Synthesis, Characterization, and X-ray Structures of Diphenyltin(IV) *N*-(2-Hydroxyacetophenone)glycinate, Its 1:1 Adduct with Triphenyltin(IV) Chloride, and Related Systems

Dainis Dakternieks*

School of Chemical and Biological Sciences, Deakin University, Geelong, Victoria 3217, Australia

Tushar S. Basu Baul* and Sushmita Dutta

Chemical Laboratory, Regional Sophisticated Instrumentation, North Eastern Hill University, Bijni Complex, Bhagyakul, Shillong 793 003, India

Edward R. T. Tiekink*

Department of Chemistry, The University of Adelaide, Australia 5005

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The compound [$Ph_2Sn(2\text{-}OC_6H_4C(CH_3){=}NCH_2COO)$], **1**, shows a distorted trigonal-bipyramidal geometry in the solid state. Reaction of **1** with Ph_3SnCl yields a 1:1 adduct in which the two tin atoms are joined via the carbonyl atom of the ligand in **1** to form a mixed diorgano/triorgano species. NMR data indicate that the 1:1 adduct dissociates in noncoordinating solvent. Similarly, [${}^tBu_2Sn(2\text{-}OC_6H_4C(CH_3){=}NCH_2COO)\cdot{}^tBu_2SnCl_2$], which has been characterized crystallographically in the solid state, is dissociated in solution. In contrast to the above behavior, monomeric [$Vin_2Sn(2\text{-}OC_6H_4C(CH_3){=}NCH_2COO)$] forms an adduct with a water molecule to yield [$Vin_2Sn(2\text{-}OC_6H_4C(CH_3){=}NCH_2COO)OH_2$] in the solid state.

Introduction

The development of dendritic chemistry is of current interest owing to the possibility of obtaining compounds whose structures result in modified and new chemical properties. These synthetic macromolecules are largely based on organic residues, however, there is also considerable interest in transition-metal-mediated dendrimers, i.e., metallodendrimers.[1] Receiving particular attention are the Ru/polybipyridyl systems owing to their exciting luminescent and redox properties.[2,3] In contrast, metallodendrimers containing main-group-element compounds, with the possible exception of those with Si, are still comparatively unexplored.[1] Our interest in this area stems from a program designed to link smaller Sn-containing entities to form organotin oxo clusters[4,5] in a rational and reliable fashion in order to control the size, shape, and tin-atom nuclearity. Such organotin oxo clusters have applications as homogeneous catalysts[6] and in new materials science.[7,8]

In a related study of synthetic and structural investigations of organotin(IV)/amino acid compounds, which are of interest owing to their putative antitumor activity,[9−13] it was observed that the isolated monomeric complexes contained additional potentially, O-containing coordination sites. These proved to be sufficiently basic to coordinate a second Sn-containing species, and hence, a thorough investigation of the nature of adduct formation was conducted in noncoordinating solvent employing ^{119}Sn NMR methods and in the solid state using X-ray crystallography. Hence, this contribution reports the preparation of diphenyltin(IV) *N*-(2-hydroxyacetophenone)glycinate and its 1:1 molecular adduct with Ph_3SnCl yielding a rare mixed diorganotin/triorganotin compound that features a nonorgano bridge as well as related studies containing other diorganotin entities.

Experimental Section

Materials and Spectroscopic Methods. Organotin chlorides (Aldrich) were used after recrystallization from hexane.

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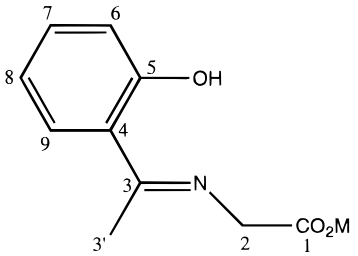
Glycine and 2-hydroxyacetophenone (Aldrich) were used as supplied. Carbon, hydrogen, and nitrogen analyses were performed with a Perkin-Elmer 2400 Series II. IR spectra were obtained on a Perkin-Elmer 1720X FT spectrophotometer in KBr disks in the range 4000−400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ solution on a Bruker ACF300 spectrometer at 300.13 and 75.47 MHz, respectively, referenced to Me$_4$Si (0.0 ppm) and CDCl$_3$ (77.0 ppm), respectively. ^{119}Sn NMR spectra were recorded, with an inverse-gated pulse delay of 2 s, using a JEOL GX 270 MHz FT NMR spectrometer operating at 100.75 MHz.

Preparation of Ligands. The ligand *N*-(2-hydroxyacetophenone)glycine (systematic name 2-{[(*E*)-1-(2-hydroxyphenyl)-ethylidene]amino}acetic acid, LH$_2$), could not be isolated and, therefore, was prepared either as its monosodium salt (LHNa) or monopotassium salt (LHK).



