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Diorganotin(IV) Complexes of Methyl 2-{[(*E*)-8-Oxo-5,8-dihydroquinolin-5-ylidene]hydrazino}benzoate

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Abstract. Three *cis*-bis{5-[(*E*)-2-(2-carbomethoxyphenyl)-1-diazenyl]quinolinolato}-diorganotin(IV), $R_2Sn(L)_2$, complexes [*R* = Me (**1**), Ph (**2**) and Bz (**3**)] were synthesized and characterized by ^{1}H-, ^{13}C-, ^{119}Sn- NMR, IR, and ^{119}Sn Mössbauer spectroscopic techniques in combination with elemental analysis. The structure of diphenyltin(IV) complex $Ph_2Sn(L)_2$ (**2**) was determined by single-crystal X-ray crystallography as its tri-benzene solvate. Each complex was found to adopt a distorted *cis*-R_2 octahedral arrangement around the tin atom with the quinolinolato ligands being *N*,*O*-chelating; the oxygen atoms are *trans* to each other. The complexes retain their solid-state structure in non-coordinating solvents as evidenced by ^{119}Sn-NMR spectroscopy.

Introduction

Although the chemistry of organotin(IV) quinolin-8-olate has been known for a long time, the structures of only a few organotin(IV) quinolin-8-olate have been investigated so far. Among these, the diorganotin(IV) *bis*(quinolin-8-olate) group of compounds has received most attention with the crystal structure determinations of R_2SnL_2 complexes, where *R* = Me,[1] *p*-ClPh and *p*-MePh,[2] *n*Bu and Cl,[3] *n*Bu,[4,5] *t*Bu,[4] Ph,[6,7] and Bz,[8] revealing molecules with a highly distorted octahedral coordination of the tin atom by bidentate quinolin-8-olate groups and essentially *cis*-*R* groups. Structural information on $R_2SnX(L)$ type complexes (e.g. *R* = $EtCO_2Me$; *X* = Cl)[9] is also available.

Recently, the reactions of $nBu_2SnCl(L^1)$ (**i**), where L^1 = acid residue of 5-[(*E*)-2-(4-methoxyphenyl)-1-diazenyl]quinolin-8-ol, with various substituted benzoic acids were investigated. These yielded dimeric mixed ligand di-*n*-butyltin(IV) complexes of composition $[nBu_2Sn(L^1)(L^{2-6})]_2$, where L^2 = benzene carboxylate (**ii**), L^3 = 2-[(*E*)-2-(2-hydroxy-5-methylphenyl)-1-diazenyl]benzoate (**iii**), L^4 = 5-[(*E*)-2-(4-methylphenyl)-1-diazenyl]-2-hydroxybenzoate (**iv**), L^5 = 2-{(*E*)-4-hydroxy-3-[(*E*)-4-chlorophenyliminomethyl]-phenyldiazenyl}benzoate (**v**), and L^6 = 2-[(*E*)-(3-formyl-4-hydroxyphenyl)-diazenyl]benzoate (**vi**)[10] (Scheme 1). In complexes **ii**–**v**, the molecules are centrosymmetric dimers in which the tin atoms are connected by asymmetric μ-O bridges through the quinolinolato oxygen atom to give a Sn_2O_2 four-membered ring. The structure of **v** displays more regular pentagonal bipyramidal coordination arrangement about each tin atom compared to those in **ii**–**iv**. In contrast, the centrosymmetric dimeric structure of **vi** involves asymmetric carboxylate bridges, resulting in a different $Sn_2C_2O_4$ motif. If the secondary interactions are considered, all the di-*n*-butyltin(IV) complexes (**ii**–**vi**) display a distorted pentagonal bipyramidal arrangement about each tin atom, in which the *n*-butyl groups occupy the axial positions. Thus, the structural results reveal a strong modulation of the tin coordination arrangement as a function of the substituent pattern on the L^{2-6} ligand. In this context, the structure of the related ligand 2-{[(*E*)-8-oxo-5,8-dihydroquinolin-5-ylidene]hydrazino}benzoate (Figure 1) was determined, which is found to exist as the phenylhydrazone tautomer in the solid-state,[11] rather than in the azo form.[12]

