APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 118–124

Preparation and structures of [2-(dimethylamino)-phenyl]diorganotin(IV) acetates substituted with organophosphorus groups in the α-position of the acetate ligand

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Received 17 June 2004; Revised 15 July 2004; Accepted 29 July 2004

Organotin(IV) carboxylates $R_2L^{NC}SnOC(O)CH_2P(E)Ph_2$, where L^{NC} is an *N*-chelating 2-(dimethylamino)phenyl group, and R/E = Ph/void (1a), Ph/O (1b), Ph/S (1c), Me/void (2a), Me/O (2b) and Me/S (2c), were synthesized, characterized by ^1H, ^{13}C, ^{31}P and ^{119}Sn NMR, IR and MS spectra, and the solid-state structures of 1b, 1c, 2b and 2c were determined by single-crystal X-ray diffraction. Spectral and structural data showed that the compounds are monomeric in $CDCl_3$ solution and the solid state, with the organophosphorus groups in the α-position of the monodentate carboxylate ligands not interacting with the tin atom. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: organotin(IV) compounds; phosphinocarboxylic acids; C,N-chelate ligand; NMR; X-ray diffraction

INTRODUCTION

Organotin(IV) compounds readily coordinate various donors to form hypervalent compounds.[1] The increase in the coordination number of the central tin atom can be accomplished not only via a formation of simple adducts but also by a modification of a substituent at tin (usually an organyl) with a donor functionality to form chelate rings via donor → Sn interactions. Among others, the latter approach has also been applied to organotin(IV) carboxylates since suitable and appropriately functionalized carboxylic acids can provide an access to hypervalent organotin(IV) compounds. Stannyl esters modified with phosphorus groups in the carboxylic part, such as $Ph_2P(E)CH_2CO_2SnR_3$ (E = O, R = Me, Et, Pr, Bu, cyclohexyl, and Ph; E = S, R = Ph),[2] $MeCH(P(O)Ph_2)CH_2CO_2SnR_3$, $\{MeCH[P(O)Ph_2]CH_2CO_2\}_2SnR_2$ (R = Me and Ph)[3], and the salts $[Ph_3P(CH_2)_2CO_2SnR_3]X$ (X = Cl, Br, I, N_3, NCS, NO_3, BPh_4 and $[Co(CO)_4]$),[4] are the representative examples. As a contribution to this field, we decided to prepare organotin(IV) acetates containing two *different* donor groups: a chelating 2-(dimethylamino)phenyl group at tin and various organophosphorus substituents in the α-position of the carboxylato ligand, relating to (diphenylphosphino)acetic acid.[5] In this paper, we report on the preparation, spectral characterization and crystal structures of new organotin carboxylates $R_2L^{NC}SnOC(O)CH_2P(E)Ph_2$, where L^{NC} = 2-(dimethylamino)phenyl, and R/E = Ph/void (**1a**), Ph/O (**1b**), Ph/S (**1c**), Me/void (**2a**), Me/O (**2b**) and Me/S (**1c**).

RESULTS AND DISCUSSION

The stannyl esters **1a**–**c** and **2a**–**c** were synthesized by salt metathesis between the respective organotin(IV) chloride (**1** and **2**) and potassium carboxylates, which were prepared *in situ* from the appropriate carboxylic acid (**3a**–**c**) and potassium *tert*-butoxide (Scheme 1). The phosphines **1a** and **2a** were obtained as non-crystallizing waxy solids, tending to firmly retain traces of solvents and reaction impurities (e.g. the educts). In addition, compound **2a** is slowly oxidized in air

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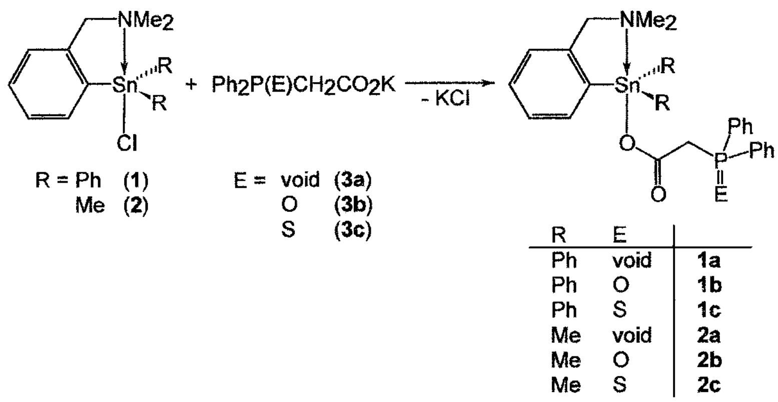
Contract/grant sponsor: Grant Agency of the Czech Republic; Contract/grant number: 203/04/223; 203/99/M037.
Contract/grant sponsor: Ministry of Education, Youth and Sports of the Czech Republic; Contract/grant number: MSM 113100001.



