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Synthesis, Characterization, and Reaction Chemistry of [2-(2-Pyridyl)ethyl]-, [2-(4-Pyridyl)ethyl]-, and [2-(2-Oxo-*N*-pyrrolidinyl)ethyl]triphenyltin(IV)

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The compounds Ph_3SnR [R = $(CH_2)_2C_5H_5N$-2 (**1**), $(CH_2)_2C_5H_5N$-4 (**2**), and $(CH_2)_2C_3H_6C(O)N$-2 (**3**)] have been synthesized by hydrostannylation of 2- or 4-vinylpyridine and *N*-vinylpyrrolidin-2-one, respectively, with Ph_3SnH. Reaction of **1**–**3** with 1 equiv of X_2 (X = Br, I) gives Ph_2RSnX, which have been used to synthesize representative compounds of general formula $Ph_2RSn(L)$, L = $S_2CNR'_2$ (R′ = Me, Et) or O_2CR' (R′ = Me, Ph). The structures of the compounds are discussed on the basis of their ^1H, ^{13}C, ^{119}Sn NMR and ^{119}Sn Mössbauer data. The structure of $Ph_2Sn[(CH_2)_2C_5H_5N\text{-}2](S_2CNMe_2)$ has been determined by X-ray crystallography: $C_{22}H_{24}N_2S_2Sn$, fw 499.28, a = 9.611 (4) Å, b = 10.255 (3) Å, c = 12.896 (9) Å, α = 75.35 (4)°, β = 70.97 (4)°, γ = 68.09 (3)°, V = 1102.2 Å^3, Z = 2, space group $P\bar{1}$, ρ_{calc} = 1.50 g cm^{-3}, μ(Mo Kα) = 12.42 cm^{-1}, λ(Mo Kα) = 0.710 69 Å, $F(000)$ = 504, R = 0.0492, R_w = 0.0542 for 2133 unique data. The tin is in a five-coordinate, trigonal bipyramidal *trans*-$NSSnPh_2R$ environment, with nitrogen and sulfur in the axial positions. The 2-ethylpyridyl ligand chelates the metal, while the dithiocarbamate is monodentate.

Introduction

We have been interested in the synthesis of organotin compounds of general type $R_2R'SnX$, where R = Bu, Ph, C_6H_{11} and R′ is a biocidally active heterocycle, such that the unsymmetrical triorganotin may offer synergic biocidal activity between the heterocycle and metal centers.[1] Such an approach differs from the majority reported over the last decade which have seen the ligand X as the favored variable, despite the fact that the most common linkages (Sn–O, N, S) are all readily cleaved under in vivo (i.e. hydrolytic) conditions.[2] Incorporation of the ligand of complimentary activity via an Sn–C bond, generally a more hydrolytically stable entity, should maintain the proximity of the two centers and may create novel activity. Despite this assertion, we have found that the Sn–C bond in *C*-organostannyl heterocycles is remarkably reactive and, in the case of triphenyltin derivatives of imidazoles, benzoxazoles, and benzothiazoles, is more susceptible to cleavage by both electrophiles (e.g. I_2) and nucleophiles (OH^-) than the Sn–C_6H_5 bond.[1] In order to mitigate this reactivity, we have sought to synthesize related compounds of general formula $R_2Sn(CH_2CH_2R')X$, in which the active heterocycle (R′) is separated from the metal by *at least two* methylene groups.[3] This effectively renders "alkyl" rather than "phenyl" or "benzyl" character on the heterocycle (i.e. none or one methylene linkage) and hence increases the stability of the Sn–C bond coupling the metal to the (now substituted) heterocycle.

In this paper we wish to report the synthesis of such compounds, in which either pyridine or pyrrolidin-2-one are thus combined with tin via a CH_2CH_2 moiety. The C_5H_5N heterocycle is a component of the well-known weedkillers "Diquat" and "Paraquat", while chloropyridines feature strongly in the herbicide market in a variety of commercial preparations.[4] Several pyridine derivatives have found applications in the poultry industry as antiparasitics and anthelmintics.[5] The pyrrolidine nucleus and its derivatives also form the basis for a number of biocidal formulations and are also present as a component of the notorious pharmaceutical thalidomide. It is, additionally, also used in a number of insecticides, fungicides, and as a diuretic.

Experimental Section

General Data. Spectra were recorded on the following instruments: Perkin-Elmer 599B (infrared spectra), JEOL GX270 (^1H, ^{13}C NMR), JEOL GX400 (^{119}Sn NMR). NMR spectra were recorded as saturated $CDCl_3$ solutions at room temperature. Coupling constants involving tin refer to $^{117,119}Sn$ nuclei as written. Unspecified ^{13}C chemical shifts refer to the numbering schemes shown in **1**–**3** of Scheme I and are given in order. ^{13}C chemical shifts for the phenyl groups are given in the order ipso, ortho, meta, and para. Details of our Mössbauer spectrometer and related procedures are given elsewhere.[6] Infrared spectra were recorded as Nujol mulls on CsI windows. Microanalyses were performed by the Microanalysis Service of the University of Bath.

Triphenyltin hydride was prepared according to the method of Van der Kerk.[7] 2- and 4-vinylpyridine were of commercial origin (Aldrich) and were distilled under reduced pressure before use. *N*-vinylpyrrolidin-2-one and *N,N*-dimethyl- and *N,N*-diethyldithiocarbamate (the latter two as their sodium salts) (Aldrich) were used as supplied. Petroleum ether (or petrol) refers to that fraction boiling in the 60–80 °C range, throughout.

Synthesis of [2-(2-Pyridyl)ethyl]triphenyltin (1). Triphenyltin hydride (2.84 g, 7.37 mmol) and 2-vinylpyridine (1.15