This paper reports the results of extending the organotin(IV) work, particularly with R_2Sn (*R* = Me, Ph, Bz) with the stable and bulkier phenylhydrazone tautomer ligand system (Figure 1). The aim of the study was to evaluate the bonding mode of the diorganotin(IV) complexes from a detailed analysis of their IR, NMR (^{1}H, ^{13}C, ^{119}Sn), and ^{119}Sn Mössbauer spectra. Further, in the course of studies in this area, the diphenyltin(IV) complex **2** (as its tri-benzene solvate) provided X-ray quality crystals enabling a detailed analysis of the coordination arrangement in the solid-state.

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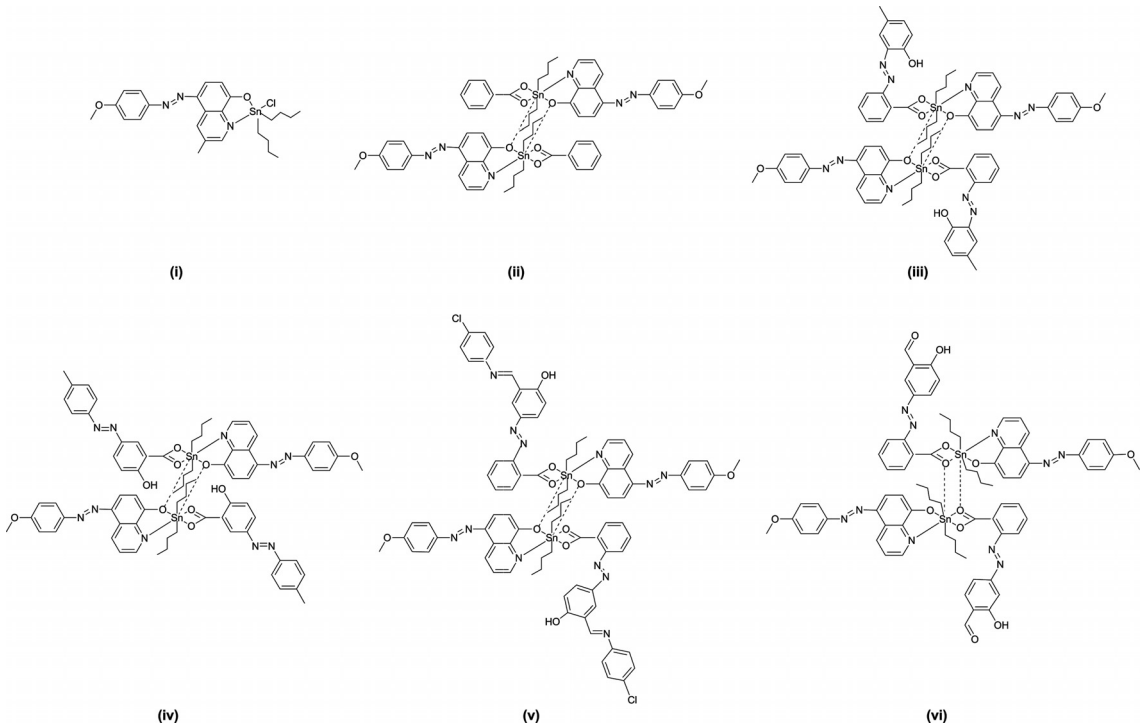

Scheme 1. Various structural motifs (**i**–**vi**) observed in $Bu_2Sn(L)$ {L = 5-[(*E*)-2-(4-methoxyphenyl)-1-diazenyl]quinolin-8-ol} with chloride and various substituted benzoic acids.

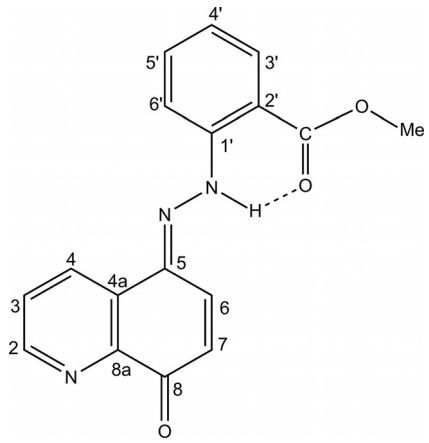

Figure 1. Structure of the ligand (LH).