Scheme 1.

Table 1. Selected NMR data for **1a–c** and **2a–c**[a]

					δ_C		
Compound	δ_P[b]	δ_{Sn}	Sn*Me*$_2$	N*Me*$_2$	NCH$_2$	PCH$_2$[d]	COO[e]
1a	17.6	217.9	—	45.59	64.73	37.13 [18]	174.70 [8]
1b	28.5	215.2	—	45.60	64.64	40.70 [63]	169.77 [4]
1c	38.7	214.0	—	45.61	64.66	45.61 [48	169.24 [6]
2a	17.6	75.5 [5[c]]	3.29	45.19	64.97	37.51 [18]	175.05 [8]
2b	28.5	71.3 [7[c]]	3.42	45.19	64.95	41.06 [64]	170.18 [5]
2c	38.9	70.1 [7[c]]	3.27	45.19	64.95	44.15 [49]	169.69 [6]

[a] Measured in $CDCl_3$ at 25 °C.
[b] Reference data: δ_P **3a**, 15.3; **3b**, 31.6; **3c**, 37.6 (this work).
[c] J_{PSn}/Hz.
[d] $\delta(PCH_2)$ [$^1J_{PC}$/Hz].
[e] $\delta(COO)$ [$^2J_{PC}$/Hz].

to the corresponding phosphine oxide **2b**. On the other hand, the phosphinoyl (**1b** and **2b**) and thiophosphoryl (**1c** and **2c**) derivatives resulted as white amorphous solids, which were further recrystallized from chloroform–hexane or ethyl acetate–hexane to give well-developed colourless crystals of analyticaly pure, air-stable compounds. All compounds were characterized by multinuclear NMR spectroscopy, IR and MS spectra, and elemental analyses (Table 1 and Experimental section). In addition, the solid state structures of **1b**, **1c**, **2b** and **2c** were established by single-crystal X-ray diffraction.

In IR spectra, the compounds show strong carboxylate bands at ca. 1630–1660 (ν_{as}) and ca. 1315–1335 cm^{-1} (ν_s), similar to $Ph_2P(O)CH_2CO_2SnR_3$.[2] The ^{119}Sn chemical shifts (Table 1) do not vary much in the series **1a–c** and **2a–c**, whereas the ^{31}P NMR parameters (Table 1) are practically identical for the pairs **1a–2a**, **1c–2c** and **1c–2c**, comparing favourably with the respective free acids. This implies similar arrangements around tin atoms and rules out a direct donor interaction between the phosphorus substituents and the tin atom. In summary, the NMR data (including the $^2J_{SnH}$ coupling constants for the tin-bonded methyl groups in **2a–c**) indicate that the solution structures of organotin carboxylates **1a–c** and **2a–c** are monomeric, most likely similar to those in the solid state (see the solid-state structures below).

The reluctance of the phosphorus groups, which are potential P, O and S donors, to ligate the tin atom can be accounted for by a saturation of the central tin atom by donation from the nitrogen and, possibly, also O1 atoms (see below) to form stable chelate rings and, simultaneously, by unfavourable steric properties of the carboxymethylene linking group. This is not unprecedented; the need for a particular arrangement can be demonstrated by the related phosphorus-modified organotin(IV) compounds, which *do* [e.g. (t-Bu)PhP(O)$CH_2CH_2SnXR_2$ (X = Cl, Br; R = Me, t-Bu),[6] $R_2P(CH_2)_3SnClMe_2$[7]] or *do not* form the chelates in solution [e.g. $R_2P(CH_2)_2SnClMe_2$[7]], depending on the properties of the tether and the substituents at tin.

X-ray crystallography

The solid-state structures of **1b**, **1c**, **2b** and **2c** have been determined by single-crystal X-ray diffraction. The views of the molecular structures are shown only for **1b** (Fig. 1) and **2c** (Fig. 2) since the structures of **1c** and **2b** are practically identical (N.B. compounds **2b** and **2c** are isostructural). The pertinent geometric parameters for all structurally characterized compounds are given in Table 2.