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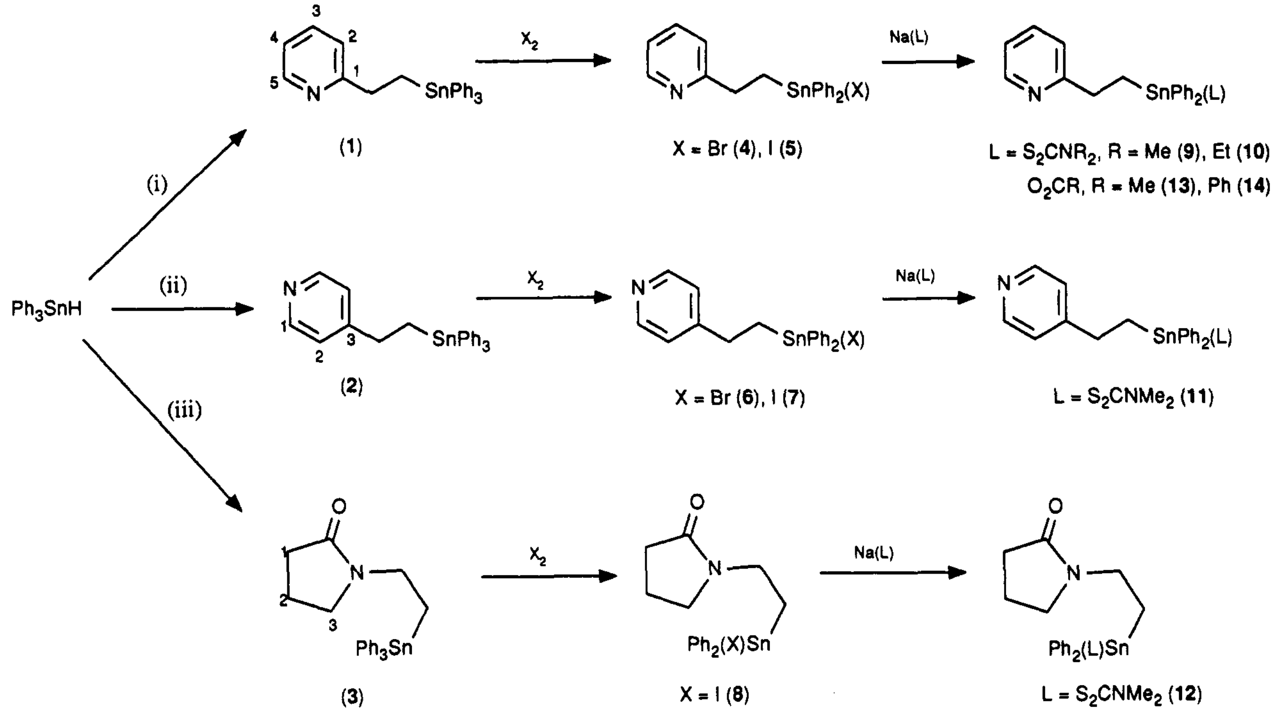
Scheme I. [a] **Reagents: (i) 2-Vinylpyridine, (ii) 4-Vinylpyridine, (iii) *N*-Vinylpyrrolidin-2-one**



[a] The numbering of carbon atoms in 1–3 refers to the listing of ^{13}C chemical shift data in the Experimental Section.

g, 11 mmol) were stirred together as a melt at 100 °C for 2 h under a dry dinitrogen atmosphere. The solid residue was recrystallized from petroleum ether to yield hexaphenylditin (0.56 g). The mother liquor was evaporated to dryness under reduced pressure, and the remaining solid recrystallized from methanol–diethyl ether (1:1) to yield the product 1 (2.71 g, 80%; mp 73 °C, lit. mp[8] 72–4 °C). Anal. Found (Calc) for $C_{25}H_{23}NSn$: C, 66.10 (65.82); H, 5.08 (5.09); N, 3.17 (3.07). ^{1}H NMR: 1.85 (t, 2 H, $\mathrm{SnCH_2C}H_2$), 3.21 (t, 2 H, $\mathrm{SnC}H_2$), 6.94–8.24 (m, 19 H, $\mathrm{C_6}H_5$, $\mathrm{C_5}H_4\mathrm{N}$) ppm; ^2J(Sn–CH$_2$) 68.6, 72.0 Hz. ^{13}C NMR: 10.5 ($\mathrm{Sn}C\mathrm{H_2}$) [^1J(Sn–C) 406, 423 Hz], 33.9 ($\mathrm{SnCH_2}C\mathrm{H_2}$), 140.3, 136.9, 128.1, 128.4 ($C_6\mathrm{H_5}$), 162.7, 122.4, 136.2, 121.0, 148.7 ($C_5\mathrm{H_4N}$).

Synthesis of [2-(4-Pyridyl)ethyl]triphenyltin (2). Following the procedure described for 1 (10-mmol scale, reaction time 30 min) yielded a solidified mass, from which 2 was crystallized using petroleum ether as solvent (4.12 g, 90%; mp 112 °C, lit. mp[9] 112–3 °C). Anal. Found (Calc) for $C_{25}H_{23}NSn$: C, 64.50 (65.82); H, 4.78 (5.09); N, 3.04 (3.07). ^{1}H NMR: 1.76 (t, 2 H, $\mathrm{SnCH_2C}H_2$), 2.95 (t, 2 H, $\mathrm{SnC}H_2$), 7.01–8.42 (m, 19 H, $\mathrm{C_6}H_5$, $\mathrm{C_5}H_4\mathrm{N}$) ppm; ^2J(Sn–CH$_2$) 44.4, 51.8 Hz. ^{13}C MMR: 11.2 ($\mathrm{Sn}C\mathrm{H_2}$) [^1J(Sn–C) 360, 376 Hz], 31.7 ($\mathrm{SnCH_2}C\mathrm{H_2}$), 137.9, 136.8, 128.5, 128.9 ($C_6\mathrm{H_5}$), 149.6, 123.1, 153.2 ($C_5\mathrm{H_4N}$).

Synthesis of [2-(2-Oxo-*N*-pyrrolidinyl)ethyl]triphenyltin (3). Following the procedure described for 1 (10-mmol scale, reaction time 4 h at 90 °C), 3 was crystallized from petrol as white rosettes (3.93 g, 85%; mp 73–5 °C, lit. mp[8] 74–6 °C). Anal. Found (Calc) for $C_{24}H_{25}NOSn$: C, 62.30 (62.37); H, 5.40 (5.46); N, 2.87 (3.03). ^{1}H NMR: 1.7 (t, 2 H, $\mathrm{SnCH_2C}H_2$), 1.72 (m, 2 H, $\mathrm{C}H_2\mathrm{CH_2CO}$), 2.12 (t, 2 H, $\mathrm{C}H_2\mathrm{CO}$), 3.33 (t, 2 H, $\mathrm{C}H_2\mathrm{N}$), 3.65 (t, 2 H, $\mathrm{SnC}H_2$), 7.22–7.64 (m, 15 H, $\mathrm{C_6}H_5$) ppm; ^2J(Sn–CH$_2$) 52.9, 56.8 Hz. ^{13}C NMR: 9.4 ($\mathrm{Sn}C\mathrm{H_2}$) [^1J(Sn–C) 344, 359 Hz], 30.9 ($\mathrm{SnCH_2}C\mathrm{H_2}$), 137.8, 136.9, 128.5, 129.0 ($C_6\mathrm{H_5}$), 46.2, 17.4, 40.3 ($C\mathrm{H_2}$, pyrrolidine), 174.4 (CO). IR: ν(C=O) 1680 cm^{-1}.