Results and Discussion

Synthesis

The diorganotin(IV) complexes (**1**–**3**) were prepared by reacting R_2SnO (R = Me, Ph, or Bz) with LH in an 1:2 molar ratio using a Dean–Stark apparatus in anhydrous toluene (reaction 1). The complexes could also be prepared by reacting stoichiometric amounts of R_2SnCl_2 and LH in benzene in the presence of triethylamine (reaction 2). While reaction 2 proceeded smoothly, it results in a complex mixture that could only be separated with great difficulty. The work-up convenience and purity considerations led to the choice of reaction 1.

$$2LH + R_2SnO \xrightarrow[\text{reflux, 4 h}]{\text{toluene}} R_2Sn(L)_2 + H_2O \quad (1)$$

$$2LH + R_2SnCl_2 + 2Et_3N \xrightarrow[\text{reflux, 3 h}]{\text{benzene}} R_2Sn(L)_2 + 2Et_3N{\cdot}HCl \quad (2)$$

The complexes could be isolated by fractional crystallization with high purity in moderate yield. The work-up details and characterization data for the complexes are described in the Experimental Section. The complexes are crystalline, stable in air and are soluble in all common organic solvents.

Spectroscopic Investigations

Diorganotin(IV) complexes **1**–**3** display a strong IR band due to ν_{as}(O–C=O) at ca. 1725 cm^{-1}, which is observed at 1673 cm^{-1} in the free LH. The lowering of the ν_{as}(O–C=O) vibration in LH is ascribed to intramolecular hydrogen bonding involving N–H···O (Figure 1) in contrast to the complexes, where such interactions are absent the ligand being stabilized in the azo-form after deprotonation (see Figure 2). A strong band at around 1320 cm^{-1} in the spectra of **1**–**3**, missing in LH as expected, is assigned to ν[C(aryl)–O] (i.e. C_8–O in Figure 1).[5,7,8,13]

The solution NMR (^1H and ^{13}C) spectroscopic data of the ligand have been reported previously[7,8] with resonances assigned by the use of correlated spectroscopy (COSY), heteronuclear single-quantum correlation (HSQC) and heteronuclear multiple-bond connectivities (HMBC) experiments. The conclusions drawn from the ligand assignments were subsequently extrapolated to the complexes **1**–**3** owing to the similarity in

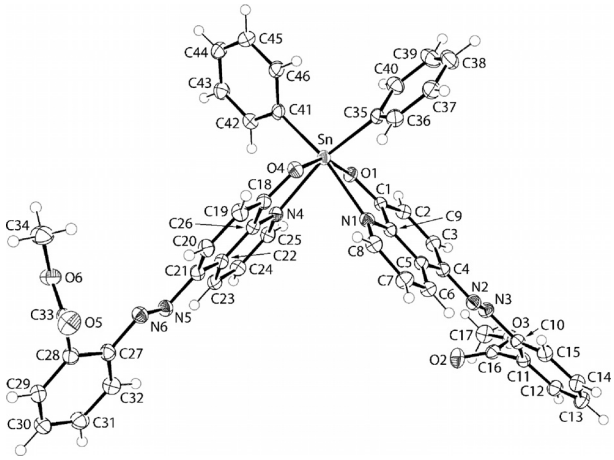

Figure 2. Molecular structure of **2** characterized as its tri-benzene solvate, showing the crystallographic numbering scheme employed; the benzene molecules of solvation are omitted. Selected structural parameters: Sn–O1 2.0940(14), Sn–O4 2.1190(15), Sn–N1 2.3446(18), Sn–N4 2.3071(17) Å; O1–Sn–O4 155.27(6), N1–Sn–C41 165.13(7), N4–Sn–C35 162.96(7), C35–Sn–C41 103.89(8)°.