As revealed by X-ray diffraction analysis, compounds **1b**, **1c**, **2b** and **2c** all involve tin atoms in a trigonal bipyramidal

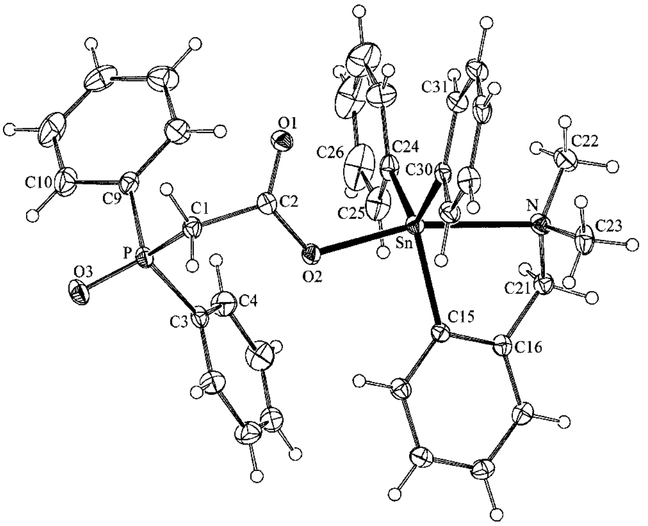


Figure 1. A view of the molecular structure of **1b** showing the atom labelling scheme. Thermal motion ellipsoids are scaled to enclose 30% probability level.

environment resulting from intramolecular N → Sn donor interactions. The nitrogen and the tin-bonded oxygen atoms are located in the axial positions of the trigonal bipyramid, the nitrogen atom being significantly more distant than the other four donor atoms around the tin. The geometric constraints imposed by the chelate ligand bring about a further deformation of the coordination sphere, namely the closure of the N–Sn–C15 angles (ca. 75°) which is, however, relaxed by an opening of the other interligand angles. The geometries of the coordination spheres are very similar in the whole series and, in addition, compare favourably with the geometries of the precursor compounds **1** [Sn-N 2.519(2), Sn-C(Ph) 2.125(3), Sn-C(L^{NC}) 2.126(3) Å][8] and **2** [Sn-N 2.488(7), Sn-C(L^{NC}) 2.129(9) Å],[9] as well as the analogous bromide $Ph_2L^{NC}SnBr$ [Sn-N 2.51(1), Sn-C(L^{NC}) 2.15(1) Å].[10]

The acetate ligands are coordinated in an unidentate fashion: the Sn–O2 distances differ only marginally from the sum of the covalent atomic radii (ca. 2.14 Å). The other oxygen atoms of the carboxylate ligands (O1) are located above the C–C–O2 faces of the coordination polyhedra (different faces for different compounds). Although the Sn· · ·O1 separations markedly exceed this limit [cf. the minimum distance of 3.094(2) Å for **1b**], they may allow for a weak tin–oxygen interactions, which would render the hypervalent tin cordinatively saturated and the polar carboxy group reluctant towards intermolecular association (the sum of the contact atomic radii for tin an oxygen is ca. 3.8 Å; see below). Such a bonding situation resembles the related organotin carboxylate 4-(4-$Me_2NC_6H_4)C_6H_4CO_2SnPh_2L^{NC}$ [**4**; data for the solvate **4**. $CHCl_3$: Sn-O 2.140(2), Sn· · ·O 2.997(1), Sn-N 2.539(2), C-O 1.231(3) and 1.304(3) Å].[11]

The intramolecular Sn· · ·O3 [**1b**, 6.581(2); **2b**, 5.010(1) Å] and Sn· · ·S [**1c**, 4.9361(5); **2c**, 5.0452(7) Å] distances as well as the mutual orientation of the molecular parts and the distribution of the molecules in the crystals clearly exclude inter- and intramolecular donor–acceptor interactions between the phosphorus groups and the tin atoms. As a result, the crystals accommodate discrete molecules packed at the distances of the normal van der Waals contacts, wherein the electronegative oxygen and sulphur atoms do not contribute significantly to intermolecular association. The exceptions are weak C6-H6· · ·O3^i [O3· · ·C6 3.269(4) Å, angle at H6 143°; *i*. $(x - 1, y, z)$] and C19-H19· · ·O3^{ii}