Synthesis of [2-(2-Pyridyl)ethyl]diphenyltin Bromide (4). 1 (5.07 g, 11.1 mmol) was dissolved in CCl_4 (75 mL), and the solution was cooled to 0 °C. Bromine (1.77 g, 11.1 mmol), also dissolved in CCl_4 (50 mL), was added dropwise with stirring over a period of 1 h, during which time the coloration due to the halogen had completely disappeared. The solvent was distilled in vacuo, and the oily residue was dissolved in hot petrol–ethyl acetate (9:1). 4 deposited as white crystalline needles on cooling (4.67 g, 91%, mp 168–9 °C). Anal. Found (Calc) for $C_{19}H_{18}BrNSn$: C, 49.20 (49.71); H, 3.93 (3.92); N, 3.04 (3.05). ^{1}H NMR: 2.08 (t, 2 H, $\mathrm{SnCH_2C}H_2$), 3.44 (t, 2 H, $\mathrm{SnC}H_2$), 7.12–7.91 (m, 14 H, $\mathrm{C_6}H_5$, $\mathrm{C_5}H_4\mathrm{N}$) ppm; ^2J(Sn–CH$_2$) 110.8, 114.8 Hz. ^{13}C NMR: 16.1 ($\mathrm{Sn}C\mathrm{H_2}$) [^1J(Sn–C) 578, 605 Hz], 31.8 ($\mathrm{SnCH_2}C\mathrm{H_2}$), 139.2, 135.9, 128.4, 128.9 ($C_6\mathrm{H_5}$), 161.2, 124.6, 136.3, 122.9, 146.3 ($C_5\mathrm{H_4N}$). IR: ν(Sn–Br) 260 cm^{-1}.

Synthesis of [2-(2-Pyridyl)ethyl]diphenyltin Iodide (5). 1 (1.0 g, 2.2 mmol) in petrol and iodine (0.55 g, 2.2 mmol) in the same solvent (100 mL) was reacted over a 1-h period. The resulting suspension was filtered and the solid recrystallized from ethyl acetate–petrol (9:1) to give 5 as yellow needles (0.85 g, 76%, mp 160 °C). Anal. Found (Calc) for $C_{19}H_{18}INSn$: C, 45.20 (45.09); H, 3.58 (3.56); N, 2.76 (2.76). ^{1}H NMR: 2.16 (t, 2 H, $\mathrm{SnCH_2C}H_2$), 3.42 (t, 2 H, $\mathrm{SnC}H_2$), 7.06–7.83 (m, 14 H, $\mathrm{C_6}H_5$, $\mathrm{C_5}H_4\mathrm{N}$) ppm; ^2J(Sn–CH$_2$) 112.9, 118.8 Hz. ^{13}C NMR: 18.9 ($\mathrm{Sn}C\mathrm{H_2}$) [^1J(Sn–C) 555 Hz, unresolved], 31.8 ($\mathrm{SnCH_2}C\mathrm{H_2}$), 141.7, 135.8, 128.2, 128.8 ($C_6\mathrm{H_5}$), 160.8, 124.6, 139.3, 122.9, 145.9 ($C_5\mathrm{H_4N}$).

Synthesis of [2-(4-Pyridyl)ethyl]diphenyltin Bromide (6). Using 2 (1.76 g, 3.85 mmol) and the methodology described for 4 gave a white suspension, which was stirred overnight. After removal of volatiles the residue was dissolved in hot ethanol, from which 6 deposited as a white powder on cooling (1.42 g, 80%, mp 137–9 °C). Anal. Found (Calc) for $C_{19}H_{18}BrNSn$: C, 50.12 (49.71); H, 3.99 (3.92); N, 2.96 (3.05). ^{1}H NMR: 2.08 (t, 2 H, $\mathrm{SnCH_2C}H_2$), 3.07 (t, 2 H, $\mathrm{SnC}H_2$), 7.02–8.45 (m, 14 H, $\mathrm{C_6}H_5$, $\mathrm{C_5}H_4\mathrm{N}$) ppm; ^2J(Sn–CH$_2$) 63.7, 66.8 Hz. ^{13}C NMR: 17.9 ($\mathrm{Sn}C\mathrm{H_2}$), 31.6 ($\mathrm{SnCH_2}C\mathrm{H_2}$), 136.9, 136.3, 129.3, 130.1 ($C_6\mathrm{H_5}$), 149.7, 123.3, 153.4 ($C_5\mathrm{H_4N}$). IR: ν(Sn–Br) 264 cm^{-1}.

[2-(4-Pyridyl)ethyl]diphenyltin iodide (7) was prepared as for 5 using $CHCl_3$ as solvent and 2 as starting material. Recrystallization from ethanol yielded 7 as small yellow rosettes (54%, mp 155–6 °C). Anal. Found (Calc) for $C_{19}H_{18}INSn$: C, 45.40 (45.09); H, 3.59 (3.56); N, 2.69 (2.76). ^{1}H NMR: 2.00 (t, 2 H, $\mathrm{SnCH_2C}H_2$), 3.04 (t, 2 H, $\mathrm{SnC}H_2$), 7.01–8.40 (m, 14 H, $\mathrm{C_6}H_5$, $\mathrm{C_5}H_4\mathrm{N}$) ppm; ^2J(Sn–CH$_2$) 65.6, 68.9 Hz. ^{13}C NMR: 17.2 ($\mathrm{Sn}C\mathrm{H_2}$), 31.9 ($\mathrm{SnCH_2}C\mathrm{H_2}$), 136.8, 135.9, 128.9, 130.0 ($C_6\mathrm{H_5}$), 149.7, 123.4, 153.2 ($C_5\mathrm{H_4N}$).

[2-(2-Oxo-*N*-pyrrolidinyl)ethyl]diphenyltin iodide (8) was prepared by the addition of iodine (1.03 g, 4.06 mmol) to 3 (1.88

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g, 4.06 mmol) using $CHCl_3$ as common solvent (200 mL) over a period of 30 min. The solution was reduced in volume and the oily residue taken up in hot ethyl acetate–petroleum ether (1:1). Cooling afforded the product as white crystals (1.77 g, 85%, mp 146 °C). Anal. Found (Calc) for $C_{19}H_{18}INSn$: C, 45.40 (45.09); H, 3.59 (3.56); N, 2.69 (2.76). ^{1}H NMR: 1.92 (m, 2 H, CH_2CH_2CO), 2.02 (t, 2 H, $SnCH_2CH_2$), 2.24 (t, 2 H, CH_2CO), 3.42 (t, 2 H, CH_2N), 3.59 (t, 2 H, $SnCH_2$), 7.23–8.04 (m, 10 H, C_6H_5) ppm; $^2J(Sn–CH_2)$ 126.0, 132.8 Hz. ^{13}C NMR: 17.9 ($SnCH_2$) [$^1J(Sn–C)$ 566 Hz, unresolved], 31.6 ($SnCH_2CH_2$), 141.4, 136.7, 128.1, 128.9 (C_6H_5), 51.0, 22.8, 45.0 (CH_2, pyrrolidine), 178.7 (CO). IR: ν(C=O) 1625 cm^{-1}.