LHNa. A hot aqueous solution (30 cm^3) of NaHCO$_3$ (3.09 g, 36.72 mmol) was added slowly to a hot aqueous solution (25 cm^3) containing glycine (2.75 g, 36.72 mmol) under stirring. After completion of CO$_2$ evolution, 2-hydroxyacetophenone (5.0 g, 36.72 mmol) in ethanol (50 cm^3) was added dropwise. The reaction mixture was then maintained between 40 and 50 °C for 2 h, after which the solvent was removed using a rotary evaporator. A thick yellow mass was precipitated with a methanol−petroleum ether mixture. This was washed thoroughly with petroleum ether and recrystallized from methanol to yield pure LHNa. Yield: 80%. Mp: 239−240 °C. Anal. Calcd for C$_{10}$H$_{10}$NNaO$_3$: C, 55.8; H, 4.7; N; 6.5. Found: C, 55.7; H, 4.5; N, 6.5. IR (cm^{-1}): 1618 ν(OCO)$_{\mathrm{asym}}$, 1606 ν(C=N), 1267 ν(Ph(C−O)).

LHK. A cold aqueous solution (25 cm^3) of KOH (2.06 g, 36.72 mmol) was mixed with a cold aqueous solution (25 cm^3) containing glycine (2.77 g, 36.72 mmol) and held at 15−20 °C in an ice bath, with continuous stirring. An ethanolic solution (50 cm^3) of 2-hydroxyacetophenone (5.0 g, 36.72 mmol) was added dropwise. A deep-yellow color developed almost immediately, and stirring was continued for 1 h followed by 5 h at room temperature. The solvent was removed using a rotary evaporator. The yellow mass was washed with petroleum ether and precipitated with a methanol−diethyl ether mixture. The crude product was recrystallized from methanol solution to yield LHK. Yield: 72%. Mp: 258−260 °C. Anal. Calcd for C$_{10}$H$_{10}$KNO$_3$: C, 51.9; H, 4.4; N; 6.1. Found: C, 51.9; H, 4.3; N, 6.0. IR (cm^{-1}): 1628 ν(OCO)$_{\mathrm{asym}}$, 1606 ν(C=N), 1267 ν(Ph(C−O)).

Preparation of Compounds. Ph$_2$SnL (1): Ph$_2$SnCl$_2$ (0.79 g, 2.32 mmol) in 30 cm^3 of methanol was added dropwise with continuous stirring to a hot methanol solution (50 cm^3) containing either LHNa or LHK (0.5 or 0.53 g, 2.32 mmol). The reaction mixture was heated at reflux temperature for 2 h, and then the solvent was removed using a rotary evaporator. The dry mass was washed thoroughly with hot hexane and then extracted into chloroform. The yellow product obtained upon concentration of the chloroform extract was recrystallized from methanol to yield yellow block crystals of [Ph$_2$Sn(2-OC$_6$H$_4$C(CH$_3$)=NCH$_2$COO)] (**1**). Yield: 82%. Mp: 221−222 °C. Anal. Calcd for C$_{22}$H$_{19}$NO$_3$Sn: C, 56.9; H, 4.1; N; 3.0. Found: C, 56.7; H, 4.0; N, 3.0. IR (cm^{-1}): 1682 ν(OCO)$_{\mathrm{asym}}$, 1602 ν(C=N), 1238 ν(Ph(C−O)). ^{1}H NMR (CDCl$_3$ solution): δ 7.85−7.89 (m, 4H, Sn−Ph(*ortho*)), 7.35−7.47 (m, 8H, H-7,9 + Sn−Ph(*meta* + *para*)), 7.15 (d, 9 Hz, 1H, H-6), 6.75 (t, 6 Hz, 1H, H-8), 4.25 (s, 2H, H-2), 2.57 (s, 3H, H-3′) ppm. ^{13}C NMR (CDCl$_3$ solution): δ 182.1 (C-1), 170.2 (C-3), 166.4 (C-5),, 136.3 (C-7), 130.7 (C-9), 123.7 (C-6), 120.3 (C-4), 117.8 (C-8), 53.5 (C-2), 22.7 (C-3′); Sn−Ph δ 137.6 (ipso), 136.6 (^2J(Sn−C) = 56.0 Hz, *ortho*), 130.5 (^4J(Sn−C) = 20.6 Hz, *para*), 128.8 (^3J(Sn−C) = 86.4 Hz, *meta*) ppm. ^{119}Sn NMR (CDCl$_3$ solution): δ −351.7 ppm.