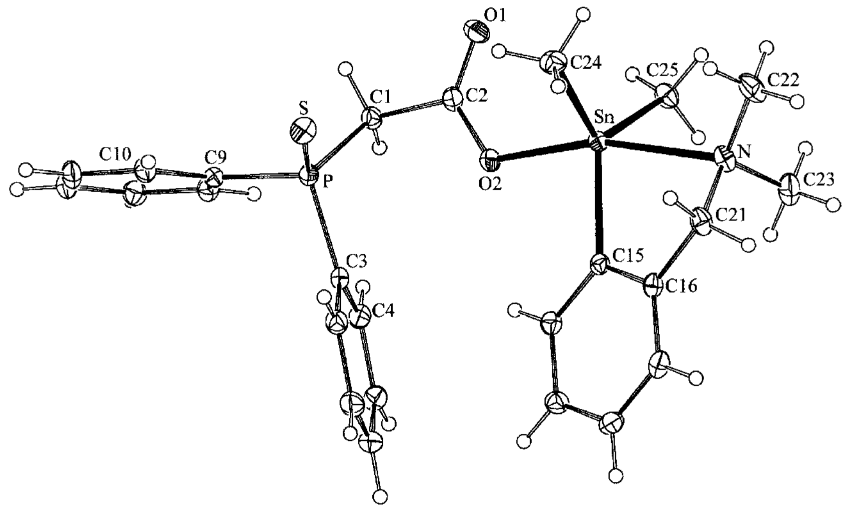


Figure 2. A view of the molecular structure of **2c** showing the atom labelling scheme. Thermal motion ellipsoids are scaled to enclose 30% probability level.

Table 2. Selected interatomic distances and angles for **1b** and **1c** (in Å and deg)

	Compound			
	1b	**1c**	**2b**	**2c**
E	O(3)	S	O(3)	S
n	30	30	25	25
Sn–O2	2.144(2)	2.138(1)	2.150(1)	2.148(1)
Sn$\cdots$O1	3.094(2)	3.242(1)	3.151(1)	3.165(2)
Sn–N	2.488(2)	2.534(2)	2.512(2)	2.524(2)
Sn–C15	2.129(2)	2.134(2)	2.138(2)	2.141(2)
Sn–C24	2.133(3)	2.130(2)	2.131(2)	2.126(2)
Sn–Cn	2.132(2)	2.126(2)	2.125(2)	2.130(2)
P=E	1.486(2)	1.9535(7)	1.483(1)	1.9412(7)
P–C1	1.816(3)	1.834(2)	1.806(2)	1.817(2)
C1–C2	1.518(3)	1.526(2)	1.524(2)	1.525(3)
C2–O1	1.225(3)	1.220(2)	1.220(2)	1.219(2)
C2–O2	1.297(3)	1.294(2)	1.296(2)	1.297(2)
P–C3	1.801(3)	1.818(2)	1.809(2)	1.815(2)
P–C9	1.804(3)	1.818(2)	1.815(2)	1.822(2)
N–Sn–O2	165.16(7)	172.22(5)	164.27(5)	164.79(5)
N–Sn–C	75.16(8)–90.54(8)[c]	74.17(6)–90.52(6)[c]	75.29(6)–90.28(6)[e]	75.07(6)–90.73(7)[e]
O2–Sn–C	90.25(8)–98.08(8)[d]	87.38(6)–101.44(6)[d]	89.06(5)–99.21(6)[f]	90.00(6)–98.41(7)[f]
C15–Sn–C24	114.2(1)	120.21(7)	121.92(6)	115.12(7)
C15–Sn–Cn	121.40(9)	114.03(7)	116.28(6)	122.91(7)
C24–Sn–Cn	121.94(9)	123.16(7)	119.08(7)	119.34(8)
O1–C2–O2	124.5(2)	125.4(2)	125.2(2)	125.7(2)
P–C1–C2	118.2(2)	112.4(1)	115.3(1)	113.6(1)
C–P–C[a]	106.2(1)–108.9(1)	103.75(8)–107.23(8)	103.12(8)–109.40(8)	102.77(8)–108.98(8)
E–P–C[b]	110.1(1)–112.1(1)	112.30(6)–114.41(6)	112.35(7)–114.28(8)	112.83(6)–113.76(6)

[a] The range of C1–P–C(3,9) and C3–P–C(9) angles.
[b] The range of E–P–C(1,3,9) angles.
[c] The range of N–Sn–C(15,24,30) angles.
[d] The range of O2–Sn–C(15,24,30) angles.
[e] The range of N–Sn–C(15,24,25) angles.
[f] The range of O2–Sn–C(15,24,25) angles.