Synthesis of [2-(2-Pyridyl)ethyl](*N*,*N*-dimethyldithiocarbamato)diphenyltin (9). 4 (1.60 g, 3.48 mmol) and the sodium salt of *N*,*N*-dimethyldithiocarbamate (0.65 g, 3.48 mmol) were dissolved in 1:1 ethanol–ethyl acetate (100 mL) and stirred together at 50 °C for 30 min and then at reflux for the same period. The solution was allowed to cool and the solvent removed in vacuo. The solid was partitioned between ethyl acetate (50 mL) and water (50 mL), the organic layer separated, dried ($MgSO_4$), reduced in volume, and cooled to give 9 as white needles (1.42 g, 81%, mp 160 °C). Anal. Found (Calc) for $C_{22}H_{24}N_2S_2Sn$: C, 52.99 (52.92); H, 4.90 (4.86); N, 5.58 (5.61). ^{1}H NMR: 2.27 (t, 2 H, $SnCH_2CH_2$), 3.39 (s, 6 H, NCH_3), 3.43 (t, 2 H, $SnCH_2$), 6.93–7.71 (m, 14 H, C_6H_5, C_5H_4N) ppm; $^2J(Sn–CH_2)$ 135.0, 141.3 Hz. ^{13}C NMR: 20.2 ($SnCH_2$) [$^1J(Sn–C)$ 666 Hz, unresolved], 32.0 ($SnCH_2CH_2$), 44.6 (NCH_3), 142.1, 136.1, 128.2, 128.6 (C_6H_5), 160.5, 123.6, 137.7, 121.9, 146.4 (C_5H_4N), 201.8 (CS_2). IR: ν(C–N) 1460, ν(C–S) 1120, 1080 cm^{-1}.

[2-(2-Pyridyl)ethyl](*N*,*N*-diethyldithiocarbamato)diphenyltin (10) was prepared as for 9 using $Et_2NCS_2Na\cdot3H_2O$ as reagent, yielding white crystals (72%, mp 145–6 °C). Anal. Found (Calc) for $C_{24}H_{28}N_2S_2Sn$: C, 54.50 (54.66); H, 5.37 (5.36); N, 5.31 (5.31). ^{1}H NMR: 1.19 (t, 6 H, CH_3CH_2N), 2.28 (t, 2 H, $SnCH_2CH_2$), 3.42 (t, 2 H, $SnCH_2$), 3.87 (q, 4 H, CH_2N), 6.92–7.70 (m, 14 H, C_6H_5, C_5H_4N) ppm; $^2J(Sn–CH_2)$ 129.8, 138.0 Hz. ^{13}C NMR: 12.1 (CH_3CH_2N), 20.3 ($SnCH_2$), 32.1 ($SnCH_2CH_2$), 48.5 (NCH_2), 144.6, 136.2, 127.9, 128.4 (C_6H_5), 160.9, 123.6, 137.3, 121.9, 146.4 (C_5H_4N), 201.8 (CS_2). IR: ν(C–N) 1450, ν(C–S) 1140, 1080 cm^{-1}.

[2-(4-Pyridyl)ethyl](*N*,*N*-dimethyldithiocarbamato)diphenyltin (11) was prepared from 6 using the method described for 9. The product was isolated as a microcrystalline solid (66%, mp 191–2 °C). Anal. Found (Calc) for $C_{22}H_{24}N_2S_2Sn$: C, 53.10 (52.92); H, 5.11 (4.86); N, 5.21 (5.61). ^{1}H NMR: 2.09 (t, 2 H, $SnCH_2CH_2$), 3.13 (t, 2 H, $SnCH_2$), 3.38 (s, 6 H, NCH_3), 7.02–8.48 (m, 14 H, C_6H_5, C_5H_4N) ppm; $^2J(Sn–CH_2)$ 64.7, 68.6 Hz. ^{13}C NMR: 20.6 ($SnCH_2$), 31.5 ($SnCH_2CH_2$), 45.8 (NCH_3), 135.6, 136.3, 128.4, 129.0 (C_6H_5), 149.5, 123.4, 153.2 (C_5H_4N), 201.2 (CS_2). IR: ν(C–N) 1465, ν(C–S) 1160, 1080 cm^{-1}.

[2-(2-Oxo-*N*-pyrrolidinyl)ethyl](*N*,*N*-dimethyldithiocarbamato)diphenyltin (12) was prepared from 8 using the methodology described for 9, yielding white crystals (81%, mp 117 °C). Anal. Found (Calc) for $C_{21}H_{26}N_2OS_2Sn$: C, 49.80 (49.91); H, 5.21 (5.20); N, 5.56 (5.54). ^{1}H NMR: 1.84 (m, 2 H, CH_2CH_2CO), 2.07 (t, 2 H, $SnCH_2CH_2$), 2.21 (t, 2 H, CH_2CO), 3.37 (t, 2 H, CH_2N), 3.42 (s, 6 H, NCH_3), 3.77 (t, 2 H, $SnCH_2$), 7.25–7.80 (m, 10 H, C_6H_5) ppm; $^2J(Sn–CH_2)$ 68.0, 72.0 Hz. ^{13}C NMR: 18.6 ($SnCH_2$) [$^1J(Sn–C)$ 483 Hz, unresolved], 31.1 ($SnCH_2CH_2$), 45.5 (NCH_3), 142.2, 136.2, 128.2, 128.8 (C_6H_5), 47.2, 17.6, 41.1 (CH_2, pyrrolidine), 174.9 (CO), 197.6 (CS_2). IR: ν(C=O) 1670, ν(C–N) 1462, ν(C–S) 1160, 1062 cm^{-1}.

Synthesis of [2-(2-Pyridyl)ethyl]diphenyltin Acetate (13). 4 (3.03 g, 6.6 mmol) and glacial acetic acid (0.40 g, 6.6 mmol) were dissolved in acetone (40 mL) and triethylamine (0.67 g, 6.6 mmol), also in acetone (10 mL), added with stirring over a 30-min period. Stirring was continued for a further 30 min, Et_3NHBr was removed by filtration, and the filtrate was evaporated to dryness. The oily residue was dissolved in hot ethyl acetate–petrol (1:9) and cooled to give the product as a white crystalline solid (2.31 g, 79%, mp 80–1 °C). Anal. Found (Calc) for $C_{21}H_{21}NO_2Sn$: C, 57.70 (57.57); H, 4.83 (4.84); N, 3.16 (3.20). ^{1}H NMR: 1.94 (t, 2 H, $SnCH_2CH_2$), 1.98 (s, 3 H, CH_3CO_2), 3.38 (t, 2 H, $SnCH_2$), 7.03–7.82 (m, 14 H, C_6H_5, C_5H_4N) ppm; $^2J(Sn–CH_2)$ 117.0, 125.0 Hz. ^{13}C NMR: 12.9 ($SnCH_2$) [$^1J(Sn–C)$ 655 Hz, unresolved], 22.9 (CH_3CO_2), 31.5 ($SnCH_2CH_2$), 144.8, 136.2, 127.4, 127.2 (C_6H_5), 160.9, 124.1, 138.5, 122.4, 146.2 (C_5H_4N), 177.4 (CO_2). IR: $\nu_{asym}(CO_2)$ 1635 cm^{-1}.