[Ph$_2$SnL·Ph$_3$SnCl] (2): This compound was prepared by the dropwise addition of an anhydrous benzene solution (30 cm^3) of Ph$_3$SnCl (1.0 g, 2.59 mmol) to a hot benzene solution (50 cm^3) containing **1** (1.2 g, 2.59 mmol). The reaction mixture was refluxed for 2 h, and excess solvent was removed using a rotary evaporator. The yellow gummy mass thus obtained was washed several times with hexane and recrystallized from chloroform solution to give **2** in 65% yield. Mp: 199−200 °C. Anal. Calcd for C$_{40}$H$_{34}$ClNO$_3$Sn$_2$: C, 56.6; H, 4.0; N; 1.7. Found: C, 56.5; H, 4.0; N, 1.5. IR (cm^{-1}): 1627 ν(OCO)$_{\mathrm{asym}}$, 1236 ν(Ph(C−O)). ^{1}H NMR (CDCl$_3$ solution): δ 7.65−7.88 (m, 10H, Sn−Ph(*ortho*)), 7.38−7.46 (m, 17H, H-7,9 + Sn−Ph(*meta* + *para*)), 7.14 (d, 9 Hz, 1H, H-6), 6.75 (t, 6 Hz, 1H, H-8), 4.24 (s, 2H, H-2), 2.59 (s, 3H, H-3′] ppm. ^{13}C NMR (CDCl$_3$ solution): δ 182.0 (C-1), 170.2 (C-3), 166.6 (C-5), 136.4 (C-7), 130.8 (C-9), 123.9 (C-6), 120.4 (C-4), 117.9 (C-8), 53.6 (C-2), 22.8 (C-3′); Sn−Ph (a and b represent signals due to Sn−Ph$_2$ and Sn−Ph$_3$, respectively) δ 137.6 (*ipso*)^{a}, 137.5 (*ipso*)^{b}, 136.7 (^2J(Sn−C) = 50.4 Hz, *ortho*)^{b}, 136.1 [^2J(Sn−C) = 55.7 Hz, *ortho*)^{a}, 130.7 (^4J(Sn−C) = 21.1 Hz, *para*)^{a} 130.5 (^4J(Sn−C) = 13.2 Hz, *para*)^{b}, 129.1 (^3J(Sn−C) = 65.0 Hz, *meta*)^{b}, 128.9 (^3J(Sn−C) = 90.5 Hz, *meta*)^{a} ppm. ^{119}Sn NMR (CDCl$_3$ solution): δ: −48.2, −350.3 ppm.

[^{t}Bu$_2$SnL·^{t}Bu$_2$SnCl$_2$] (3): This compound was isolated from the reaction of ^{t}Bu$_2$SnCl$_2$ and LHK (1:1) in methanol solution employing the procedure described for **1**. The yellow product was obtained upon concentration of a chloroform extract and recrystallized from chloroform solution to give yellow blocks in 55% yield. Mp: 132−133 °C. Anal. Calcd for C$_{26}$H$_{45}$Cl$_2$NO$_3$Sn$_2$: C, 42.9; H, 6.2; N; 1.9. Found: C, 42.8; H, 6.2; N, 1.9. IR (cm^{-1}): 1681 ν(OCO)$_{\mathrm{asym}}$, 1237 ν(Ph(C−O)). ^{1}H NMR (CDCl$_3$ solution): δ 7.45 (d, 6 Hz, 1H, H-7), 7.34 (t, 6 Hz, 1H, H-9), 6.87 (d, 9 Hz, 1H, H-6), 6.72 (m, 6 Hz, 1H, H-8), 4.25 (s, 2H, H-2), 2.67 (s, 3H, H-3′), 1.26 (s, 36H, Sn-^{t}Bu) ppm. ^{13}C NMR (CDCl$_3$ solution): δ 181.2 (C-1), 170.9 (C-3), 167.2 (C-5), 135.6 (C-7), 130.2 (C-9), 123.7 (C-6), 120.8 (C-1), 117.0 (C-8), 53.9 (C-2), 22.8 (C-3′), 29.8 (Sn−^{t}Bu); 40.7 (Sn−^{t}Bu) ppm. ^{119}Sn NMR (CDCl$_3$ solution): δ 57.2, −302.4 ppm.