[O3$\cdots$C19 3.445(3) Å, angle at H19 167°; *ii.* $(2 - x, -y, 2 - z)$] intermolecular hydrogen bonds in **1b**, and even weaker *intra*molecular C20-H20$\cdots$S interactions [C20$\cdots$S 3.666(2) Å, angle at H20 158°] in **1c**. The structure of **1c** shows numerous stacking interactions of the exactly parallel but offset aromatic rings, although with rather long distances of the respective ring centroids (cf. the separation of the layers in α-graphite of ca. 3.35 Å): $\mathrm{Ph}^1\cdots\mathrm{Ph}^{1,iii}$ 4.288(1) Å, $\mathrm{Ph}^2\cdots\mathrm{Ph}^{2,iv}$ 5.199(1), $\mathrm{Ph}^2\cdots\mathrm{Ph}^{2,v}$ 5.313(1) and $\mathrm{Ph}^3\cdots\mathrm{Ph}^{3,vi}$ 5.423(1) Å, where $\mathrm{Ph}^1 =$ C(3–8), $\mathrm{Ph}^2 =$ C(30–35), and $\mathrm{Ph}^3 =$ C(9–14); *iii* $(-x, -y, 1 - z)$, *iv* $(2 - x, 1 - y, 1 - z)$, *v* $(1 - x, 1 - y, 1 - z)$, and *vi* $(-x, -y, -z)$.

EXPERIMENTAL

General comments

All syntheses were carried out under an argon atmosphere. Dichloromethane (Merck, p.a.) was dried over anhydrous potassium carbonate. Solvents used in the work-up and for crystallizations were used as purchased (Lachema). Compounds **1**,[12] **2**,[9,13] and **3a**[14] were synthesized according to the literature methods. Other chemicals were commercial products and were used as received from the suppliers (Fluka).

NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer (^{1}H, 399.95; ^{13}C, 100.58; ^{31}P, 161.9; ^{119}Sn 149.14 MHz) at 298 K. Chemical shifts (δ/ppm) are given relative to internal tetramethylsilane (^{1}H and ^{13}C), external 85% aqueous H_3PO_4 (^{31}P), and external neat $SnMe_4$ (^{119}Sn). IR spectra were recorded on an a Perkin-Elmer 684 FT IR spectrometer in the range 400–4000 cm.^{1} Electrospray ionization (ESI) mass spectra were measured on a Bruker Esquire 3000 instrument operating in the positive ion mode. The samples were dissolved in acetonitrile or in acetonitrile–chloroform. Unless noted otherwise, the data are given for isotopomers containing ^{120}Sn, ^{12}C, ^{14}N, ^{16}O, ^{31}P and ^{32}S.

Syntheses

*Preparation of **3b** and **3c***

For (diphenylphosphoryl)acetic acid (**3b**), hydrogen peroxide (0.77 ml 30%, ca. 7.5 mmol) was added to an ice-cooled solution of (diphenylphosphino)acetic acid (1.221 g, 5.0 mmol) in acetone (10 ml). After stirring at 0 °C for 30 min, the mixture was diluted with water and acidified with 3 M HCl (5 ml). Acetone was removed under reduced pressure, and the aqueous suspension extracted into chloroform. A subsequent drying of the organic extract over magnesium sulphate and evaporation afforded pure **3b** as a white solid. The yield was 1.105 g (85%).

M.p. 139–141 °C (Issleib and Thomas,[15] 142–144 °C). ^{1}H NMR ($CDCl_3$): δ 3.51 (d, $^2J_{PH} = 13.7$ Hz, 2 H, PCH_2), 7.46–7.88 (m, 10 H, PPh_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.6. IR (Nujol): ν/cm^{-1} 1710 vs 1169 br s, 1217 m, 1144 s, 1128 s, 1093 s, 1095 br m, 905 m, 840 s, 813 m, 754 s, 694 s, 600 m, 510 s.

