geometry of organotin(IV) derivatives is reflected in their NMR parameters.[16] Thus, the values of the $^2J(^{119}SnC^1H)$ and $^1J(^{119}Sn^{13}C)$ coupling constants fall in the region for six-co-ordinate tin in the case of diorganotin derivatives, and four-co-ordinate tin in the case of $SnMe_3[(OPPh_2)(SPPh_2)N]$.[19] Table 1 contains the calculated C–Sn–C angles based on reported relationships with $^2J(^{119}SnC^1H)$ and $^1J(^{119}Sn^{13}C)$.[17,19–21] The deviations from 180° (established by X-ray diffraction, see below) for the diorganotin(IV) derivatives, $SnR_2[(OPPh_2)(SPPh_2)N]_2$, might be the result of structural changes which occur during the transition from solid state to solution. A similar behaviour was noted for $SnMe_2[(OCMe)_2CH]_2$ [in solution, $^1J(^{119}Sn^{13}C)$ 977 Hz,[22] estimated C–Sn–C angle 163°;[20] in solid state, $^1J(^{119}Sn^{13}C)$ 1175 Hz, estimated C–Sn–C angle 180°,[19] confirmed by X-ray diffraction[6]]. For the trimethyltin(IV) derivative, $SnMe_3[(OPPh_2)(SPPh_2)N]$, the estimated C–Sn–C angle (113°) is slightly larger than 109° expected for a tetrahedral geometry, so that five-co-ordination as found for the dithio derivative[4] cannot be definitely ruled out.

The solid-state structures of $SnR_2[(OPPh_2)(SPPh_2)N]_2$, R = Me **1** or Ph **2**, were determined by single-crystal X-ray diffraction. Selected bond distances and angles are listed in Table 2. Figs. 1 and 2 show the ORTEP-like view of the molecular structures with the atom numbering schemes. In both cases the crystal contains discrete molecular units, separated by normal van der Waals distances. Since the two structures are very similar a general description for both compounds is given.

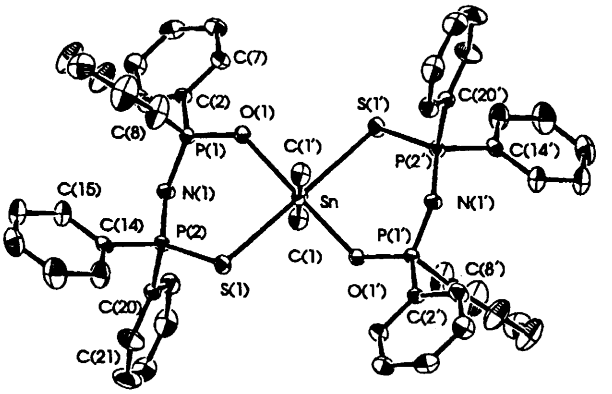


Fig. 1 An ORTEP-like drawing of the molecular structure of $SnMe_2[(OPPh_2)(SPPh_2)N]_2$

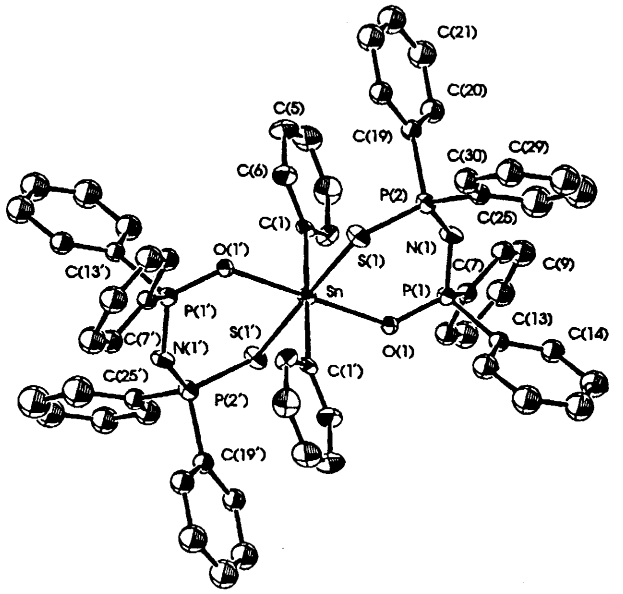


Fig. 2 An ORTEP-like drawing of the molecular structure of $SnPh_2[(OPPh_2)(SPPh_2)N]_2$

The central tin atom occupies a centre of inversion. The SnC_2 unit is linear (C–Sn–C 180°), in contrast with the angular arrangement inferred from NMR data in solution. The two asymmetric ligand moieties are monometallic biconnective, thus resulting in a distorted-octahedral co-ordination around tin, with the carbon atoms of the organic groups in axial positions. The equatorial SnO_2S_2 system is planar, with the *trans* positions occupied by pairs of the same donor chalcogen atoms (O–Sn–O and S–Sn–S angles 180°). Thus, of two possible isomers **IV** (S *trans* S, O *trans* O) and **V** (S *trans* O) only **IV** is observed.