[Vin$_2$SnL·OH$_2$] (4): This compound was prepared from the reaction of [Vin$_2$SnCl$_2$] and LHNa in methanol solution (1:2 molar proportions) as described for **1**. The colorless product was obtained upon concentration of a chloroform extract and recrystallized from benzene solution to give colorless blocks in 58% yield. Mp: 163−164 °C. Anal. Calcd for C$_{14}$H$_{17}$NO$_4$Sn: C, 44.0; H, 4.5; N; 3.7. Found: C, 43.9; H, 4.2; N, 3.6. IR (cm^{-1}): 1658 ν(OCO)$_{\mathrm{asym}}$, 1605 ν(C=N), 1240 ν(Ph(C−O)). ^{1}H NMR (CDCl$_3$ solution): δ 7.50 (d, 9 Hz, 1H, H-7), 7.38 (t, 9 Hz, 1H, H-6), 6.78 (t, 6 Hz, 1H, H-9), 6.28−6.80 (m, 6H, Sn−Vin), 4.27 (s, 2H, H-2), 2.66 (s, 3H, H-3′) ppm. ^{13}C NMR (CDCl$_3$ solution): δ 182.7 (C-1), 170.3 (C-3), 166.2 (C-5), 136.0 (C-7), 130.5 (C-9), 123.5 (C-6), 120.6 (C-1), 117.9 (C-8), 53.3 (C-2), 22.8 (C-3′), 135.0 (Sn−Vin), 139.5 (Sn−Vin) ppm. ^{119}Sn NMR (CDCl$_3$ solution): δ −344.6 ppm.

Crystallography. Intensity data were collected at room temperature on a Rigaku AFC6R diffractometer employing the $\omega-2\theta$ scan technique and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The data sets were corrected routinely for Lorentz and polarization effects,[14] and an empirical absorption correction[15] was applied in each case. The

Table 1. Crystallographic Data and Refinement Details for 1−4

	1	**2**	**3**	**4**
formula	$C_{22}H_{19}NO_3Sn$	$C_{40}H_{34}ClNO_3Sn_2$	$C_{30}H_{45}Cl_2NO_3Sn_2$	$C_{14}H_{17}NO_4Sn$
fw	464.1	849.6	776.0	382.0
cryst size, mm	0.19 × 0.32 × 0.48	0.02 × 0.12 × 0.15	0.07 × 0.19 × 0.52	0.10 × 0.18 × 0.32
cryst syst	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	20.280(4)	13.073(2)	12.748(2)	9.323(4)
b, Å	20.597(5)	13.961(2)	16.531(4)	10.03(1)
c, Å	9.366(1)	11.591(2)	8.117(1)	8.756(5)
α, deg		92.06(1)	96.79(2)	96.61(8)
β, deg	92.06(1)	115.39(1)	96.67(1)	106.08(5)
γ, deg		110.67(1)	72.45(1)	104.47(5)
V, Å^3	3909(1)	1743.6(7)	1613.7(5)	746(1)
Z	8	2	2	2
D_{calcd}, g cm^{-3}	1.577	1.618	1.597	1.699
μ, cm^{-1}	13.28	15.48	17.43	17.22
transmission factors	0.969−1	0.963−1	0.905−1	0.910−1
θ range, deg	3.0−27.5	3.0−25.0	3.0−27.5	3.0−27.5
no. of data collcd	9848	6467	7790	3661
no. of unique data	9298	6173	7457	3452
no. of data used	4767	3509	4018	2890
R	0.042	0.038	0.042	0.039
R_w	0.044	0.037	0.042	0.049
residual e$^-$/Å^3	0.37	0.50	0.52	1.31

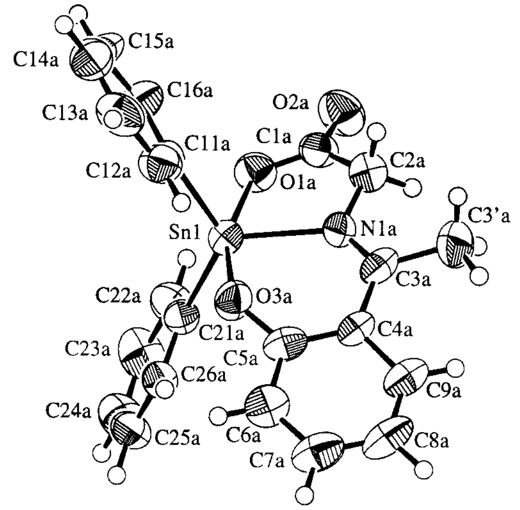


Figure 1. Molecular structure and crystallographic numbering scheme for molecule a of $[Ph_2Sn(2\text{-}OC_6H_4C(CH_3){=}NCH_2COO)]$ (**1**).