the data. The ^{1}H- NMR integration values were completely consistent with the formulation of the products. The ^{1}H and ^{13}C NMR chemical shift assignment of the diorganotin moiety is straightforward from the multiplicity pattern, resonance intensities and also by examining the $^{n}J(^{13}C–^{119/117}Sn)$ coupling constants. In the ^{1}H and ^{13}C NMR spectra of **1–3** there is only one set of NMR signals for both the organo groups (Sn–*R*; *R* = Me, Ph, Bz) and for the ligand L, which confirms for the magnetic equivalence of both the Sn–*R* and both ligands in solution. This indicates their relative symmetrical arrangement in the coordination sphere of the tin atom in solution. The chemical shifts $\delta(^{13}C)$ of the carbon atoms of the Sn–*R* are not very sensitive to changes in the coordination of the central tin atom. The value of the coupling constants $^{n}J[^{119}Sn–^{13}C(Sn–R)]$ of **1–3** matches (see Experimental Section) closely with the data for respective hexacoordinate $[Me_2Sn(Ox)_2]$,[14] $[Ph_2Sn(Ox)_2]$, $[Ph_2Sn(AzOx)_2]$,[7,15] and $[Bz_2Sn(AzOx)_2]$[8,15] {Ox = deprotonated quinolin-8-ol, AzOx = 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-ol} complexes in $CDCl_3$ solution. Further structural conclusions were extracted from the solution ^{119}Sn NMR spectra. Complexes **1–3** display a sharp singlet at –221, –384, and –323 ppm, respectively, and these values match well with those reported for six-coordinate diorganotin(IV) quinolinolates ($[Me_2Sn(Ox)_2]$ = –237 ppm[16] or –236 ppm,[17] $[Ph_2Sn(Ox)_2]$ = –394 ppm,[15] $[Ph_2Sn(AzOx)_2]$ = –386 ppm,[7] $[Bz_2Sn(Ox)_2]$ = –335 ppm,[15] and $[Bz_2Sn(AzOx)_2]$ = –326 ppm[8] in $CDCl_3$ solution. Thus, the ^{119}Sn NMR spectroscopic data indicate the structures in solution to be rather similar to the structures observed in the solid state (see Mössbauer and X-ray discussion, vide infra).

The Mössbauer data, i.e. isomer shift (δ), quadrupole splittings (Δ) and the widths at half-height of the resonant peaks (Γ), for the diorganotin(IV) complexes are given in the Experimental Section. The diorganotin(IV) complexes **1–3** display δ values in the range 0.81–0.88 mm·s^{-1}, which are typical of diorganotin(IV) derivatives[18] and fall within the limits of δ values observed for related diorganotin(IV) quinolinolates: $[Me_2Sn(Ox)_2]$ = 0.88 mm·s^{-1},[19] $[Me_2Sn(AzOx)_2]$ = 0.93 mm·s^{-1},[20] $[Ph_2Sn(Ox)_2]$ = 0.78 mm·s^{-1},[19] $[Ph_2Sn(AzOx)_2]$ = 0.65–1.10 mm·s^{-1},[7,20] and $[Bz_2Sn(AzOx)_2]$ = 0.81–0.93 mm·s^{-1}.[8] On the other hand, Δ was proved useful in distinguishing between a *cis* and a *trans* configuration in octahedral complexes. The Mössbauer spectra of the complexes **1–3** are characterized by symmetrical doublets with Δ values in the range 1.72–2.04 mm·s^{-1}, which is typical of *cis*-R_2 octahedral R_2Sn^{IV} derivatives.[21,22] The Δ values for **1–3** compare well with the data for related diorganotin(IV) quinolinolates, e.g. $[Me_2Sn(Ox)_2]$ = 1.98 mm·s^{-1},[19] $[Me_2Sn(AzOx)_2]$ = 2.18 mm·s^{-1},[20] $[Ph_2Sn(Ox)_2]$ = 1.64 mm·s^{-1},[19] $[Ph_2Sn(AzOx)_2]$ = 1.68–2.20 mm·s^{-1},[7,20] and $[Bz_2Sn(AzOx)_2]$ = 1.58–1.77 mm·s^{-1},[8] having a *cis*-R_2Sn octahedral arrangement as confirmed by single-crystal X-ray crystallography (vide infra). The similar magnitudes of the δ and Δ values in **1–3**, further indicate that the complexes are isostructural. Thus, Mössbauer spectroscopic data suggest a *cis*-R_2Sn octahedral arrangement for **1–3**, where the equatorial positions are defined by two oxygen atoms, one nitrogen atom, and one organo group, whereas the axial site is occupied by an organo group and a nitrogen atom. The structure of a representative complex **2** has been confirmed from the diffraction study (see below).