The distortion of the co-ordination octahedron is due to the differences between the equatorial Sn–O and Sn–S lengths, as well as between the endocyclic [average 91.2(3)°] and exocyclic [average 88.8(3)°] O–Sn–S angles, and the slight deviation of the C–Sn–C axis from orthogonality to the equatorial plane [C–Sn–X range 87.8(2)–92.2(2)°]. The Sn–O [average 2.194(6) Å] and Sn–S [average 2.72(5) Å] bonds in $SnR_2[(OPPh_2)(SPPh_2)N]_2$ are of the same magnitude as observed in analogues containing symmetric ligand units: $SnBu^n{}_2[(OPPh_2)_2N]_2$, average Sn–O 2.203(1) Å;[5] $SnMe_2[(SPPh_2)_2N]_2$, average Sn–S 2.735(3) Å.[3] However it should be noted that in compound **2**, R = Ph, the Sn–S bond is significantly shorter [2.680(4) Å] than in **1**, R = Me [2.758(1) Å], which reflects the difference in the electronic effects of the organic groups attached to tin. As a result the O···S bite in the ligand unit is also smaller in **2** [3.489(7) Å] compared to **1** [3.772(3) Å], thus supporting the high flexibility of the OPNPS skeleton.

In the ligand the P–S [average 2.021(3) Å] bonds are intermediate between single and double bonds [*cf.* the methyl ester, $MeS–PPh_2{=}N–Ph_2P{=}S$: P–S 2.069(3), P=S 1.956(3) Å],[23] while the P–O [average 1.527(4) Å] bonds are of the same magnitude as the single phosphorus–oxygen bond in $Ph_2P(=O)OH$ [P–O 1.526(6), P=O 1.486(6) Å].[24] Within a ligand unit the two non-equivalent phosphorus–nitrogen bonds are intermediate [range 1.578(3)–1.599(3) Å] between single and double bonds [*cf.* the methyl ester, $MeS–PPh_2{=}N–Ph_2P{=}S$: P–N 1.619(4), P=N 1.568(4) Å],[23] thus suggesting partial double-bond character. As a consequence, the ligand might be regarded as relatively more strongly bonded to tin through oxygen, although there is still strong co-ordination through sulfur.

The bidentate nature of the monothio ligand units leads to an inorganic bicyclic system, $NP_2SOSnOSP_2N$, with the metal as spiro atom. Although some delocalization of the π electrons over the OPNPS systems is suggested by the magnitude of the bonds, the $SnOSP_2N$ rings are not planar, but they exhibit a twisted-boat conformation [deviations from the SOSnOS plane: P(1) 0.593, P(2) 1.038, N(1) 1.417 Å for **1**, and P(1) 0.664, P(2) 1.246, N(1) 1.461 Å for **2**] (Fig. 3). In contrast, the SnO_2C_3 rings in $SnMe_2[(OCMe)_2CH]_2$ are planar,[6] while in $SnMe_2$-

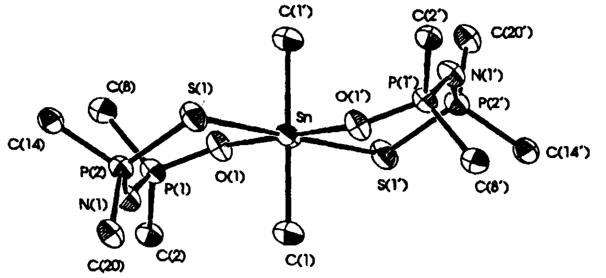
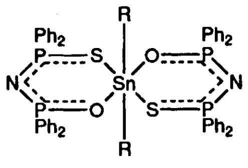
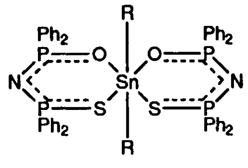


