APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2004; **18**: 353–358
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.653

Solid-state NMR study of $[(Ph_3SnF)_2(Ph_3SnO_2PPh_2)]$, a novel coordination polymer prepared from $Bu_4N[Ph_3SnF_2]$ and $[Ph_3SnOPPh_2OSnPh_3](O_3SCF_3)$

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Received 3 March 2004; Revised 23 March 2004; Accepted 24 March 2004

The coordination polymer $[(Ph_3SnF)_2(Ph_3SnO_2PPh_2)]$ (3), prepared by the reaction of $[Ph_3SnOPPh_2OSnPh_3](O_3SCF_3)$ (4) with $Bu_4N[Ph_3SnF_2]$ (5), was investigated by multinuclear magic angle spinning magnetic resonance spectroscopy and the results compared with those of the polymeric parent compounds Ph_3SnF (1) and $Ph_3SnO_2PPh_2$ (2). The crystal structure of 4 was determined by X-ray crystallography. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: tin; coordination polymer; solid state NMR; triflate

INTRODUCTION

Triorganotin(IV) compounds, R_3SnX (R = alkyl, aryl; X = halogen, OH, OR, O_2CR, O_2PR_2) show a strong tendency to self-associate when the substituent X contains an electronegative atom or group.[1,2] The degree and strength of the self-association is governed by the steric demand of the organic groups and by the donor strength of the substituent X. Thus, the combination of reasonably small organic groups and strong donors gives rise to the formation of strong coordination polymers, typical examples being Ph_3SnF (**1**)[3–5] and $Ph_3SnO_2PPh_2$ (**2**)[6–9] (Scheme 1). The geometry of the tin atoms in these polymers comprises trigonal bipyramids, in which the organic groups are situated in the equatorial positions and the electronegative substituents X occupy the apical positions, where they link adjacent tin atoms. Despite the fact that coordination polymers of the type R_3SnX (R = alkyl, aryl; X = halogen, OH, OR, O_2CR, O_2PR_2) are numerous, there are only a few examples, such as $(Me_3SnCl)(Me_3SnTaF_6)$,[10] $(Me_3SnNH_2)(Me_3SnCl)_2$,[11] $(Me_3SnOH)(Me_3SnN_3)$[12,13] and $(Me_3SnOH)(Me_3SnNCO)$,[14] in which different electronegative substituents X are present within the same polymer. Thus, the aim of this study was to develop a strategy for the preparation of a coordination polymer with mixed donors, namely $[(Ph_3SnF)_2(Ph_3SnO_2PPh_2)]$ (**3**), which may be regarded as a derivative of the parent compounds **1** and **2** (Scheme 1).

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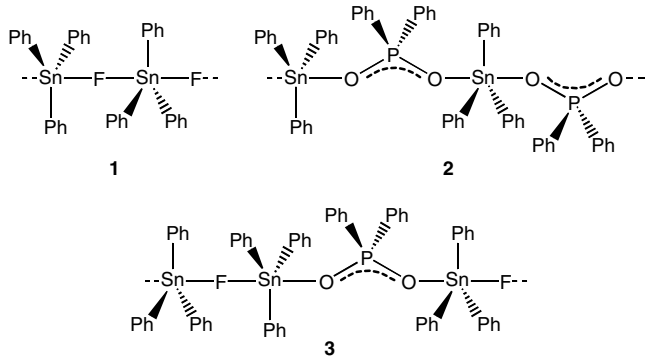
Contract/grant sponsor: ARC.