X-ray Crystallography

Crystals of $Ph_2Sn(L)_2$ (**2**) were isolated from re-crystallization of its benzene solution and the X-ray crystal structure was determined on its tri-benzene solvate. The molecular structure, Figure 2, confirms the spectroscopic studies, with the tin atom being coordinated by *cis*-*ispo*-C atoms derived from the two phenyl groups, and two chelating *N*,*O*-quinolinato ligands (selected geometric parameters are collected in the caption to Figure 2).

The oxygen atoms occupy approximately *trans* positions with O1–Sn–O4 155.27(6)°, and the nitrogen atoms are each approximately *trans* to a phenyl-*C*. Distortions from the ideal octahedral arrangement are related, in part, to the restricted bite angles of the quinolinato chelate rings. There are twists evident in each of the ligands and these are quantified in terms of the dihedral angles formed between the quinolinato residue and the terminal aromatic ring, i.e. 31.60(8) and 22.61(8)° for the O1 and O4 ligands, respectively. In each case, the methoxy residue is twisted out of the plane of the aromatic ring, to which it is connected; the C10–C11–C16–O2 and C27–C28–C33–O5 torsion angles are 54.5(3) and 112.9(2)°, respectively.

There are three diphenyltin *bis*(quinolin-8-olate) structures bearing similar azo functionality available in the literature for comparison[7] with terminal phenyl (crystallized as an acetone monosolvate), 4-bromophenyl and 4-methylphenyl groups; the molecules with substituted phenyl rings have twofold symmetry. Each of these structures features a virtually superimposable coordination arrangement to that observed in compound **2** and the ranges of Sn–O and Sn–N bond lengths are 2.092(4) to 2.099(3) Å and 2.2833(12) to 2.3868(12) Å, respectively.

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The Sn–O4 bond length in **2** of 2.1190(15) Å lies out of the observed range but, variations in geometric parameters in organotin compounds are notorious for their non-systematic variations.[23]

In the crystal structure of **2** the most prominent intermolecular interactions are of the type C–H···O [shortest interaction: C25–H25···O5^{i} = 2.40 Å, C25···O5^{i} = 3.273(3) Å, angle at H25 = 153° for *i*: *x*, 1/2–*y*, 1/2+*z*] and C–H···π [shortest interaction: C17–H17b···Cg1^{ii} = 2.70 Å, C17..Cg1^{ii} = 3.639(3) Å, angle at H17b = 162°, where Cg1 is the ring centroid of (C41–C46) and *ii*: –*x*, 1–*y*, 2–*z*]. Globally, the molecules stack to form columns aligned along the *a* axis, in which reside the solvent benzene molecules (Figure 3).

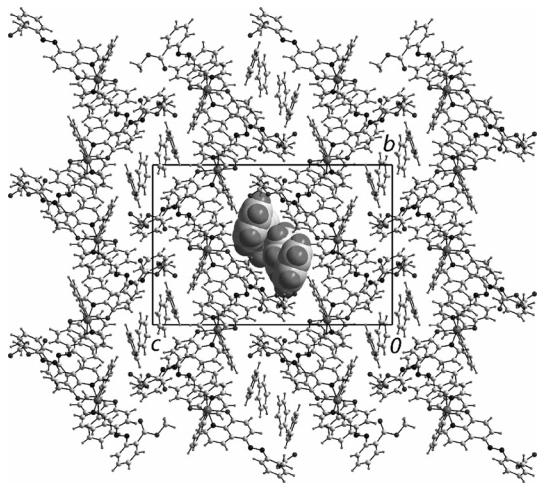


Figure 3. A view of the unit cell contents in projection down the *a* axis for **2**·3C_6H_6. Molecules of **2** define channels parallel to the *a* axis, in which reside the benzene molecules. The benzene molecules occupying one channel are highlighted in space filling mode.