Fig. 3 Conformation of the inorganic $SnOSP_2N$ chelate rings in $SnMe_2[(OPPh_2)(SPPh_2)N]_2$ (only *ipso*-carbon atoms of the phenyl groups are shown for clarity)



IV



V

Table 1 Correlations between $^{119}SnC^1H$ and $^{119}Sn^{13}C$ coupling constants (in Hz) and C–Sn–C angles (°) in $SnR_n[(OPPh_2)(SPPh_2)N]_{4-n}$

	^1H		^{13}C	
Compound	$^2J(^{119}SnC^1H)$	C–Sn–C	$^1J(^{119}Sn^{13}C)$	C–Sn–C
$SnMe_2[(OPPh_2)(SPPh_2)N]_2$	101.1[a]	165[b]		
$SnBu^n{}_2[(OPPh_2)(SPPh_2)N]_2$			774.7	152[c]
$SnMe_3[(OPPh_2)(SPPh_2)N]$	60.6	113[b]	408.3	113[d]

[a] The mean value of $^2J(^{119,117}SnC^1H)$. [b] $\theta = 0.0161|^2J|^2 - 1.32|^2J| + 133.4$.[20] [c] $|^1J| = 9.99\theta - 746$.[21] [d] $|^1J| = 11.4\theta - 875$.[19]

Table 2 Selected interatomic distances (Å) and angles (°) in $SnMe_2[(OPPh_2)(SPPh_2)N]_2$ **1** and $SnPh_2[(OPPh_2)(SPPh_2)N]_2$ **2** with estimated standard deviations (e.s.d.s) in parentheses *

	1	**2**		**1**	**2**
Sn–O(1)	2.199(2)	2.189(5)	P(2)–N(1)	1.578(3)	1.581(7)
Sn–S(1)	2.758(1)	2.680(4)	P(2)–S(1)	2.023(1)	2.018(3)
Sn–C(1)	2.116(3)	2.135(8)	O(1)···S(1)	3.772(3)	3.489(7)
P(1)–O(1)	1.524(2)	1.530(5)	O(1')···S(1)	3.483(3)	3.431(6)
P(1)–N(1)	1.599(3)	1.593(7)			
O(1)–Sn–S(1)	91.48(7)	91.0(2)	C(1')–Sn–S(1)	88.4(1)	87.8(2)
O(1)–Sn–S(1')	88.52(8)	89.0(2)	C(1')–Sn–S(1')	91.6(1)	92.2(2)
O(1)–Sn–O(1')	180.00	180.00	C(1')–Sn–O(1)	89.0(1)	89.1(1)
S(1)–Sn–S(1')	180.00	180.00	C(1')–Sn–O(1')	91.0(1)	90.9(3)
S(1)–Sn–O(1')	88.52(8)	89.0(2)			
S(1')–Sn–O(1')	91.48(7)	91.0(2)	Sn–O(1)–P(1)	131.7(1)	132.1(3)
C(1)–Sn–C(1')	180.00	180.00	O(1)–P(1)–N(1)	116.4(1)	117.7(3)
C(1)–Sn–O(1)	91.0(1)	90.9(3)	P(1)–N(1)–P(2)	132.0(2)	134.1(4)
C(1)–Sn–S(1)	91.6(1)	92.2(2)	S(1)–P(2)–N(1)	117.8(1)	119.6(3)
C(1)–Sn–O(1')	89.0(1)	89.1(1)	Sn–S(1)–P(2)	104.91(5)	103.8(1)
C(1)–Sn–S(1')	88.4(1)	87.8(2)			

* Symmetry-equivalent positions $1 - x, 1 - y, -z$ for compound **1** and $1 - x, -y, 1 - z$ for **2** are denoted by primes.

[(OCMe)(SCMe)CH]$_2$ the SnOSC$_3$ rings are folded along the O···S axis.[7]

A comparison of the structure of the present diorganotin(IV) compounds with those containing 1,1-dithio ligands as well as the related monothiophosphinate, SnMe$_2$(OSPEt$_2$)$_2$, β-diketonates and monothio-β-diketonates reveals interesting structural features. Selected molecular dimensions for some representative compounds are listed in Table 3 and the co-ordination cores are shown in Fig. 4.