DISCUSSION

The equimolar reaction of hexaphenyldistannoxane (or two equivalents of Ph_3SnOH)[15] with triflic acid in MeCN afforded a clear solution, which presumably consists of solvated and dissociated $[Ph_3SnOHSnPh_3](O_3SCF_3)$. Notably, attempts to isolate this compound by removal of the solvent led to partial phenyl group cleavage and formation of the dimeric tetraorganodistannoxane $[Ph_2(HO)SnOSn(O_3SCF_3)Ph_2]_2$ in modest yield.[15] The subsequent addition of one equivalent of diphenylphosphinic acid to this solution provided the crystalline $[Ph_3SnOPPh_2OSnPh_3](O_3SCF_3)$ (**4**) in high yield:

$$Ph_3SnOSnPh_3 + F_3CSO_3H + Ph_2PO_2H \xrightarrow[-H_2O]{MeCN} \underset{\mathbf{4}}{[Ph_3SnOPPh_2OSnPh_3](O_3SCF_3)} \quad (1)$$



Scheme 1.

The crystal structure of **4** contains an alternating sequence of loosely associated $[Ph_3SnOPPh_2OSnPh_3]^+$ cations and triflate anions (ion pairing), whose symmetry translation gives rise to the formation of a weak one-dimensional coordination polymer that proceeds in the direction of the crystallographic *c*-axis (symmetry operation: a $= x, 1.5 - y, 0.5 + z$) as shown in Fig. 1; selected bond parameters are collected in Table 1. The $[Ph_3SnOPPh_2OSnPh_3]^+$ cation consists of two crystallographically independent, albeit similar, triphenyltin moieties with pentacoordinated tin atoms that adopt distorted trigonal bipyramidal geometries (4 + 1 coordination) defined by equatorial carbon atoms and apical oxygen atoms (geometrical goodness:[16] $\Delta\sum(\theta)$ 79.7 for Sn1 and $\Delta\sum(\theta)$ 77.2 for Sn2, where $\Delta\sum(\theta) = \sum(\theta_{eq}) - \sum(\theta_{ax})$; 0°(tetrahedron) $\leq \Delta\sum(\theta) \leq$ 90°(trigonal bipyramid)). The degree of distortion is evidenced in the different Sn–O distances (2.150(2) and 2.464(2) Å for Sn1 and 2.111(2) and 2.515(2) Å for Sn2) and bond orders[16–18] calculated thereof (0.61 and 0.22 for Sn1 and 0.70 and 0.19 for Sn2, where the bond order BO $= 10^{-\Delta d \times 1.41}$, and $\Delta d = d - d_{ref}$ with $d_{ref} = 2.00$ for Sn–O). The P–O bond lengths are almost identical (1.511(2) and 1.516(2) Å), suggesting an equal charge distribution for O1 and O2 and that the geometry differences of Sn1 and Sn2 may originate from crystal packing or, alternatively, arise from steric hindrance within the cation. Consistent with the two crystallographically independent tin sites, the ^{119}Sn magic angle spinning (MAS) NMR spectrum of **4** recorded at 149.05 MHz with an MAS frequency of 9.5 kHz, reveals two signals at δ −204.9 and −215.7 that are accompanied by sets of spinning sidebands, indicative for large shielding anisotropies (SAs). A tensor analysis according to the method of Herzfeld and Berger was performed and the results collected in Table 2.[19,20] The ^{31}P MAS NMR spectrum of **4** shows a signal at δ 29.6. The IR spectrum (KBr) of **4** displays absorptions at 1129 and 1038 cm^{-1}, which were tentatively assigned to the asymmetric and symmetric PO_2 stretching vibrations.[6–9] IR spectroscopy also confirmed the association of the triflate anions (C_s symmetry) with the $[Ph_3SnOPPh_2OSnPh_3]^+$ cations in the solid state by revealing two absorptions for the asymmetric SO_3 stretching vibration at 1300 and 1218 cm^{-1}.[23,24] For non-coordinating triflate anions (C_{3v} symmetry) this vibration is expected to be doubly degenerate, giving rise to only one absorption at approximately 1273 cm^{-1}, as reported for $Bu_4N(O_3SCF_3)$.[21,22] The symmetric SO_3 stretching vibration was observed at 1024 cm^{-1}.