Experimental Section

Materials and Methods: Me_2SnCl_2 (Merck), Ph_2SnO (Aldrich), methyl anthranilate (Lancaster) and oxine (Merck) were used without further purification. Bz_2SnCl_2 (dibenzyltin dichloride) was prepared by the method reported earlier.[24] Me_2SnO and Bz_2SnO were prepared by literature methods.[25,26] The solvents used in the reactions were of AR grade and dried using standard procedures. Benzene was distilled from sodium benzophenone ketyl. Methyl 2-{[(*E*)-8-oxo-5,8-dihydroquinolin-5-ylidene]hydrazino}benzoate (LH) was prepared by following literature method.[11]

Carbon, hydrogen, and nitrogen analyses were performed with a Perkin–Elmer 2400 series II instrument. IR spectra in the range 4000–400 cm^{-1} were obtained with a Perkin–Elmer Spectrum BX series FT-IR spectrophotometer as KBr discs. ^{1}H-, ^{13}C- and ^{119}Sn-NMR spectra were recorded with a Bruker AMX 400 spectrometer and measured at 400.13, 100.62, and 149.18 MHz, respectively. The ^{1}H, ^{13}C and ^{119}Sn chemical shifts were referenced to Me_4Si set at δ = 0.00 ppm, $CDCl_3$ set at δ = 77.0 ppm, and Me_4Sn set at δ = 0.00 ppm, respectively. The Mössbauer spectra were recorded with a conventional spectrometer operating in the transmission mode. The source was $Ca^{119}SnO_3$ (Ritverc GmbH, St. Petersburg, Russia; 10 mCi), moving at room temperature with constant acceleration in a triangular waveform. The driving system was from Halder (Seehausen, Germany), and the NaI (Tl) detector from Harshaw (De Meern, The Netherlands). The multichannel analyzer and the related electronics were from Takes (Bergamo, Italy). The solid absorber samples, containing ca 0.5 mg ^{119}Sn cm^{-2}, were held at 77.3 K in a MNC 200 liquid-nitrogen cryostat (AERE, Harwell, UK). The velocity calibration was made with a ^{57}Co Mössbauer source (Ritverc GmbH, St. Petersburg, Russia, 10 mCi), and an iron foil as absorber. The isomer shifts are relative to room temperature $Ca^{119}SnO_3$.

Synthesis of $Me_2Sn(L)_2$ (1): The compound was synthesized by reacting LH (0.37 g, 1.20 mmol) and Me_2SnO (0.10 g, 0.60 mmol) in anhydrous toluene (50 mL) in a flask equipped with a Dean–Stark moisture trap and water cooled condenser. The reaction mixture was heated to reflux for 4 h. Afterwards, the solvent was distilled off to dryness and the residue was dried in vacuo. The solid mass was washed with hexane and recrystallized from a mixture of chloroform and ethanol (v/v 1:2), which afforded red crystals. Yield 0.41 g (79 %), M.p. 208–210 °C. $C_{36}H_{30}N_6O_6Sn$ (760.93): calcd. C 56.77, H 3.97, N 11.04 %; found: C 56.70, H 4.05, N 11.10 %. **IR** (KBr): $\tilde{\nu}$ = 1727 [ν_{as}(O–C=O)], 1320 [ν(C(aryl)O)] cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ_H = 9.33 [dd, 2 H, H4], 8.87 [dd, 2 H, H2], 8.03 [d, 2 H, H6], 7.74 [d, 2 H, H6'], 7.61 [d, 2 H, H3], 7.59 [t, 2 H, H4'], 7.36 [m, 6 H, H3', H5' & H7], 3.82 [s, 6 H, CO_2Me], 0.59 [s, 6 H, Sn-Me]. **^{13}C NMR** ($CDCl_3$): δ_C = 168.5 [CO_2], 162.1 [C8], 152.3 [C1'], 142.9 [C2], 136.4 [C5], 135.9 [C2'], 135.1 [C8a], 131.6 [C4], 129.5 [C3'], 128.9 [C4'], 128.5 [C4a], 128.1 [C5'], 122.9 [C3], 120.9 [C6'], 119.7 [C6], 114.2 [C7], 52.3 [CO_2Me], 7.4 [Sn-Me; ^{1}J (^{119}Sn,^{13}C) = 620 Hz]. **^{119}Sn NMR** ($CDCl_3$): δ_{Sn} = –221.2. **^{119}Sn Mössbauer**: δ = 0.84, Δ = 2.04, Γ = 0.80 mm·s^{-1}, ρ = 2.43.