In complexes of type SnR$_2$(S$_2$Z)$_2$ [Z = COR′, CNR′$_2$, P(OR′)$_2$, PR′$_2$ or AsR′$_2$], with very few exceptions, the 1,1-dithio ligands are asymmetric monometallic biconnective. This results in a strongly distorted octahedral (or skew-trapezoidal bipyramidal) geometry around tin, with *cis* short Sn–S (range 2.47–2.57 Å) and long Sn···S bonds (range 2.92–3.52 Å).[1] The angle between the primary Sn–S bonds is much smaller (range 80–87°) than that between the secondary Sn···S bonds (range 135–151°), while the SnC$_2$ system is angular (range 122–150°). As a typical example the structural parameters of SnMe$_2$(S$_2$PEt$_2$)$_2$ [Fig. 4(*a*)][26] were included in Table 3. Many diorganotin(IV) carboxylates display an analogous co-ordination geometry around tin[28,29] [*cf.* SnPh$_2$(O$_2$CMe)$_2$:[28] short Sn–O (average) 2.078(2), long Sn···O (average) 2.56(4) Å, C–Sn–C 131.4(2), exocyclic O–Sn–O 82.0(3), O···Sn···O 167.8(1)°, O···O bite (average) 2.181 Å, endocyclic O–Sn···O (average) 55.0, calculated from published atomic coordinates]. A similar structure was found for the related monothiophosphinate, SnMe$_2$(OSPEt$_2$)$_2$ [Fig. 4(*c*)],[25] with the ligands primarily bonded through oxygen atoms and occupying *cis* positions in an almost planar SnO$_2$S$_2$ system.

So far only in SnPh$_2$[S$_2$P(OPr^i)$_2$]$_2$ [Fig. 4(*b*)] the 1,1-dithio ligands were found to act as symmetric chelating units, resulting in a centrosymmetric structure with a nearly perfect octahedral co-ordination geometry around tin [average Sn–S 2.684(8) Å, C–Sn–C 180.0°, S–Sn–S (*trans*) 180.0°].[27] A similar centrosymmetric structure is exhibited by SnMe$_2$[(SPPh$_2$)$_2$N]$_2$,[3] SnBu$^n{}_2$[(OPPh$_2$)$_2$N]$_2$,[5] the present SnR$_2$[(OPPh$_2$)(SPPh$_2$)N]$_2$ [Fig. 4(*f*)] and the β-diketonato derivative SnMe$_2$[(OCMe)$_2$CH]$_2$ [Fig. 4(*e*)].[6] All these compounds contain two six-membered rings joined together by the tin spiro atom, with a planar X$_2$SnY$_2$ (X, Y = O or S) system and a linear SnC$_2$ fragment. Both the ligand bite and the flexibility of the XPNPY ligand skeleton (resulting in a diminished strain in the six-membered SnXYP$_2$N chelate ring *vs.* the four-membered