Compound **4** exhibits good solubility in organic solvents such as $CHCl_3$, tetrahydrofuran (THF) or MeCN. The ^{119}Sn NMR spectrum of **4** in MeCN-d_3 exhibits a reasonably sharp doublet centred at δ −212.0 with a $^2J(^{119}Sn–O–^{31}P)$ coupling of 145 Hz and the ^{31}P NMR spectrum in MeCN-d_3 shows a singlet at δ 26.2 with unresolved tin satellites indicative for a $^2J(^{31}P–O–^{117/119}Sn)$ coupling of 140 Hz. The ^{119}Sn NMR spectrum of **4** in $CDCl_3$ shows

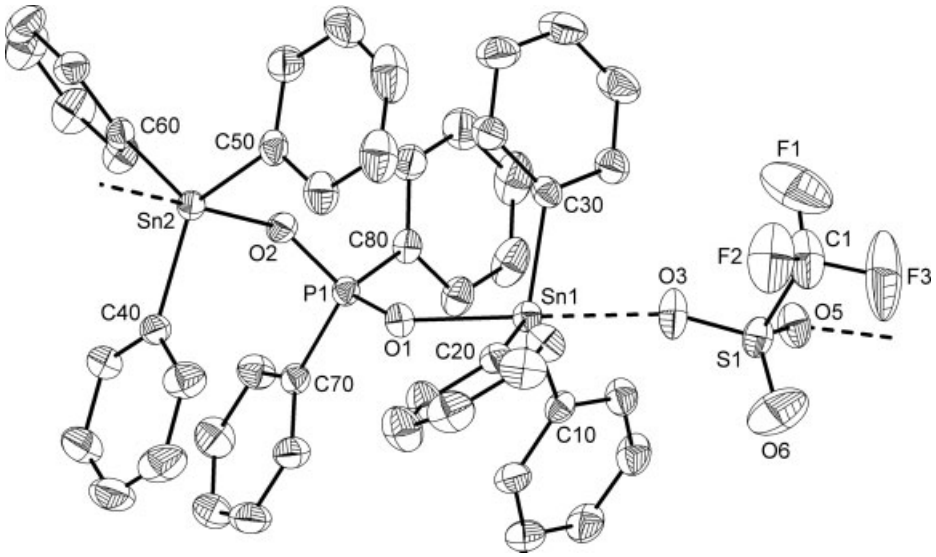


Figure 1. General view of **4** showing 30% probability displacement ellipsoids and the atom numbering scheme.

Table 1. Selected bond lengths (Å) and bond angles (°) for **4**[a]

Sn1–O1	2.150(2)	Sn1–O3	2.464(2)
Sn1–C10	2.109(2)	Sn1–C20	2.127(2)
Sn1–C30	2.100(2)	Sn2–O2	2.111(2)
Sn2–O5[a]	2.515(2)	Sn2–C40	2.110(2)
Sn2–C50	2.107(2)	Sn2–C60	2.111(2)
P1–O1	1.511(2)	P1–O2	1.516(2)
P1–C70	1.790(2)	P1–C80	1.787(2)
O1–Sn1–O3	178.72(6)	O1–Sn1–C10	92.26(7)
O1–Sn1–C20	90.63(7)	O1–Sn1–C30	96.47(8)
O3–Sn1–C10	88.15(8)	O3–Sn1–C20	88.10(8)
O3–Sn1–C30	84.38(8)	C10–Sn1–C20	116.98(8)
C10–Sn1–C30	119.30(9)	C20–Sn1–C30	122.82(9)
O2–Sn2–O5[a]	179.47(6)	O2–Sn2–C40	95.10(8)
O2–Sn2–C50	94.70(8)	O2–Sn2–C60	91.69(7)
O5[a]–Sn2–C40	84.37(8)	O5[a]–Sn2–C50	85.52(7)
O5[a]–Sn2–C60	88.62(7)	C40–Sn2–C50	122.9(1)
C40–Sn2–C60	115.86(9)	C50–Sn2–C60	119.9(1)
O1–P1–O2	114.2(1)	O1–P1–C70	108.2(1)
O1–P1–C80	110.8(1)	O2–P1–C70	109.4(1)
O2–P1–C80	107.0(1)	C70–P1–C80	107.0(1)
Sn1–O1–P1	138.64(9)	Sn2–O2–P1	140.7(1)