structures were solved by direct methods (**1**, **3**;[16a] **2**, **4**[16b]) and each refined by a full-matrix least-squares procedure based on *F*.[14] Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms included in the models at their calculated positions (C−H = 0.97 Å). A σ weighting scheme was applied, i.e., $w = 1/\sigma^2(F)$, and the refinement continued until convergence in each case. Neutral scattering factors employed were as included in teXsan,[14] and diagrams were drawn with ORTEP[17] at the 50% probability level. Crystallographic data and refinement details are given in Table 1. Crystallographic information files for all structures are available upon request from E.R.T.T. (etiekink@chemistry.adelaide.edu.au).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1−4

	1a	**1b**	**2**[a]	**3**[b]	**4**[c]
Sn−O(1)	2.127(4)	2.131(4)	2.167(6)	2.184(4)	2.249(4)
Sn−O(3)	2.064(4)	2.059(4)	2.055(6)	2.057(4)	2.105(4)
Sn−N(1)	2.190(5)	2.178(5)	2.174(6)	2.190(5)	2.254(4)
Sn−C(11)	2.120(6)	2.102(7)	2.127(7)	2.148(8)	2.101(5)
Sn−C(21)	2.138(6)	2.111(6)	2.122(8)	2.152(8)	2.100(5)
O(1)−C(1)	1.280(7)	1.276(8)	1.27(1)	1.254(8)	1.263(6)
O(2)−C(1)	1.213(7)	1.217(7)	1.24(1)	1.256(7)	1.234(6)
O(3)−C(5)	1.330(7)	1.322(7)	1.311(7)	1.335(8)	1.334(6)
N(1)−C(2)	1.459(8)	1.470(7)	1.46(1)	1.474(8)	1.467(7)
N(1)−C(3)	1.285(7)	1.299(7)	1.293(9)	1.307(8)	1.298(6)
O(1)−Sn−O(3)	160.3(2)	158.6(2)	160.1(2)	155.0(2)	152.4(1)
O(1)−Sn−N(1)	77.2(2)	76.2(2)	76.3(2)	74.6(2)	72.8(1)
O(1)−Sn−C(11)	96.0(2)	93.9(2)	93.2(2)	91.6(2)	86.3(2)
O(1)−Sn−C(21)	93.6(2)	94.9(2)	94.0(3)	95.2(2)	90.0(2)
O(3)−Sn−N(1)	83.1(2)	82.6(2)	84.0(2)	81.7(2)	79.6(1)
O(3)−Sn−C(11)	92.3(2)	93.8(2)	92.0(3)	93.4(2)	99.2(2)
O(3)−Sn−C(21)	95.8(2)	96.5(2)	95.2(3)	101.4(3)	91.8(2)
N(1)−Sn−C(11)	113.5(2)	120.2(2)	111.8(3)	120.2(3)	97.7(2)
N(1)−Sn−C(21)	120.5(2)	113.4(2)	110.8(2)	112.8(3)	97.2(2)
C(11)−Sn−C(21)	126.0(2)	126.2(2)	137.4(3)	126.4(3)	162.8(2)
Sn−O(1)−C(1)	118.8(4)	118.8(4)	117.9(5)	120.5(4)	117.9(3)
Sn−O(3)−C(5)	126.7(4)	123.1(4)	127.4(6)	125.9(4)	121.6(3)
Sn−N(1)−C(2)	111.5(4)	111.8(4)	112.7(4)	113.7(4)	112.6(3)
Sn−N(1)−C(3)	128.2(5)	127.2(4)	127.8(6)	128.4(4)	127.9(4)
O(1)−C(1)−O(2)	124.6(7)	125.4(6)	125.5(7)	127.6(6)	125.1(5)
C(2)−N(1)−C(3)	120.2(5)	120.9(5)	119.5(7)	117.9(6)	119.5(4)

[a] Sn(2)−Cl(1) 2.446(3), Sn(2)−O(2) 2.453(6), Cl(1)−Sn(2)−O(2) 176.5(2). [b] Sn(2)−Cl(1) 2.480(2), Sn(2)−Cl(2) 2.370(2), Sn(2)−O(2) 2.335(2), Sn(2)−C(31) 2.156(8), Sn(2)−C(41) 2.160(8), Cl(1)−Sn(2)−Cl(2) 86.89(7), Cl(1)−Sn(2)−O(2) 166.5(1), Cl(2)−Sn(2)−O(2) 79.9(1), C(31)−Sn(2)−C(41) 125.3(3). [c] Sn−O(4) 2.358(4), O(1)−Sn−O(4) 128.5(1), O(3)−Sn−O(4) 79.0(1), O(4)−Sn−N(1) 158.7(1), O(4)−Sn−C(11) 85.1(2), O(4)−Sn−C(21) 84.1(2).