Table I. Crystal and Data Collection Parameters for [2-(2-Pyridyl)ethyl]diphenyltin *N*,*N*-Dimethyldithiocarbamate

formula	$C_{22}H_{24}N_2S_2Sn$
fw	499.28
a, Å	9.611 (4)
b, Å	10.255 (3)
c, Å	12.896 (9)
α, deg	75.35 (4)
β, deg	70.97 (4)
γ, deg	68.09 (3)
V, Å^3	1102.2
Z	2
space group	$P\bar{1}$
ρ_{calc}, g cm^{-3}	1.50
μ(Mo Kα), cm^{-1}	12.42
λ(Mo Kα), Å	0.710 69
F(000)	504
temp, K	298
scan technique	ω–2θ
2θ limit, deg	44
quadrant collcd	h 0→10; k, +11→–11; l, +13→–13
no. data collcd	2893
no. unique data	2440
no. obsd data $I > 3\sigma(I)$	2133
R	0.0492
R_w	0.0542
no. of variable params	154
max, min residual density, e Å^{-3}	0.29, –0.36
max shift/esd	0.009

Table II. ^{119}Sn Mössbauer[a,b] and NMR Data[c]

	$\delta(^{119}Sn)$	IS	QS
1	–110.8	1.22	0.63
2	–101.8	1.25	0.32
3	–109.3	1.23	0.39
4	–143.5	1.32	2.98
5	–109.3	1.35	2.95
6	–85.8	1.33	2.95
7	–61.7	1.34	2.92
8	–147.2	1.33	3.14
9	–202.0	1.27	2.55
10	–198.2	1.27	2.35
11	–128.1	1.27	2.55
12	–182.8	1.30	2.18
13	–177.3	1.26	2.71
14	–175.2	1.26	2.41

[a] mm s^{-1}. [b] Full width at half-height in the range 0.87–0.99 mm s^{-1} for all compounds except 6, which has Γ = 1.38, 1.55 mm s^{-1}. [c] All shifts in ppm relative to Me_4Sn.

[2-(2-Pyridyl)ethyl]diphenyltin benzoate (14) was prepared as for 13 using benzoic acid as reagent. The product was isolated as a microcrystalline white solid (61%, mp 140–4 °C). Anal. Found (Calc) for $C_{26}H_{23}NO_2Sn$: C, 62.32 (62.43); H, 4.58 (4.64); N, 2.77 (2.80). ^{1}H NMR: 1.94 (t, 2 H, $SnCH_2CH_2$), 3.38 (t, 2 H, $SnCH_2$), 7.03–7.82 (m, 19 H, C_6H_5Sn, $C_6H_5CO_2$, C_5H_4N) ppm; $^2J(Sn–CH_2)$ 117.0, 124.2 Hz. ^{13}C NMR: 13.2 ($SnCH_2$), 30.0 ($SnCH_2CH_2$), 144.8, 136.2, 127.4, 127.2 (C_6H_5Sn), 160.2, 123.7, 138.2, 121.9, 146.1 (C_5H_4N), 130.6, 129.7, 128.5, 132.9 ($C_6H_5CO_2$), 169.8 (CO_2). IR: $\nu_{asym}(CO_2)$ 1640 cm^{-1}.

Crystallographic Analysis of [2-(2-Pyridyl)ethyl]diphenyltin *N*,*N*-Dimethyldithiocarbamate. Crystals suitable for X-ray diffraction were obtained by recrystallization from a petrol–ethyl acetate mixture (1:1). A crystal of approximate dimensions 0.2 × 0.2 × 0.1 mm was used for data collection. Crystal data and parameters associated with the data collection and treatment are given in Table I. Unit cell parameters are based upon 12 centered reflections with $\theta > 11°$. Data were collected at room temperature on a Hilger and Watts Y290 automatic four-circle diffractometer. A monitor reflection, measured at 75-min intervals, indicated no systematic intensity

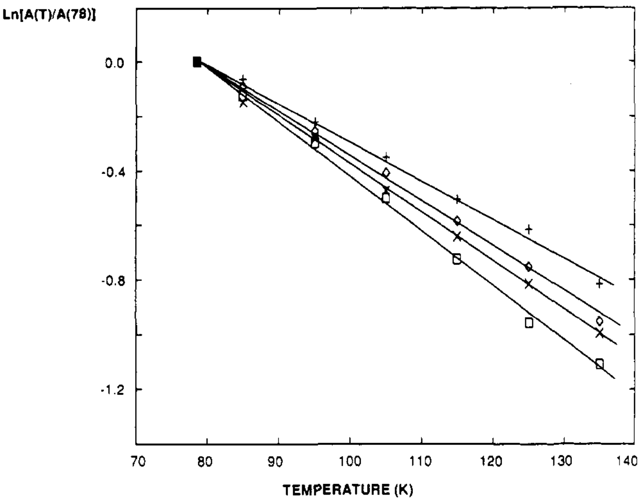

Figure 1. Temperature dependence of the Mössbauer spectral areas for (1) (□), (2) (◇), (4) (×) and (7) (+). Slopes of the best fit straight lines (-10^2d ln A/dT, K^{-1}) are (1) 1.96, (2) 1.60, (4) 1.75, and (7) 1.37.

decay. Data were corrected for Lorentz and polarization, but not absorption. The structure was solved and refined using conventional Patterson and Fourier methods (SHELX76,[10] SHELX86[11]). In the final stages of refinement, Sn, S, N, and C(1)–C(5) were treated anisotropically. The remaining atoms were refined with isotropic thermal parameters. Atomic scattering factors were taken from the usual sources.[12]

The asymmetric unit with the labeling scheme used in the text is given in Figure 2. Fractional atomic coordinates and selected bond distances and angles are given in Tables III and IV, respectively.

Results and Discussion

The synthetic procedures carried out in this study are represented in Scheme I. The three tetraorganotin compounds **1**–**3** have each been synthesized by the addition of Sn–H across the unsaturated C=C bonds of either 2- or 4-vinylpyridine or N-vinylpyrrolidin-2-one, respectively. The reactions proceed over a 2–4-h period at ca. 100 °C, without the addition of catalyst. Yields are in excess of 80%. The course of the reaction can be monitored by the disappearance of ν(Sn–H) (1825 cm^{-1}) and, in the case of the pyrrolidin-2-one, ν(C=C) (1630 cm^{-1}), which is unobscured by vibrational modes of any aromatic functionalities. The nature of the final reaction product seems dependent on the purity of Ph_3SnH used, since undistilled hydride leads to the formation of Ph_6Sn_2 as the major, sometimes quantitative, product.