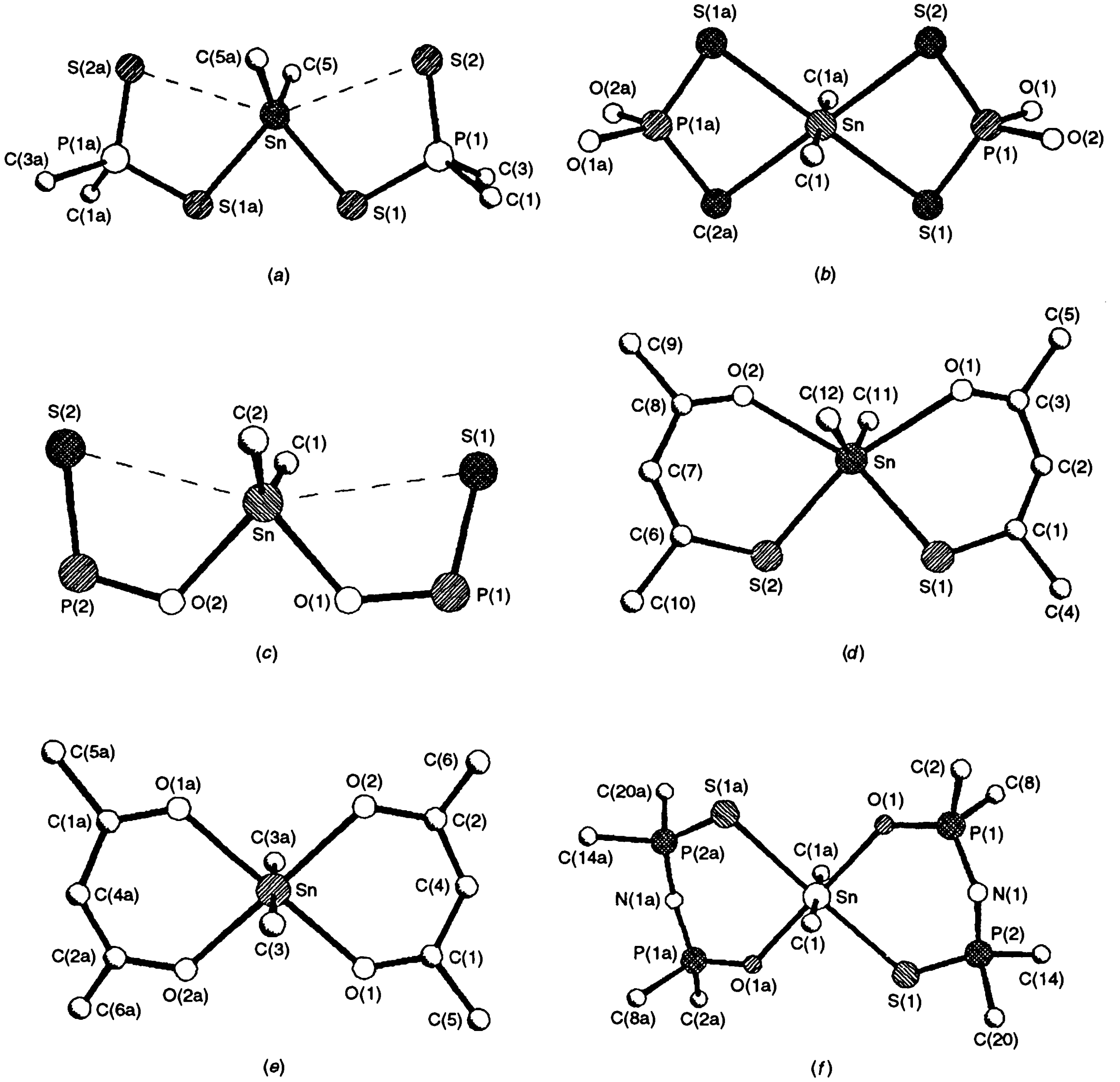


Fig. 4 The C$_2$SnX$_2$Y$_2$ (X, Y = O or S) cores in SnMe$_2$(S$_2$PEt$_2$)$_2$ (*a*), SnPh$_2$[S$_2$P(OPr^i)$_2$]$_2$ (*b*), SnMe$_2$(OSPEt$_2$)$_2$ (*c*), SnMe$_2$[(OCMe)(SCMe)CH]$_2$ (*d*), SnMe$_2$[(OCMe)$_2$CH]$_2$ (*e*) and SnMe$_2$[(OPPh$_2$)(SPPh$_2$)N]$_2$ (*f*)

Table 3 Comparative structural data for compounds **1**, **2** and some related six-co-ordinated diorganotin(IV) derivatives[a]