Results and Discussion

Crystal Structures. The molecular structure of **1** is shown in Figure 1, and selected interatomic parameters are collected in Table 2. The compound crystallizes with two independent molecules in the crystallographic asymmetric unit, labeled a and b, that do not differ from each other significantly (see below; the numbering scheme for molecule b (not illustrated) is as for molecule a). The structure is molecular with the closest intermolecular contact involving the non-hydro-

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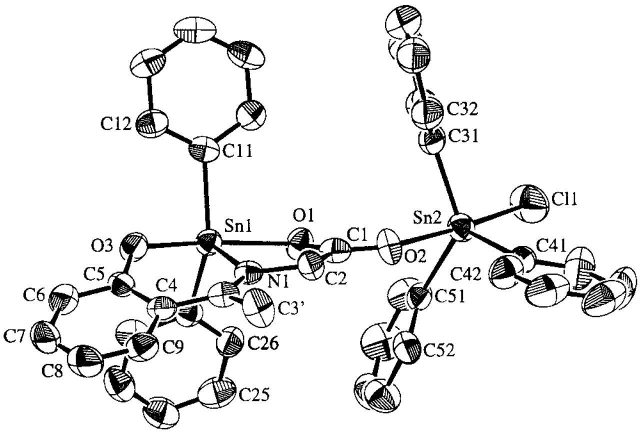

Figure 2. Molecular structure and crystallographic numbering scheme for [Ph$_2$Sn(2-OC$_6$H$_4$C(CH$_3$)=NCH$_2$COO)-SnPh$_3$Cl] (**2**).

gen atoms of 3.382(8) Å occurring between O(2)b and C(2)b^i (symmetry operation $i = x, 0.5 - y, 0.5 + z$). The coordination geometry about the tin atom is defined by two phenyl groups, an oxygen (O(1), derived from a unidentate carboxylate group), a phenoxide O(3) atom, and the imino N(1) atom. The arrangement of the donor set is distorted trigonal bipyramidal with the two oxygen atoms defining the axial positions: O−Sn−O 160.3(2)° for molecule a and 158.6(2)° for molecule b. Distortions from the ideal geometry may be traced to the restricted bite angles of the tridentate ligand. Neither of the five- or six-membered rings formed upon chelation are planar, as seen in the following torsion angles (value for molecule *b* follows in parentheses): Sn/O(1)/C(1)/C(2) −0.2(8)° (10.5(8)°), Sn/N(1)/C(2)/C(1) −19.7(7)° (−18.9(6)°), Sn/O(3)/C(5)/C(4) 37.7(8)° (42.1(7)°), and Sn/N(1)/C(3)/C(4) 10.9(9)° (−1.6(8)°). Similar features are found in structures **2**−**4** described below. The tin atom lies 0.0267(4) Å (0.0457(5) Å) out of the NC$_2$ trigonal plane in the direction of the more tightly held O(3) atom. In addition to the differences between molecules *a* and *b* reflected in the above torsion angles, there are several minor differences in their derived interatomic parameters with the most significant of these being the Sn−O(3)−C(5) angle (Table 2). The geometry found about the tin atom in **1** is almost identical to that found about the Sn(1) atom in **2**.

The molecular structure of **2** is illustrated in Figure 2, and further details are given in Table 2. The closest non-hydrogen intermolecular contact in the lattice of 3.455(9) Å occurs between C(11) and C(16)^i (symmetry operation $i = -x, 1 - y, 1 - z$). The compound is dinuclear and may be considered as an adduct formed between **1** and Ph$_3$SnCl. A comparison of chemically equivalent geometric parameters for **1** with those about the Sn(1) atom in **2** shows a remarkable consistency; the Sn(1) atom lies 0.0376(5) Å out of the trigonal plane in the direction of the O(3) atom. The only significant difference in the coordination geometries is found in the C−Sn−C angle, which has expanded to 137.4(3)° in **2** compared with 126.0(2)° and 126.2(2)° for molecules a and b, respectively, in **1**. The other major difference between the geometries may be related to the formation of the O(2)→Sn(2) interaction. Thus, the Sn(1)−O(1) bond is longer in **2** owing to the withdrawal of electron density from O(2) and donation to the Sn(2) atom via the carboxylate group. This is also manifested in the apparent lengthening of the C(1)−O(2) bond in **2** compared with the comparable distances in **1**, i.e., consistent with the IR results (see below). The geometry about the Sn(2) atom is also distorted trigonal bipyramidal with the Cl and O(2) atoms defining the axial positions. The Sn(2) atom lies 0.2057(5) Å above the C$_3$ trigonal plane.