The triorganotin bromides **4** and **6** and iodides **5**, **7**, and **8** were prepared from their parent tetraorganotin by halogen cleavage. Under the reaction stoichiometry used only one Sn–C bond was cleaved and this was without exception an Sn–C(Ph) moiety. The resulting unsymmetrical triorganotin halides have been used as starting materials for the synthesis of other triorganotin derivatives, based on simple metathesis reactions with dithiocarbamate, **9**–**12**, acetate, **13**, or benzoate, **14**, anions. All of the compounds reported are stable under normal aerobic conditions.

The three tetraorganotins are all tetrahedral in nature, but each exhibits a narrow quadrupole splitting (QS) in its Mössbauer spectrum, reflecting electronic differences in the Sn–Ph and Sn–CH_2 bonds. Older data on the related compounds such as $Ph_3Sn(CH_2)_3CO_2Me$[13] or $Ph_3SnCH_2CH{=}CH_2$[14] have each been reported as having singlet spectra.

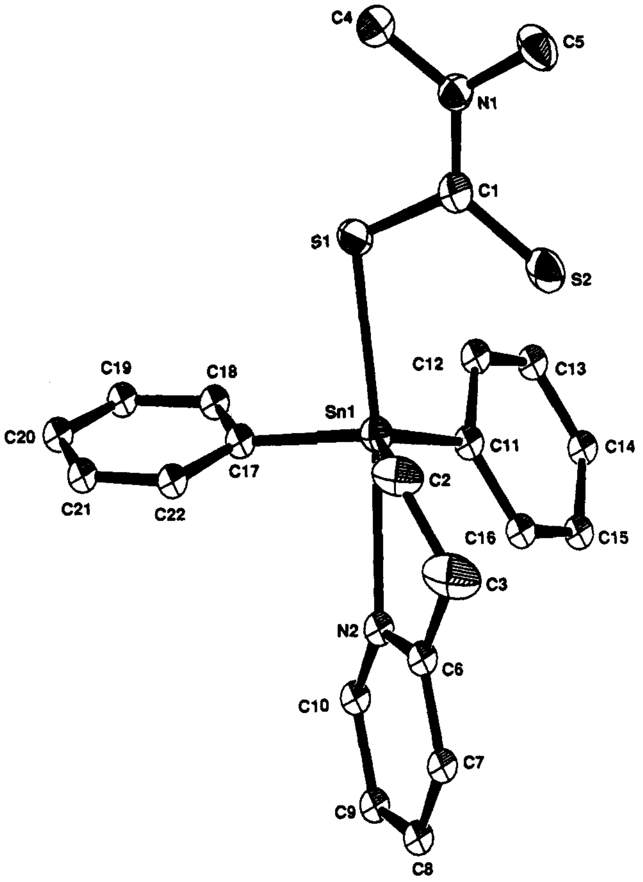

Figure 2. Structure of [2-(2-pyridyl)ethyl]diphenyltin N,N-dimethyldithiocarbamate (**9**), showing the atomic labeling scheme used in the text.

Table III. Fractional Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for [2-(2-Pyridyl)ethyl]diphenyltin N,N-Dimethyldithiocarbamate

atom	x	y	z	U_{iso} or U_{eq} (*)
Sn	0.15987 (6)	0.31457 (6)	0.25367 (5)	0.0444 (4)*
S1	0.4416 (2)	0.2157 (2)	0.2668 (2)	0.057 (1)*
S2	0.3405 (3)	−0.0426 (3)	0.3343 (2)	0.070 (2)*
N1	0.6064 (8)	−0.0345 (8)	0.3467 (7)	0.055 (5)*
C1	0.4735 (9)	0.0349 (9)	0.3195 (7)	0.048 (5)*
C2	0.0458 (11)	0.2742 (12)	0.4261 (8)	0.065 (6)*
C3	−0.1131 (13)	0.2612 (15)	0.4392 (10)	0.091 (9)*
C4	0.7192 (11)	0.0364 (11)	0.3391 (10)	0.076 (7)*
C5	0.6448 (13)	−0.1876 (10)	0.3926 (10)	0.076 (7)*
N2	−0.1230 (8)	0.4302 (7)	0.2710 (6)	0.051 (2)
C6	−0.2013 (10)	0.3692 (9)	0.3647 (8)	0.056 (2)
C7	−0.3642 (12)	0.4052 (11)	0.3885 (10)	0.070 (3)
C8	−0.4395 (12)	0.4995 (11)	0.3127 (10)	0.072 (3)
C9	−0.3544 (12)	0.5600 (12)	0.2131 (10)	0.077 (3)
C10	−0.1957 (11)	0.5216 (10)	0.1973 (9)	0.066 (2)
C11	0.1729 (9)	0.2206 (8)	0.1191 (7)	0.044 (2)
C12	0.3157 (10)	0.1741 (9)	0.0449 (8)	0.054 (2)
C13	0.3255 (12)	0.1189 (11)	−0.0491 (9)	0.070 (3)
C14	0.1990 (13)	0.1055 (12)	−0.0641 (10)	0.080 (3)
C15	0.0549 (12)	0.1509 (12)	0.0098 (10)	0.078 (3)
C16	0.0423 (10)	0.2084 (9)	0.1019 (8)	0.059 (2)
C17	0.1911 (9)	0.5190 (8)	0.2005 (7)	0.047 (2)
C18	0.2831 (11)	0.5548 (10)	0.0962 (9)	0.064 (2)
C19	0.3126 (12)	0.6838 (11)	0.0663 (10)	0.073 (3)
C20	0.2506 (12)	0.7799 (11)	0.1415 (9)	0.072 (3)
C21	0.1583 (12)	0.7505 (11)	0.2410 (10)	0.073 (3)
C22	0.1245 (10)	0.6226 (10)	0.2730 (8)	0.062 (2)

The five organotin halides divide into two structurally

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[10] Sheldrick, G. M. SHELX 76, Program for Crystal Structure Determination. University of Göttingen, Germany, 1976.

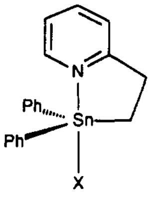
[11] Sheldrick, G. M. SHELX 86, Program for Crystal Structure Determination. University of Göttingen, Germany, 1986.

[12] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.