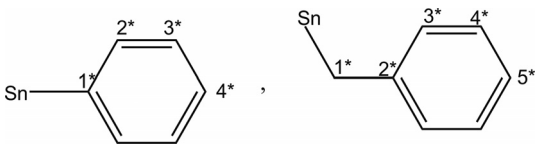
Alternatively, compound **1** can also be synthesized by dropwise addition of hot anhydrous benzene solution (30 mL) of LH (0.30 g, 0.98 mmol) to a stirred benzene solution (10 mL) containing Me_2SnCl_2 (0.11 g, 0.50 mmol). The reaction mixture was heated to reflux for 1 h, subsequently triethylamine (0.05 g, 0.50 mmol) was added and heating to reflux was continued for additional 3 h. The reaction mixture was cooled to room temperature and filtered to remove Et_3N·HCl. The filtrate was collected; volatiles were removed and the residue dried in vacuo. The residue was washed with hexane three times, dried in vacuo and finally recrystallized from a mixture of chloroform and ethanol (v/v 1:2), which afforded red crystals in 32 % yield. Analytical and spectroscopic data match well with those of the compound obtained by the former procedure.

Synthesis of $Ph_2Sn(L)_2$ (2): A similar synthetic procedure as for **1** was used except that Me_2SnO was replaced by Ph_2SnO, giving maroon crystals from a mixture of benzene and hexane (v/v 1:1). Yield 85 %. M.p. 120–122 °C. $C_{46}H_{34}N_6O_6Sn$ (884.96): calcd. C 62.38, H 3.87, N 9.49 %; found: C 62.10, H 3.78, N 9.40 %. **IR** (KBr): $\tilde{\nu}$ = 1725 [ν_{as}(O–C=O)], 1317 [ν(C(aryl)O)] cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ_H = 9.29 [dd, 2 H, H4], 8.63 [dd, 2 H, H2], 8.27 [d, 2 H, H6], 7.76 [d, 2 H, H6'], 7.68 [d, 2 H, H3], 7.56 [m, 6 H, H4'& H2*], 7.42 [m, 12 H, H3', H5', H7, H3*& H4*], 3.85 [s, 6 H, CO_2Me]. **^{13}C NMR** ($CDCl_3$): δ_C = 168.6 [CO_2], 161.9 [C8], 152.3 [C1'], 148.4 [C1*; ^{1}J (^{119}Sn,^{13}C) = 925 Hz],143.4 [C2], 136.4 [C5], 136.4 [C2'], 135.1 [C2*; ^{2}J (^{119}Sn,^{13}C) = 52 Hz], 134.8 [C8a], 134.6 [C4], 131.6 [C3'], 129.5 [C4*; ^{4}J (^{119}Sn,^{13}C) = 20 Hz], 128.9 [C4'], 128.6 [C4a], 128.3 [C3*; ^{3}J (^{119}Sn,^{13}C) = 70 Hz], 127.9 [C5'], 123.0 [C3], 121.0 [C6'], 119.5 [C6], 114.6 [C7], 52.3 [CO_2Me]. **^{119}Sn NMR** ($CDCl_3$): δ_{Sn} = –384.1. **^{119}Sn Mössbauer**: δ = 0.81, Δ = 1.80, Γ = 0.80 mm·s^{-1}, ρ = 2.22.