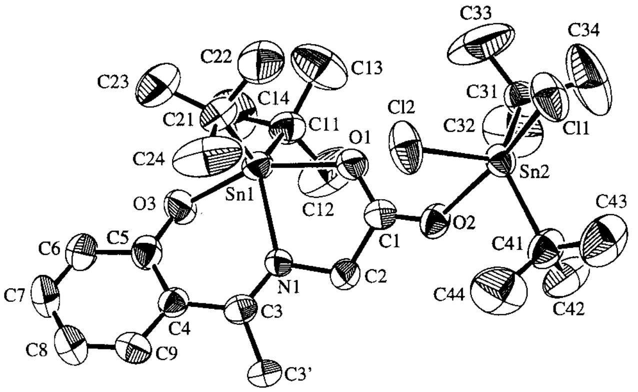

Figure 3. Molecular structure and crystallographic numbering scheme for [^{t}Bu$_2$Sn(2-OC$_6$H$_4$C(CH$_3$)=NCH$_2$COO)·^{t}Bu$_2$SnCl$_2$] (**3**).

The presence of bidentate bridging carboxylate residues in organotin carboxylate structures is well established,[18] however, this is the first example of an isolated ditin structure held together in this fashion, i.e., in which the two tin atoms are not connected via an organo link. Further, crystal structures of mixed diorgano/triorgano tin are also rare, with one example containing a Sn−Sn bond[19] and the other having the tin centers linked via a central platinum atom.[20]

A similar structure to **2** is found for **3** (Figure 3), and selected parameters are collected in Table 2. In this case, the adduct involves two diorganotin centers. A distorted trigonal-bipyramidal geometry is found about the Sn(1) atom in which the Sn atom lies 0.0930(5) Å out of the NC$_2$ plane in the direction of the O(3) atom. With the exception of the elongation of the Sn(1)−C bonds in **3**, the geometry is essentially as found in **2**; however, it is noted that the disparity in the C−O(1), O(2) distances is not as pronounced in **3** owing to the shorter Sn(2)−O(2) interaction of 2.335(2) Å, a result that may be correlated with the enhanced Lewis acidity of ^{t}Bu$_2$SnCl$_2$ compared with Ph$_3$SnCl. The strength of the Sn(2)−O(2) contact is responsible for the elongation of the Sn(2)−Cl(2) bond; O(2)−Sn(2)−Cl(2) is 166.5(1)°.

The final structure is that of **4**, which was shown to be five-coordinate in solution (see below) but six-coordinate in the solid-state owing to the coordination of a water molecule; see Figure 4 and Table 2 for details. The geometry is distorted octahedral with the two vinyl groups occupying trans positions (C−Sn−C 162.8(2)°) above and below a NO$_3$ equatorial plane. Similar coordination geometries to those seen in **4** have been found in some related 2,6-pyridinedicarboxylate[21,22] and *N*-methyliminidiacetate[22] structures, however, in these

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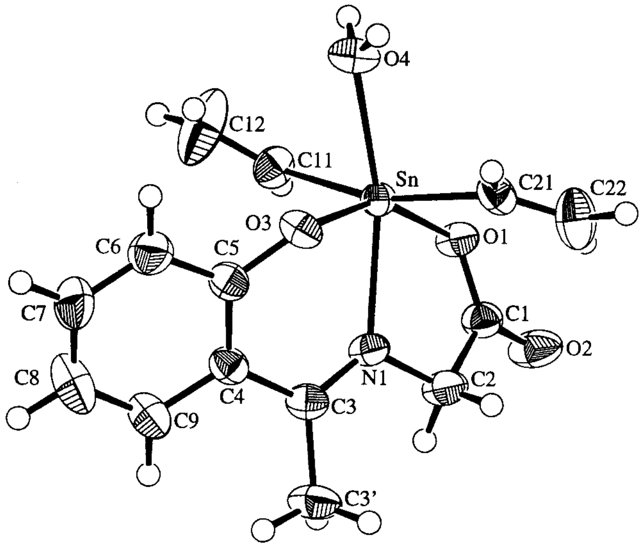

Figure 4. Molecular structure and crystallographic numbering scheme for [$Vin_2Sn(2\text{-}OC_6H_4C(CH_3){=}NCH_2COO)OH_2$] (**4**).

structures, association (2.5−2.8 Å) via one of the carboxylate oxygen atoms leads to the formation centrosymmetric dimers featuring central Sn_2O_2 cores. In **4**, the closest Sn···O(1)^i intermolecular contact is 3.319(4) Å (symmetry operation i = 1 − *x*, 1 − *y*, 1 − *z*).