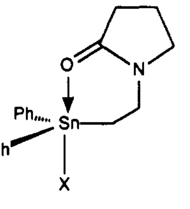
Table IV. Selected Bond Lengths (pm) and Angles (deg) for [2-(2-Pyridyl)ethyl]diphenyltin *N*,*N*-Dimethyldithiocarbamate

Sn–S1	2.559 (2)	Sn–N2	2.486 (7)
Sn-C2	2.145 (9)	Sn–C11	2.138 (8)
Sn–C17	2.136 (8)	C3–C6	1.470 (16)
S1–C1	1.752 (9)	S2–C1	1.680 (8)
N1–C1	1.322 (11)	N1–C4	1.483 (12)
N1–C5	1.480 (12)	N2–C6	1.340 (12)
N2–C10	1.327 (13)	C2–C3	1.534 (14)
N2–Sn–S1	169.6 (2)	C2–Sn–S1	99.0 (3)
C2–Sn–N2	73.5 (3)	C11–Sn–S1	101.8 (2)
C11–Sn–N2	88.5 (3)	C11–Sn–C2	128.8 (3)
C17–Sn–S1	87.4 (2)	C17–Sn–N2	89.3 (3)
C17–Sn–C2	114.7 (4)	C17–Sn–C11	112.6 (3)
C4–N1–C1	122.6 (7)	C5–N1–C1	120.5 (8)
C5–N1–C4	116.8 (8)	C6–N2–Sn	108.9 (6)
C10–N2–Sn	129.5 (6)	C10–N2–C6	120.9 (8)
S2–C1–S1	120.9 (5)	N1–C1–S1	116.0 (6)
N1–C1–S2	123.1 (7)	C3–C2–Sn	110.2 (7)
C6–C3–C2	113.7 (9)	C3–C6–N2	118.4 (8)
C7–C6–N2	120.2 (9)	C7–C6–C3	121.3 (9)
C1–S1–Sn	105.5 (3)		

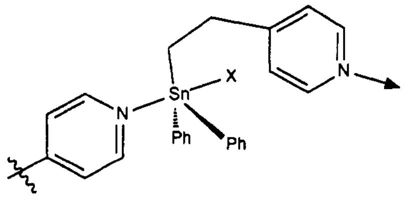
dissimilar groups. Compounds 4, 5, and 8 all have ^2J(^{119}Sn–C–^{1}H) (114–132 Hz) and ^1J(^{119}Sn–^{13}C) couplings (555–605 Hz), which are markedly enhanced over their four-coordinate parents 1 or 3 (^2J, 57–72 Hz; ^1J, 359–423 Hz), and have ^{119}Sn chemical shifts upfield of the same precursors. Only the iodide 5 has a ^{119}Sn shift similar to that of its parent, though it is notable that another iodide, 7, which has a coordination number of 4, shows a more downfield shift than its tetrahedral precursor 2, so the somewhat anomalous shift data for these iodides may be an artefact of the halogen. In addition, the ^{13}C chemical shifts of the ipso carbon atoms of the phenyl rings are below 140 ppm for both 5 and 8, a criterion used by others to assign a coordination number of greater than 4 at tin.[15] The Mössbauer QS values are in the range 2.95–3.14 mm s^{-1}, indicative of a *trans*-X_2SnR_3 geometry about the metal.[16] Collectively, these data indicate a coordination number of 5 for the three compounds in both the solid and solution states, which in the cases of 4 and 5 can only arise from intramolecular chelation by the 2-pyridylethyl (I).



(I)



(II)



(III)

Moreover, the ^{13}C chemical shifts for the pyridine ring atoms are moved relative to their positions in 1, most notably for carbons in the sites either side of nitrogen, again suggesting an N:→Sn interaction. For 8, lowering of ν(C=O) (1625 cm^{-1}) relative to both *N*-vinylpyrrolidin-2-one (1700 cm^{-1}) and 3 (1680 cm^{-1}) indicates coordination enhancement, as depicted in II.

The two halide derivatives containing the 4-pyridylethyl moiety (6, 7) have ^2J(^{119}Sn–C–^{1}H) couplings (67, 69 Hz) similar to that of 2 (52 Hz), ^{13}C chemical shifts for the ipso carbon atoms of the aromatic groups less than 140 ppm,[15] and ^{119}Sn chemical shifts downfield of that of 2, all factors which specify a coordination number of 4 at tin in solution. Since the Mössbauer QS values for the two compounds are similar to those for the first group of triorganotin halides, the solid-state structures must again incorporate a *trans*-X_2SnR_3 unit. Data for the two phases are reconciled by the intermolecularly coordinated structure (III), which is to be expected from the geometrical constraints of this particular ligand substitution pattern.

This conclusion is supported by comparison of the temperature dependence of the Mössbauer spectral areas for compounds 1, 2, 4, and 7, shown in Figure 1. Briefly, the decay of the spectral area (normalized to the 78 K point to facilitate comparison) is logarithmically related to temperature and is most marked for compounds showing the weakest intermolecular interactions. In such lattices, the vibrational motion of the Mössbauer atom increases most rapidly with temperature, decreasing the recoil-free fraction of interactions between γ-photons and the Mössbauer nuclei and hence diminishing the spectral area.[17] It can be seen in Figure 1 that 1, 2, and 4, all of which have lattices comprising discrete molecular units, show the steepest plots (rapidly decaying spectral areas), with slopes typical of noninteracting lattice units (-1.60 to -1.96×10^{-2} K^{-1}).[17] On the other hand 7, for which we propose structure III, shows the shallowest decay plot, whose slope (-1.37×10^{-2} K^{-1}) is typical of a flexible but nonetheless tangible linkage between metal centers.[17]

Dithiocarbamate derivatives of the differing pyridine-based ligands also fall into two groups, whose structures parallel the two classes of halide complexes. Both 9 and 10 have large ^2J(^{119}Sn–C–^{1}H) (141, 138 Hz) and ^1J(^{119}Sn–^{13}C) couplings (666 Hz for 9) and more upfield ^{119}Sn chemical shifts (ca. -200 ppm) than 1. Indeed, the sizable upfield shifts in ^{119}Sn resonance may reflect a coordination number greater than 5 at tin, a point more fully discussed in terms of the crystal structure of 9, below. The QS data for the two compounds are similar, and thus both have the *trans*-$NSSnR_3$ structure confirmed crystallographically for 9, despite the fact that such a splitting is generally lower than normally associated with a geometry of this type.[16] It is worth noting, however, that point charge calculations based on this coordination sphere, a ligand arrangement believed to be implicated in the binding of triorganotin units by the cysteine and histidine residues of proteins,[2] predict QS = 1.68 or 2.13 mm s^{-1} (R = Ph, alkyl, respectively),[18] somewhat lower than found for either 9 or 10. While these species essentially adopt structure I (X = monodentate S_2CNR_2) in both solid and solution

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[13] Abbas, S. Z.; Poller, R. C. *J. Chem. Soc., Dalton Trans.* **1974**, 1769.

[14] Clark, H. C.; Poller, R. C. *Can. J. Chem.* **1970**, *48*, 928.

[15] Holeček, J.; Nadvornik, M.; Handir, K.; Lycka, A. *J. Organomet. Chem.* **1983**, *241*, 177. This methodology, we feel, should be treated with caution. 4 has ^{13}C for C_i at 139.2 ppm despite the weight of evidence suggesting it has a coordination number of 5. On the other hand, tetrahedral 1 has a shift of 140.3 ppm (i.e. above 140 ppm) for the corresponding ipso carbon atom.

[16] Molloy, K. C. In *Chemistry of Tin*; Harrison, P. G., Ed.; Blackie: Glasgow, 1989; p 205.