For (diphenylthiophosphoryl)acetic acid (**3c**), the procedure was modified from Issleib and Thomas.[16] A suspension of (diphenylphosphino)acetic acid (1.221 g, 5.0 mmol) and sulphur (0.164 g, 5.1 mmol) in toluene (10 ml) was heated to reflux for 90 min. The resulting clear solution was cooled to 0 °C and the product, which separated, was filtered off, washed with little toluene and dried in air. The yield of **3c** was 1.200 g, 87%; white microcrystalline solid.

M.p. 187–188 °C (Issleib and Thomas,[16] 190 °C). ^{1}H NMR ($CDCl_3$): δ 3.65 (d, $^2J_{PH} = 13.7$ Hz, 2 H, PCH_2), 7.46–7.88 (m, 10 H, PPh_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.6. IR (Nujol): ν/cm^{-1} 1698 vs 1304 vs 1207 m, 1132 s, 1097 s, 958 br m, 918 m, 863 m, 807 s, 749 s, 696 s, 639 s, 579 m, 502 m, 479 s.

Preparation of tin carboxylates

Potassium *tert*-butoxide (0.058 g, 0.52 mmol) and the appropriate acid (0.50 mmol; **3a**, 0.122 g, **3b**, 0.130 g; and **3c**, 0.138 g) were dissolved in dichloromethane (10 ml) and the solution was stirred for 1 h (the mixture deposited white precipitate of the respective potassium carboxylates). Then a solution of organotin halide (0.50 mmol; **1**, 0.221 g; and **2**, 0.159 g) in dichloromethane (5 ml) was introduced, whereupon the most of the precipitated salt dissolved (a clear solution resulted in some cases). The mixture was stirred overnight, the solvents were removed under reduced pressure, and the residue extracted with chloroform–hexane (1 : 1, v/v). The extract was filtered and evaporated under vacuum to give the products. Compounds **1b**, **1c**, **2b** and **2c** were further purified by recrystallization from chloroform–hexane or ethyl acetate–hexane.

Compound **1a**. Yield: 0.147 g (45%), yellowish solid. ^{1}H NMR ($CDCl_3$): δ 1.75 (s, 6 H, NMe_2), 3.04 (d, $^2J_{PH} = 0.9$ Hz, 2 H, PCH_2), 3.46 (s, 2 H, NCH_2), 7.08–7.97 (m, 24 H, aromatics). IR (Nujol): ν/cm^{-1} 1652 vs br, 1333 vs 1195 m, 1099 m, 1019 m, 865 s, 751 vs 718 vs 624 w, 530 m, 478 s. ESI MS: m/z 690 ($[M+K]^+$), 674 ($[M+Na]^+$), 408 ($[(C_6H_4CH_2NMe_2)SnPh_2]^+$). HR MS: calculated for $C_{29}H_{29}NO_2P^{118}Sn$ ($[M-Ph]^+$) 572.0952, found 572.0975; calculated for $C_{29}H_{29}NO_2P^{119}Sn$ ($[M-Ph]^+$), 573.0969; found, 573.1010; calculated for $C_{29}H_{29}NO_2P^{120}Sn$ ($[M-Ph]^+$), 574.0958; found, 574.1045.

Compound **1b**. Yield: 0.171 g (51%), white solid. ^{1}H NMR ($CDCl_3$): δ 1.74 (s, 6 H, NMe_2), 3.40 (d, $^2J_{PH} = 16$ Hz, 2 H, PCH_2), 3.45 (s, 2 H, NCH_2), 7.08–7.93 (m, 24 H, aromatics). IR (Nujol): ν/cm^{-1} 1647 vs 1315 vs 1195 s, 1124 s, 997 m, 844 s, 729 s, 696 vs, 610 m, 509 s, 454 m. ESI MS: m/z 706 ($[M+K]^+$), 690 ($[M+Na]^+$), 408 ($[(C_6H_4CH_2NMe_2)SnPh_2]^+$). Analysis calculated for $C_{35}H_{34}O_3PSn$—C, 63.09; H, 5.14; N, 2.10%; found—C, 63.00; H, 5.23; N, 2.00%.