[a] Symmetry operation used to generate equivalent atoms: a = x, 1.5 − y, 0.5 + z.

a significantly broader signal at δ −162.0 ($W_{1/2}$ = 400 Hz). The ^{119}Sn NMR chemical shift difference of 50 ppm, as well as the different linewidth of the signals, is consistent with (i) an electrolytic dissociation of **4** into solvated $[Ph_3SnOPPh_2OSnPh_3]^+$ cations and triflate anions, whereby the tin atoms are strongly coordinated by MeCN and (ii) a weak association of the $[Ph_3SnOPPh_2OSnPh_3]^+$ cations and triflate anions in $CDCl_3$ (ion pairing). A conductivity measurement of **4** in MeCN ($\Lambda = 116\ S\ cm^2\ mol^{-1}$) agrees with this interpretation by confirming the presence of considerable amounts of electrolyte in solution.[25] Furthermore, the electrospray mass (ES) spectrum of **4** in MeCN (cone voltage 50 V, positive mode) shows an intense mass cluster at 917.1 Da that is unambiguously assigned to the $[Ph_3SnOPPh_2OSnPh_3]^+$ cation. The same spectrum also shows two less intense mass clusters at 351.0 Da and 1483.2 Da, which were assigned respectively to the cations $[Ph_3Sn]^+$ and $[Ph_3Sn(OPPh_2OSnPh_3)_2]^+$ presumably related to **4** by autoionization.[26]

The equimolar reaction of $[Ph_3SnOPPh_2OSnPh_3](O_3SCF_3)$ (**4**) and $Bu_4N[Ph_3SnF_2]$ (**5**)[4,22] in THF provided $[(Ph_3SnF)_2(Ph_3SnO_2PPh_2)]$ (**3**) as an amorphous high-melting-point material in almost quantitative yields

$$\underset{\mathbf{4}}{[Ph_3SnOPPh_2OSnPh_3](O_3SCF_3)} + \underset{\mathbf{5}}{Bu_4N[Ph_3SnF_2]} \xrightarrow[-Bu_4N(O_3SCF_3)]{THF} \underset{\mathbf{3}}{[(Ph_3SnF)_2(Ph_3SnO_2PPh_2)]} \quad (2)$$

Like its parent compounds, Ph_3SnF (**1**)[3–5] and $Ph_3SnO_2PPh_2$ (**2**),[6–9] $[(Ph_3SnF)_2(Ph_3SnO_2PPh_2)]$ (**3**) is virtually insoluble in common organic solvents at room temperature. The characterization of **3** was achieved mainly by ^{119}Sn, ^{31}P and ^{19}F MAS NMR spectroscopy and comparison of the results with those of the parent compounds **1** and **2**, as well as with the starting materials **4** and **5** (Table 2). The ^{119}Sn MAS NMR spectrum of Ph_3SnF (**1**), already reported and discussed by Harris and co-workers,[21] reveals a triplet centred at δ −211.9 with a $^1J(^{119}Sn-^{19}F)$ coupling of 1530 Hz, and is entirely consistent with the crystal structure determined by Tudela *et al*.[5] A sample of Ph_3SnF (**1**) prepared for this study according to the method of Gingras[4] and investigated by ^{119}Sn MAS NMR was consistent with these results. However, the ^{19}F MAS NMR of the same sample shows a reasonably sharp signal at δ −119.9 (integral 20%) and a broad signal at δ −146.3 (integral 80%). X-ray powder diffraction data collected for this material were consistent with the simulated data from the single-crystal X-ray experiment.[5] Since the crystal structure shows only one type of independent fluorine site, the major signal (δ −146.3) is tentatively assigned to crystalline Ph_3SnF and the minor signal (δ −119.9) to amorphous Ph_3SnF. Alternatively, the signal at δ −119.9 may be assigned to a small amount of amorphous KF, which might be adsorbed on the Ph_3SnF. This idea is supported by the reported ^{19}F NMR chemical shift of KF adsorbed on alumina (δ −115).[27] The second parent compound, $Ph_3SnO_2PPh_2$ (**2**), prepared by condensation of Ph_3SnOH and Ph_2PO_2H