	SnMe$_2$-[(SPPh$_2$)$_2$N]$_2$	SnBu$_2$-[(OPPh$_2$)N]$_2$	**1** SnMe$_2$[(OPPh$_2$)-(SPPh$_2$)N]$_2$	**2** SnPh$_2$[(OPPh$_2$)-(SPPh$_2$)N]$_2$	SnMe$_2$(acac)$_2$	SnMe$_2$-[(OCMe)(SCMe)]$_2$	SnMe$_2$-[(OCPh)(SCPh)CH]$_2$	SnMe$_2$-(OSPEt$_2$)$_2$[b]	SnMe$_2$(S$_2$PEt$_2$)$_2$	SnPh$_2$-[S$_2$P(OPr^i)$_2$]$_2$
Ref.	3	5	This work	This work	6	7	7	25	26	27
SnC$_2$S$_4$ core geometry	*O$_h$*	*O$_h$*	*O$_h$*	*O$_h$*	*O$_h$*	*c*	*c*	*c*	*c*	*O$_h$*
Sn–O		2.202(5) 2.204(5)	2.199(2)	2.189(5)	2.20(1) 2.18(1)	2.452(6) 2.501(7)	2.514(3) 2.489(3)	2.00(2) 2.12(3)		
Sn–S	2.733(2) 2.737(2)		2.758(1)	2.680(4)		2.502(2) 2.528(2)	2.526(2) 2.535(2)		2.476(2)	2.689(1) 2.678(1)
Sn · · · S								3.41(1) 3.17(1)	3.336(2)	
P–O		1.520(6) 1.527(6)	1.524(2)	1.530(5)				1.60(2) 1.54(3)		
P–S	2.009(3) 2.019(3)		2.023(1)	2.018(3)					2.054(2)	1.998(2) 2.006(2)
P=S								1.97(1) 1.99(2)	1.961(2)	
X · · · Y bite	4.122[d]	3.073[d]	3.772(3)	3.489(7)	2.989[d]	3.187[d] 3.186[d]	3.183[d] 3.179[d]	2.895[d] 2.924[d]	3.333[d]	3.305[d]
Sn–O–P		129.7(3) 131.4(3)	131.7(1)	132.1(3)	127(1)[e] 126(1)[e]	127.2(5)[e] 128.8(5)[e]	127.8(3)[e] 137.2(3)[e]	126(1) 115(1)		
Sn–S–P	106.1(1) 106.0(1)		104.91(5)	103.8(1)		109.9(3)[f] 110.4(3)[f]	113.0(2)[f] 115.7(1)[f]		101.1(1)	86.26(5) 85.38(5)
Sn · · · S–P								67[d] 70[d]	78.3(1)	
C–Sn–C	180.0(1)	180.0(0)	180.00	180.00	180(0)	139.4(3)	134.2(2)	138(1)	123.7(4)	180
X–Sn–Y (endocyclic)	97.8(1)	88.5(2)	91.48(7)	91.0(2)	86(1)	80.1(1) 78.6(1)	78.3(1) 78.5(1)	58.1(6) 63.6(8)	68.1(1)	76.03(3)
X–Sn–Y (exocyclic) (*cis*)	82.2(1)	91.5(2)	88.52(8)[g]	89.0(2)[g]	94[d]	82.6(1)[h] 118.6(2)[i]	75.8(1)[h] 127.4(1)[i]	83.0(9)[i] 155.4(4)[h]	80.6(2) 143.4(2)	103.97
X–Sn–Y (exocyclic) (*trans*)	180.0(1)	180.0(0)	180.00[j]	180.00[j]	180[d]	162.7(1)[g] 161.1(1)[g]	154.1(1)[g] 154.2(1)[g]	146.2(6)[g] 138.9(8)[g]	148.4[d]	180

[a] acac = (OCMe)$_2$CH. [b] In space group *Pna*$_1$. [c] Distorted octahedral or skew-trapezoidal bipyramidal. [d] Calculated from published atomic coordinates. [e] Sn–O–C angle. [f] Sn–S–C angle. [g] O–Sn–S angle. [h] S–Sn–S angle. [i] O–Sn–O angle. [j] O–Sn–O or S–Sn–S angle.

Table 4 Crystallographic data[a]

	1 $SnMe_2[(OPPh_2)(SPPh_2)N]_2$	**2** $SnPh_2[(OPPh_2)(SPPh_2)N]_2$
Molecular formula	$C_{50}H_{46}N_2O_2P_4S_2Sn$	$C_{60}H_{50}N_2O_2P_4S_2Sn$
M	1013.63	1137.77
a/Å	10.713(7)	9.72(1)
b/Å	18.873(4)	17.718(9)
c/Å	12.144(6)	15.91(1)
β/°	104.44(4)	99.24(8)
U/Å^3	2377(1)	1577(1)
D_c/g cm^{-3}	1.42	1.72
Crystal dimensions/mm	0.23 × 0.25 × 0.32	0.19 × 0.24 × 0.35
μ(Mo-Kα)/cm^{-1}	8.01	7.13
F(000)	1036	1164
Reflections measured	4581	5243
Observed reflections [$I > 3\sigma(I)$], N_o	2911	2294
Parameters refined, N_p	277	202
R	0.0328	0.0547
R'[b]	0.0244	0.0448
Goodness of fit, S[c]	1.98	1.92

[a] Details in common: monoclinic, space group $P2_1/c$, $Z = 2$, 2θ range 2–50°. [b] $w = 1/\sigma^2(F_o)$. [c] $S = [\Sigma(|F_o| - |F_c|)/\sigma]/(N_o - N_p)$.