Synthesis of $Bz_2Sn(L)_2$ (3): A similar synthetic procedure as for **1** was used except that Me_2SnO was replaced by Bz_2SnO, giving orange crystals from a mixture of benzene and hexane (v/v 1:1). Yield 44 %,

M.p. 155–56 °C. $C_{48}H_{38}N_6O_6Sn$ (912.99): calcd. C 63.09, H 4.19, N 9.20%; found: C 63.01, H 4.25, N 9.30%. **IR** (KBr): $\tilde{\nu}$ = 1725 [ν_{as}(O–C=O)], 1319 [ν(C(aryl)O)] cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ_H = 9.15 [dd, 2 H, H4], 8.20 [d, 2 H, H6], 8.13 [dd, 2 H, H2], 8.03 [m, 4 H, H3 & H6'], 7.59 [t, 2 H, H4'], 7.45 [t, 2 H, H3'], 7.25 [m, 4 H, H5'& H7], 6.75 [m, 10 H, H3*, H4*& H5*], 3.85 [s, 6 H, CO_2Me], 2.70 [d, 4 H, H1*]. **^{13}C NMR** ($CDCl_3$): δ_C = 168.7 [CO_2], 162.2 [C8], 152.3 [C1'], 143.0 [C2], 140.8 [C2*; $^2J(^{119}Sn,^{13}C)$ = 55 Hz], 136.2 [C5], 135.9 [C2'], 135.1 [C8a], 131.6 [C4], 129.5 [C3'], 129.2 [C4'], 128.9 [C3*; $^3J(^{119}Sn,^{13}C)$ = 30 Hz], 128.2 [C4a], 128.0 [C5'], 127.6 [C4*; $^4J(^{119}Sn,^{13}C)$ = 20 Hz], 123.1 [C3], 122.6 [C-5*; $^5J(^{119}Sn,^{13}C)$ = 25 Hz], 120.5 [C6'], 120.0 [C6], 114.0 [C7], 52.3 [CO_2Me], 33.5 [C1*; $^1J(^{119}Sn,^{13}C)$ = 530 Hz]. **^{119}Sn NMR** ($CDCl_3$): δ_{Sn} = –322.9 ppm. **^{119}Sn Mössbauer**: δ = 0.88, Δ = 1.72, Γ = 0.89 mm·s^{-1}, ρ = 1.95.

Ligand numbering scheme as shown in Figure 1 and numbering schemes for Sn–Ph and Sn–Bz skeletons as shown below:



Crystal Structure Determination: Crystal data for **2**·3C_6H_6: $C_{46}H_{34}N_6O_6Sn.3C_6H_6$: M = 1119.8, T = 98(2) K, monoclinic, $P2_1/c$, a = 13.007(4), b = 16.810(4), c = 25.207(6) Å, β = 92.191(7)°, V = 5508(2) Å^3, Z = 4, D_x = 1.350, $F(000)$ = 2304, μ = 0.522 mm^{-1}, 58465 data measured (Rigaku AFC12κ/SATURN724 CCD using Mo-K_α radiation, θ_{max} = 26.5°[27]), no. absorption corrected,[28] unique data = 11403, no. of parameters = 696, R [10907 data with $I \geq 2\sigma(I)$] = 0.037, wR (all data) = 0.098. The structure was solved by direct-methods (SHELXS97[29]) and refined (anisotropic displacement parameters, hydrogen atoms in the riding model approximation and a weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.057P)^2 + 2.851P]$ where $P = (F_o^2 + 2F_c^2)/3$) with SHELXL97 on F^2.[28] The maximum and minimum residual electron density peaks of 1.26 and 0.72 e·Å^{-3}, respectively, were located 1.20 and 0.73 Å from the C35 and tin atoms, respectively. Figure 2 was drawn with ORTEP-3[30] at the 50% probability level, and Figure 3, with DIAMOND[31] with arbitrary spheres. Data manipulation and interpretation were with WinGX[32] and PLATON.[33]

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-847466 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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