The solid-state IR spectrum of **1** displays a band at 1682 cm^{-1}, which may be assigned to a $\nu(OCO)_{asym}$ vibration, and in **2**, this vibration appears at 1627 cm^{-1}. The shift of the $\nu(OCO)_{asym}$ band at ca. 55 cm^{-1} to lower wavenumbers in **2** confirms the interaction of Ph_3SnCl with the carbonyl oxygen atom of complex **1**. In these compounds, the v(C=N) band appears[23] as a single sharp band at the same frequency and is assigned as being due to C=N→Sn coordination in the solid state. The band at ca. 1270 cm^{-1} of the Na/K salts moves toward lower frequency by 30 cm^{-1} in the complexes, owing to the coordination of phenolic oxygen to tin atom.[24] Thus, the IR results provide strong evidence for the complexation of the potentially multidentate ligand.

Given the availability of a series of crystal structures, it was thought of interest to probe the solution-state structures in order to ascertain whether the observed association in the solid-state persisted in solution.

Solution Structures. Compound **1** (room temperature in CH_2Cl_2 solution) shows one ^{119}Sn resonance at δ −351.7 ppm; a similar value was found for the in situ reaction of 1:1 mol equiv of LHNa with Ph_2SnCl_2 in the same solvent. Compound **2** gives two ^{119}Sn resonances of equal intensity (δ −49.9 and −351.4 ppm) in CH_2Cl_2 solution. The signal at δ −351.4 ppm is assigned to the five-coordinate tin center in the Ph_2SnL core and the resonance at δ −49.9 ppm is assigned to the Ph_3SnCl moiety (cf δ −47.0 ppm for Ph_3SnCl in CH_2Cl_2 solution). A similar spectrum was obtained when equimolar amounts of **1** and Ph_3SnCl were mixed in the same solvent, which indicates that compound **2** completely dissociates into **1** and Ph_3SnCl under these conditions. Cooling the solution of **2** to −10 °C causes only a minor shift of the low-frequency ^{119}Sn resonance (δ −350.9) but a more substantive shift of the higher frequency resonance (δ −83.5 ppm). At −95 °C, the two ^{119}Sn resonances occur at −223.0 and −347.4 ppm, which indicates that the equilibrium between Ph_3SnCl and **1** has moved substantively toward formation of **2**. The ^{119}Sn shift of the adducted Ph_3SnCl is comparable to that found for other similar five-coordinate species:[25] ($Ph_3SnClO_2^-$ δ −251 at −95 °C in CH_2Cl_2; $Ph_3SnCl\cdot$pyridine δ −219 in pyridine at room temperature).

The ^{119}Sn NMR spectrum at room temperature of a CH_2Cl_2 solution of **1** to which an equimolar amount of Ph_2SnCl_2 was added shows resonances at −114.0 (cf −33 ppm for Ph_2SnCl_2 at room temperature[25]) and −348.0 ppm, indicating substantial adduct formation. On cooling, the resonance at −114.0 moves progressively to lower frequency, and at −95 °C, the ^{119}Sn NMR spectrum contains two resonances at −236.8 and −342.7 ppm. Clearly, the magnitude of the interaction between **1** and an additional tin moiety is dependent on the Lewis acidity of the latter.

The ^{119}Sn NMR spectrum at room temperature of a CH_2Cl_2 solution of **3** shows resonances at 57.2 (cf 56.0 for $^tBu_2SnCl_2$ in CH_2Cl_2) and −302.4 ppm, indicating negligible interaction between these two species in solution. The magnitude of the interaction is not changed much on cooling the solution to −95 °C (δ 47.8 and −297.8 ppm).

The ^{119}Sn NMR spectrum of [$Vin_2SnL\cdot OH_2$] (**4**) in $CHCl_3$ shows a single resonance at −344.6 ppm indicative of five-coordinate tin (by comparison to other compounds described above), indicating that water is not coordinated in solution contrary to the X-ray study (see above).

The ^1H and ^{13}C NMR spectra of **1**−**4** show the expected resonances and integration (see Experimental Section).

Conclusion

Compounds of the form $R_2Sn(2\text{-}OC_6H_4C(CH_3){=}NCH_2COO)$ have been shown to form adducts with R_3SnCl and R_2SnCl_2 in the solid state as shown by X-ray crystallography. ^{119}Sn NMR shows extensive adduct formation at low temperature but extensive dissociation at room temperature.

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Supporting Information Available: Tables of the structure determinations for **1**−**4**, including atomic coordinates, bond distances and angles, and thermal parameters (25 pages). Ordering information is given on any current masthead page.

OM9800290

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