Compound **1c**. Yield: 0.230 g (67%), yellowish solid. ^{1}H NMR ($CDCl_3$): δ 1.75 (s, 6 H, NMe_2), 3.45 (s, 2 H, NCH_2), 3.55 (d, $^2J_{PH} = 15$ Hz, 2 H, PCH_2), 7.08–7.99 (m, 24 H, aromatics). IR (Nujol): ν/cm^{-1} 1649 s, 1317 s, 1119 m, 1101 m, 748 m, 731 m, 698 m, 647 m, 587 m. ESI MS: m/z 722 ($[M+K]^+$), 706 ($[M+Na]^+$), 408 ($[(C_6H_4CH_2NMe_2)SnPh_2]^+$). Analysis calculated for $C_{35}H_{34}O_2PSSn$—C, 61.60; H, 5.02; N, 2.05%; found—C, 60.91; H, 5.08; N, 1.92%.

Compound **2a**. Yield: 0.232 g (88%), yellowish waxy solid. ^{1}H NMR ($CDCl_3$): δ 0.51 (s with tin satellites: $^2J_{119SnH} = 68.4$, $^2J_{117SnH} = 65.4$ Hz, 6 H, $SnMe_2$), 2.24 (s, 6 H, NMe_2), 3.20 (d, $^2J_{PH} = 0.5$ Hz, 2 H, PCH_2), 3.54 (s, 2 H, NCH_2), 7.06–7.92 (m, 14 H, aromatics). IR (Nujol): ν/cm^{-1} 1632 vs 1318 vs 1103 m, 1014 m, 925 m, 846 m, 739 s, 694 s, 605 m, 507 m. ESI MS: m/z 566 ($[M+K]^+$), 550 ($[M+Na]^+$), 284 ($[(C_6H_4CH_2NMe_2)SnMe_2]^+$). HR MS: calculated for $C_{24}H_{27}NO_2P^{118}Sn$ ($[M-Me]^+$), 510.0796; found, 510.0814; calculated for $C_{24}H_{27}NO_2P^{119}Sn$ ($[M-Me]^+$), 511.0813; found, 511.0828; calculated for $C_{24}H_{27}NO_2P^{120}Sn$ ($[M-Me]^+$), 512.0801; found, 512.0842.

Compound **2b**. Yield: 0.190 g (70%), yellowish solid. ^{1}H NMR ($CDCl_3$): δ 0.44 (s with tin satellites: $^2J_{119SnH} = 68.4$, $^2J_{117SnH} = 65.5$ Hz, 6 H, $SnMe_2$), 2.22 (s, 6 H, NMe_2), 3.53 (s, 2 H, NCH_2), 3.59 (d, $^2J_{PH} = 15.2$ Hz, 2 H, PCH_2), 7.02–7.92 (m, 14 H, aromatics). IR (Nujol): ν/cm^{-1} 1646 vs 1332 vs 1226 m, 1208 s, 1142 m, 1036 w, 1013 w, 936 m, 845 m, 710–775 s composite, 607 m, 544 s, 516 s. ESI MS: m/z 582 ($[M+K]^+$), 566 ($[M+Na]^+$), 284 ($[(C_6H_4CH_2NMe_2)SnMe_2]^+$). Analysis calculated for $C_{25}H_{30}O_3PSn$: C, 55.38; H, 5.58; N 2.58%; found: C, 54.99; H, 5.72; N 2.49%.

Compound **2c**. Yield: 0.166 g (59%), white solid. ^{1}H NMR ($CDCl_3$): δ 0.48 (s with tin satellites: $^2J_{119SnH} = 68.7$, $^2J_{117SnH} = 65.6$ Hz, 6 H, $SnMe_2$), 2.23 (s, 6 H, NMe_2), 3.53 (s, 2 H, NCH_2), 3.72 (d, $^2J_{PH} = 14.3$ Hz, 2 H, PCH_2), 7.06–7.99 (m, 14 H, aromatics). IR (Nujol): ν/cm^{-1} 1661 vs 1336 vs 1149 m, 1117 m, 1045 m, 1026 m, 875 m, 715–780 s composite, 659 m, 605 s, 631 m, 504 s. ESI MS: m/z 598 ($[M+K]^+$), 582 ($[M+Na]^+$), 284 ($[(C_6H_4CH_2NMe_2)SnMe_2]^+$). Analysis calculated for $C_{25}H_{30}O_2PSSn$—C, 53.79; H, 5.42; N, 2.51%; found—C, 53.50; H, 5.56; N, 2.43%.