[17] Molloy, K. C.; Quill, K. *J. Chem. Soc., Dalton Trans.* **1985**, 1417.

[18] Barbieri, R.; Di Bianca, F.; Rivarola, F.; Huber, F. *Inorg. Chim. Acta* **1985**, *108*, 141.

states, **11** exhibits the same structural duality between phases described for **6** and **7**. Thus, ${}^{2}J({}^{119}\mathrm{Sn}\text{–}\mathrm{C}\text{–}{}^{1}\mathrm{H})$ is similar to that of **2** and only a small increase in δ (^{119}Sn) compared to the same compound in solution can be contrasted with a solid-state QS value, similar to the case of **9** and **10**. Thus, the compound is most likely a tetrahedral monomer in solution and an N-bridged polymer in the solid state, the dithiocarbamate being monodentate in both cases.

The remaining dithiocarbamate complex (**12**) affords spectral data suggesting a potentially differing coordination sphere about tin. In solution, small increases in ${}^{2}J({}^{119}\mathrm{Sn}\text{–}\mathrm{C}\text{–}{}^{1}\mathrm{H})$ (72 Hz), ${}^{1}J(\mathrm{Sn}\text{–}\mathrm{C})$ (483 Hz) and $\delta({}^{119}\mathrm{Sn})$ (−182.8 ppm) suggest that the coordination about tin is marginally greater than four; i.e. any additional coordination is extremely weak, much less so than in **9** or **10**. Infrared data [ν(C=O) 1670 cm^{-1}] rule out any significant coordination of the carbonyl oxygen to tin, implying a weakly bidentate mode for the dithiocarbamate. Indeed, the ^{119}Sn chemical shift is similar to that of other dithiocarbamates[19] which have been described as monodentate.[20] Such compounds generally exhibit Mössbauer QS values of ca. 1.90 mm s^{-1},[21,22] so the value recorded for **12** might reflect the *cis*-S_2SnR_3 arrangement generated by a weakly chelating ligand. On the other hand, the enhanced QS value merely parallels those of **9** and **10** (see above) and may be thought of as receiving an additional contribution from the electronic mismatch in differing Sn–C bonds. Clearly, the case for proposing a coordination number of 5 for tin in **12** is, as best, borderline.

The two carboxylates **13** and **14** present a more clear cut picture. As with the halides **4** and **5**, and the dithiocarbamates **9** and **10**, the large ${}^{2}J$ couplings (ca. 125 Hz) and $\delta({}^{119}\mathrm{Sn})$ (ca. −175 ppm) significantly upfield from carboxylates known to be four-coordinate in solution (e.g. Ph_3SnO_2CR, $\delta \approx -120$ ppm[19]) specify a coordination of five at tin in this phase. Moreover, ${}^{1}J({}^{119}\mathrm{Sn}\text{–}{}^{13}\mathrm{C})$ of 655 Hz for **13** is very similar to that of the five-coordinate thiocarbamate **9**. Infrared data rule out any C=O→Sn interactions [ν(C=O) ca. 1635 cm^{-1}],[23] so again the 2-pyridylethyl ligand chelates the tin (I, X = monodentate carboxylate). Changes in the ^{13}C shifts of the pyridine carbon nuclei reflect this situation. The Mössbauer QS values (2.41, 2.71 mms^{-1}) are in accordance with a *trans*-$ONSnR_3$ coordination sphere and reflect an upward trend in QS from a *trans*-$SNSnR_3$ arrangement (QS 2.35–2.55 mms^{-1}) to the *trans*-O_2SnR_3 (QS ca. 3.3 mm s^{-1} [21]) structure which is common in polymeric organotin carboxylates.[16]

Structure of [2-(2-Pyridyl)ethyl]diphenyltin *N,N*-Dimethyldithiocarbamate. The crystallographically determined structure of **9** is shown in Figure 2 and clearly confirms both the chelating nature of the 2-pyridylethyl ligand and the *trans*-$SNSnR_3$ coordination about tin. The geometries of organotin dithiocarbamates have been collated by Zuckerman,[20] and some selected data are given in Table V for comparison with data for **9**. The Sn–N_{ax} bond is typical, though the chelating limitations of the ligand are reflected in distortions in the ∠N–Sn–S (169.6°). The dithiocarbamate is monodentate, the longer of the two Sn–S distances (346.6 pm) being outside the range generally associated with chelation, though within the sum of the van der Waals radii. Moreover, the two C–S distances (168.0, 175.2 pm) are clearly typical of distinct single and double bond character, which becomes less distinct in structures with a bidentate ligand. However, the shorter of the two Sn–S distances (255.9 pm) is long for a monodentate dithiocarbamate and is noticeably influenced by its axial position trans to a donor ligand. For comparison, the axial Sn–Br bonds in the tabulated examples (263, 268.3 pm) are also longer than the same bond in a representative tetrahedral compound, e.g. Ph_3SnBr (249.0 pm).[24]

Table V. Selected Crystallographic Data (pm) for Organotin Dithiocarbamates and Related Compounds

	Sn—N_{ax}	Sn—S	S:→Sn	S—C	S=C	ref
9	248.6	255.9	346.6	175.2	168.0	this work
$BuPh_2SnS_2CNMe_2$		246.6	307.9	176.2	168.0	22
$Ph_3SnS_2CN(CH_2)_4$		246.8	310.6	177.6	170.2	20
${}^{t}Bu_2Sn(S_2CNMe_2)_2$		257.3[a]	353.2	175.2	168.6	26
		248.9[b]	279.5	173.8	170.9	
$Ph_2(Br)SnR$[c]	251					27
$Ph_2(Br)SnR'$[d]	247.6					28

[a] Monodentate dithiocarbamate. [b] Bidentate dithiocarbamate. [c] R = $C_6H_4CH_2NMe_2$-2. [d] R′ = $C_6H_4CH(Me)NMe_2$-2.

Despite the bond length data which are in accordance with a monodentate dithiocarbamate ligand, it is interesting that the equatorial ∠C2–Sn–C11, which is bisected by the long Sn–S vector, is opened to 128.8°. Whilst one would expect, on the rehybridization arguments of Bent,[25] that the equatorial angle involving the more electronegative phenyl groups would be compressed (more p character in the sp^2 hybrids) at the expense of those involving the CH_2 moiety, this is not what is observed. Thus, while the ∠C11–Sn–C17 is indeed smaller than the ideal 120° (112.6°), the ∠C2–Sn–C17 angle is also compressed (114.7°). It would seem, then, that while the Sn–S2 distance does not represent a bonding interaction, the proximity of Sn and the sterically sizable S2 is sufficient to induce a marked perturbation of the bond angles about the metal.

Acknowledgment. We thank the SERC and the International Tin Research Institute (Uxbridge, U.K.) for financial support in the form of a studentship (to P.C.W.)

Supplementary Material Available: Tables of thermal parameters (Table 6) and bond distances and angles (Table 7) (3 pages). Ordering information is given on any current masthead page.

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