Table 5 Atomic coordinates for $SnMe_2[(OPPh_2)(SPPh_2)N]_2$ **1**

Atom	x	y	z
Sn	0.5	0.5	0
S(1)	0.673 3(1)	0.398 71(6)	0.108 13(8)
P(1)	0.726 1(1)	0.591 01(5)	0.196 34(8)
P(2)	0.762 7(1)	0.442 70(6)	0.259 10(8)
O(1)	0.628 8(2)	0.586 1(1)	0.081 2(2)
N(1)	0.736 6(3)	0.523 5(1)	0.277 7(2)
C(1)	0.406 3(3)	0.500 3(3)	0.134 2(3)
C(2)	0.684 5(3)	0.664 5(2)	0.273 6(3)
C(3)	0.740 7(4)	0.672 4(2)	0.389 8(3)
C(4)	0.715 0(5)	0.732 0(2)	0.446 2(3)
C(5)	0.634 7(4)	0.783 0(2)	0.391 3(4)
C(6)	0.575 8(4)	0.775 2(2)	0.276 9(4)
C(7)	0.601 9(4)	0.716 3(2)	0.219 3(3)
C(8)	0.879 3(4)	0.612 6(2)	0.168 3(3)
C(9)	0.971 5(5)	0.652 5(3)	0.240 8(4)
C(10)	1.091 1(5)	0.663 3(3)	0.220 2(5)
C(11)	1.120 5(5)	0.633 4(3)	0.127 7(5)
C(12)	1.032 1(5)	0.594 5(3)	0.056 8(4)
C(13)	0.912 7(5)	0.584 6(3)	0.075 8(4)
C(14)	0.933 2(4)	0.424 9(2)	0.282 3(3)
C(15)	1.019 7(4)	0.470 5(2)	0.349 3(3)
C(16)	1.151 7(5)	0.459 7(3)	0.365 2(4)
C(17)	1.197 5(5)	0.403 7(3)	0.317 1(4)
C(18)	1.111 9(5)	0.358 6(3)	0.252 8(4)
C(19)	0.980 9(5)	0.368 7(3)	0.234 3(4)
C(20)	0.711 4(4)	0.396 6(2)	0.371 0(3)
C(21)	0.756 8(5)	0.330 4(3)	0.405 5(4)
C(22)	0.711 1(6)	0.293 4(3)	0.487 2(4)
C(23)	0.621 6(5)	0.324 0(3)	0.533 0(4)
C(24)	0.573 9(4)	0.389 4(3)	0.499 8(4)
C(25)	0.619 6(4)	0.425 7(2)	0.419 0(3)

Table 6 Atomic coordinates for $SnPh_2[(OPPh_2)(SPPh_2)N]_2$ **2**

Atom	x	y	z
Sn	0.5	0	0.5
S(1)	0.7437(2)	−0.0132(1)	0.4428(1)
P(1)	0.4460(2)	0.0851(1)	0.3054(1)
P(2)	0.7462(2)	0.0765(1)	0.3650(2)
O(1)	0.3964(5)	0.0366(3)	0.3743(3)
N(1)	0.6039(7)	0.1129(4)	0.3214(4)
C(1)	0.5424(9)	0.1144(4)	0.5378(5)
C(2)	0.4453(9)	0.1704(5)	0.5102(6)
C(3)	0.470(1)	0.2453(5)	0.5333(7)
C(4)	0.592(1)	0.2641(6)	0.5819(8)
C(5)	0.690(1)	0.2104(6)	0.6124(7)
C(6)	0.664(1)	0.1347(5)	0.5883(6)
C(7)	0.3386(9)	0.1681(5)	0.2860(5)
C(8)	0.389(1)	0.2333(5)	0.2548(6)
C(9)	0.299(1)	0.2958(6)	0.2349(7)
C(10)	0.166(1)	0.2908(6)	0.2517(7)
C(11)	0.114(1)	0.2267(6)	0.2828(7)
C(12)	0.203(1)	0.1642(5)	0.3022(6)
C(13)	0.4101(9)	0.0333(5)	0.2077(6)
C(14)	0.360(1)	0.0653(5)	0.1314(6)
C(15)	0.343(1)	0.0227(6)	0.0555(7)
C(16)	0.379(1)	−0.0521(7)	0.0605(8)
C(17)	0.425(1)	−0.0856(6)	0.1346(8)
C(18)	0.443(1)	−0.0441(6)	0.2100(7)
C(19)	0.8477(9)	0.1534(5)	0.4187(5)
C(20)	0.803(1)	0.2285(5)	0.4027(6)
C(21)	0.887(1)	0.2862(6)	0.4429(7)
C(22)	1.006(1)	0.2700(6)	0.498(1)
C(23)	1.050(1)	0.1975(6)	0.5135(7)
C(24)	0.969(1)	0.1396(5)	0.4740(6)
C(25)	0.8494(9)	0.0468(5)	0.2854(6)
C(26)	0.815(1)	0.0736(7)	0.2037(8)
C(27)	0.900(1)	0.0547(7)	0.1420(8)
C(28)	1.004(1)	0.0050(8)	0.1615(7)
C(29)	1.039(1)	−0.0218(6)	0.2402(7)
C(30)	0.9589(9)	−0.0014(7)	0.3025(5)