Table 2. Solid-state ^{119}Sn, ^{31}P and ^{19}F NMR parameters of **1**–**5**[a]

Compound	^{119}Sn MAS δ_{iso}	ζ	η	σ_{11}	σ_{22}	σ_{33}	^{31}P MAS δ_{iso}	^{19}F MAS δ_{iso}
Ph_3SnF (**1**)	−198.1[b]	−306	0.0	351	351	−108		−119.9, −146.3[c]
	−211.9	−255	0.0	340	340	−43		
	−225.5	−188	0.0	321	321	37		
$Ph_3SnO_2PPh_2$ (**2**)	−283.3						17.4, 16.4, 15.9	
	−290.8[d]						15.1, 12.7[e]	
$[(Ph_3SnF)_2(Ph_3SnO_2PPh_2)]$ (**3**)	−225						28.2	−76.6
	−260[f]						17.7[g]	−137.2, −143.9[h]
$[Ph_3SnOPPh_2OSnPh_3](O_3SCF_3)$ (**4**)	−204.9[i]	−258	0.2	360	308	−53	29.6	
	−215.7	−226	0.2	351	306	−10		
$Bu_4N[Ph_3SnF_2]$ (**5**)	−348.8[j]	−277	0.2	515	459	72		−158.5, −164.2[k]
	−362.7	−223	0.0	474	474	140		
	−376.5	−158	0.2	471	440	219		

[a] δ_{iso} (ppm) $= -\sigma_{iso} = -(\sigma_{11} + \sigma_{22} + \sigma_{33})/3$; ζ (ppm) $= \sigma_{33} - \sigma_{iso}$ and $\eta = |\sigma_{22} - \sigma_{11}|/|\sigma_{33} - \sigma_{iso}|$, where σ_{11}, σ_{22} and σ_{33} (ppm) are the principal tensor components of the chemical SA, sorted as follows: $|\sigma_{33} - \sigma_{iso}| > |\sigma_{11} - \sigma_{iso}| > |\sigma_{22} - \sigma_{iso}|$.
[b] Components of a triplet ($^1J(^{119}Sn-\ ^{19}F) = 1530$ Hz);[21] ^{119}Sn data obtained at 111.9 MHz.
[c] Two signals with an integral ratio of 20:80.
[d] At least two overlapping signals; no tensor analysis was performed.
[e] At least five overlapping signals.
[f] ^{119}Sn data obtained at 37.3 MHz with a rotor synchronized Hahn echo.
[g] Two signals with an integral ratio of 7 : 93; first signal is presumably due to compound **4**.
[h] Three signals with integral ratio of 8 : 32 : 60; the first signal is tentatively assigned to a triflate group.
[i] Integral 50 : 50; two crystallographically independent sites.
[j] Components of a triplet ($^1J(^{119}Sn-\ ^{19}F) = 1971$ Hz);[22] ^{119}Sn data obtained at 149.2 MHz.
[k] Integral 50 : 50; two crystallographically independent sites.