X-ray crystallography

Crystals suitable for X-ray diffraction analyses were grown by liquid phase diffusion of hexane into ethyl acetate solutions

Table 3. Crystallographic, data collection and structure refinement parameters for **1b**, **1c**, **2b** and **2c**

	Compound			
	1b	**1c**	**2b**	**2c**
Formula	$C_{35}H_{34}NO_3PSn$	$C_{35}H_{34}NO_2PSSn$	$C_{25}H_{30}NO_3PSn$	$C_{25}H_{30}NO_2PSSn$
M (g mol^{1})	666.3	682.4	542.2	558.2
Crystal system	Monoclinic	Triclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$ (no. 14)	P1bar (no. 2)	$Pbca$ (no. 61)	$Pbca$ (no. 61)
a (Å)	8.2976(1)	8.3590(1)	18.7651(2)	19.5153(2)
b (Å)	30.6485(5)	11.9386(2)	12.4174(1)	12.3509(1)
c (Å)	12.2163(2)	16.3032(3)	20.3543(2)	20.6332(2)
α (°)	90	92.2537(6)	90	90
β (°)	99.5325(9)	99.9387(6)	90	90
γ (°)	90	104.764(1)	90	90
V (Å^3)	3063.82(8)	1543.71(4)	4742.83(8)	4973.25(8)
Z	4	2	8	8
D_c (g cm^{-3})	1.444	1.468	1.519	1.491
μ (Mo Kα) (mm^{-1})	0.922	0.980	1.171	1.197
$T_{\min}$, $T_{\max}$[a]	0.800, 0.915	0.873, 0.931	0.658, 0.710	0.660, 0.703
Diffractions total	37821	27668	72167	75728
Unique/observed[b] diffractions	7016/5333	7093/6426	5438/4947	5687/5098
R_{int} (%)[c]	5.44	3.62	3.34	3.43
No. parameters	372	372	284	284
R observed diffractions (%)[d]	3.43	2.45	2.24	2.34
R, wR all data (%)[d]	5.59, 7.68	2.94, 5.63	2.57, 5.36	2.76, 5.74
$\Delta\rho$ (e Å^{-3})	0.99, −0.69	0.45, −0.86	0.43, −0.64	0.48, −0.60

[a] Transmission coefficient range.

[b] Diffractions with $F_o > 4\ \Sigma(F_o)$.

[c] $R_{\mathrm{int}} = \Sigma|F_o{}^2 - F_{o,\mathrm{mean}}{}^2|/\Sigma|F_o{}^2|$.

[d] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR(F^2) = [\Sigma\{w(F_o{}^2 - F_c{}^2)^2\}/\Sigma w(F_o{}^2)^2]^{1/2}$.

(**1b**, colourless prism, 0.10 × 0.10 × 0.38 mm^3; **2b**, colourless prism, 0.30 × 0.33 × 0.40 mm^3) or similarly from hexane–chloroform (**1c**, colourless plate, 0.08 × 0.23 × 0.40 mm^3; **2c**, colourless prism, 0.30 × 0.30 × 0.38 mm^3). Full-set diffraction data ($\pm h$ $\pm k$ $\pm l$) with $2\theta \leq 55°$ were collected on a Nonius Kappa CCD diffractometer equipped with Cryostream Cooler (Oxford Cryosystems) at 150(2) K using graphite monochromatized MoKα radiation ($\lambda = 0.71073$ Å) and analysed with HKL program package[17] (Table 3). The data were corrected for absorption using a numeric method based on intensity variation in multiply measured diffractions (SORTAV routine as incorporated in the diffractometer software[18]).

The structures were solved by direct methods (SIR97[19]) and refined by weighted full-matrix least squares on F^2 (SHELXL97[20]). All non-hydrogen atoms were refined with anisotropic thermal motion parameters. The hydrogen atoms were included in the calculated positions [C–H bond lengths: 0.93 (aromatic), 0.97 (methylene) and 0.96 (methyl) Å] and assigned $U_{\mathrm{iso}}(\mathrm{H}) = 1.2\ U_{\mathrm{eq}}(\mathrm{C})$ (aromatic and methylene) or $1.5\ U_{\mathrm{eq}}(\mathrm{C})$ (methyl). The final geometric calculations were carried out with a recent version of Platon program.[21] CCDC refence numbers: CCDC-240262 (**1b**), CCDC-240263 (**1c**), CCDC-240264 (**2b**) and CCDC-240265 (**2c**).

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