SnXYP ring) might account for the differences noted in the angles at tin and chalcogen atoms, respectively (Table 3).

It should be noted that in symmetric complexes like $SnPh_2[S_2P(OPr^i)_2]_2$ and $SnMe_2[(SPPh_2)_2N]_2$ the Sn–S bond lengths [range 2.678(1)–2.737(2) Å] are intermediate between the values observed for primary Sn–S and secondary Sn ··· S bonds in unsymmetric complexes [*e.g.* $SnMe_2(S_2PEt_2)_2$:[26] Sn–S 2.476(2), Sn ··· S 3.336(2) Å]. In the oxothio complexes investigated in this work the tin–sulfur interatomic distances [2.758(1) Å in **1**, 2.680(4) Å in **2**] are also longer than primary Sn–S bonds (*ca.* 2.40–2.50 Å). The same observation is valid for the tin–oxygen interatomic distances [range 2.189(5)–2.204(5) Å] in $SnR_2[(OPPh_2)(SPPh_2)N]_2$ and $SnBu^n{}_2[(OPPh_2)_2N]_2$ in comparison with primary Sn–O and secondary Sn ··· O bonds in diorganotin carboxylates [*e.g.* $SnPh_2(O_2CMe)_2$:[28] Sn–O (average) 2.078(2), Sn ··· O (average) 2.56(4) Å].

By contrast, the related diorganotin(IV) derivatives of monothio-β-diketones, $SnMe_2[(OCR)(SCR)CH]_2$ (R = Me or Ph) [Fig. 4(*d*)],[7] display a different structure, *i.e.* angular SnC_2 fragment in a strongly distorted-octahedral environment around tin, very similar to that found for the $SnR_2(S_2Z)_2$ and $SnMe_2(OSPEt_2)_2$ compounds. However, the Sn–O bonds in the monothio-β-diketonates are significantly weaker [range 2.452(6)–2.514(3) Å] than normally observed in other oxo ligand organotin derivatives (see Table 3), and the O–Sn–O angle is more opened than the S–Sn–S, a reversed situation compared to that found for the related $SnMe_2(OSPEt_2)_2$.[25] Since oxothio anions are ambidentate, two types of structures can be formed:

with primary (short) bonds to oxygen and secondary (long) bonds to sulfur and *vice versa*. The data in Table 3 allow one to distinguish between these two possibilities, although alternatives are not always clear cut.

Moreover, the symmetric structure of $SnR_2[(XPPh_2)(YPPh_2)N]_2$ is not only the simple result of a better co-ordinating ability of the ligand. Thus, in the monothio derivatives, $SnR_2[(OPPh_2)(SPPh_2)N]_2$, the oxygen and sulfur atoms occupy *trans* positions in the equatorial plane and not *cis* positions as one would expect due to stronger sulfur–tin interactions in a $C_2SnO_2S_2$ core of the type observed for $SnMe_2(OSPEt_2)_2$ [Fig. 4(*c*)] or $SnMe_2[(OCR)(SCR)CH]_2$ (R = Me or Ph) [Fig. 4(*d*)].

As a conclusion, the structural features of the diorganotin(IV) derivatives discussed above suggest that, although the X ··· Y bite distances (Table 3) for 1,1-dichalcogenide ligands are significantly shorter than for 1,3-dichalcogenes, neither this difference nor the relative co-ordinating ability of a particular type of ligand seem to be uniquely responsible for the changes observed in the geometry at the tin atom.

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