according to a literature procedure,[9] has not previously been investigated by solid-state NMR spectroscopy or X-ray crystallography. The ^{119}Sn MAS NMR spectrum of **2**, recorded at 149.05 MHz with an MAS frequency of 8 kHz, was of insufficient quality for a tensor analysis, but it reveals at least two overlapping signals at δ −283.3 and −290.8 and two accompanying sets of spinning sidebands. The ^{31}P MAS NMR spectrum of **2** shows at least five overlapping signals at δ 17.4, 16.4, 15.9, 15.1 and 12.7, indicative for a number of magnetically inequivalent phosphorus sites. The ^{119}Sn MAS NMR spectrum of $[(Ph_3SnF)_2(Ph_3SnO_2PPh_2)]$ (**3**), recorded at 111.89 MHz with an MAS frequency of 13 kHz, displays a broad signal ($W_{1/2} = 4500$ Hz) around δ −220 with one spinning side band on each side. When recorded at a lower field (37.3 MHz) using an MAS synchronized Hahn echo (45°–τ–90°–τ–acq.–recycling delay, $\tau = 80$ µs and $\nu_{MAS} = 12\,500$ Hz), the ^{119}Sn MAS NMR spectrum shows two narrower ($W_{1/2} = 1000$ Hz) overlapping isotropic resonances, at −225 (integral 38%) and −260 ppm (integral 62%), with no spinning sideband. These two signals can be assigned to the environments expected in **3**, i.e. F–Sn–F and F–Sn–$OPPh_2O$. The one at higher frequency (δ −225) is similar to the isotropic chemical shift of Ph_3SnF (**1**) and can be assigned to the F–Sn–F sites. No signal is observed around δ −350, which indicates the absence of $Bu_4N[Ph_3SnF_2]$ (**5**). The ^{31}P MAS NMR spectrum of **3** shows a signal of high intensity at δ 17.7 (integral 93%), which is assigned to a phosphorus site having an Sn–$OPPh_2O$–Sn environment. This assignment is supported by the observation of similar ^{31}P NMR chemical shifts for $Ph_3SnO_2PPh_2$ (**2**). Also present in the ^{31}P MAS NMR spectrum of **3** is a minor signal at δ 28.2 (integral 7%), which is reminiscent of the starting material **4** and could indicate the presence of a small amount of such compound. The ^{19}F MAS NMR spectrum of $[(Ph_3SnF)_2(Ph_3SnO_2PPh_2)]$ (**3**) shows two intense overlapping signals at δ −143.9 and −137.2 (integral 60% and 32% respectively) that are assigned to magnetically inequivalent fluorine sites in an Sn–F–Sn environment. This assignment is supported by the ^{19}F chemical shift of δ −146.3 assigned to crystalline Ph_3SnF (**1**). The two observed chemical shifts, which differ only by 6.7 ppm, most likely correspond to very similar environments, as such a chemical shift difference is also observed for the two non-equivalent yet very similar fluorine sites of $Bu_4N[Ph_3SnF_2]$ (**5**). A minor signal at δ −76.6 (integral 8%) is also observed and tentatively assigned to a triflate anion, supporting the idea that a small amount of the starting material **4** is present. Given the data at hand, $[(Ph_3SnF)_2(Ph_3SnO_2PPh_2)]$ (**3**) appears to have a regular structure with an alternating sequence of two Ph_3SnF groups and one $Ph_3SnO_2PPh_2$ group, rather than a random structure involving longer—$[Ph_3SnOPPh_2O]_n$– and –$[Ph_3SnF]_n$– sequences.

EXPERIMENTAL

All solvents were dried over the appropriate desiccants and distilled prior to use. Ph_3SnF (**1**),[4] $Ph_3SnO_2PPh_2$ (**2**),[9] and $Bu_4N[Ph_3SnF_2]$ (**5**)[22] were prepared according to literature procedures. The solution ^{119}Sn and ^{31}P NMR spectra were measured using a Jeol Eclipse Plus 400 spectrometer and were referenced to Me_4Sn and H_3PO_4 respectively. The ^{119}Sn, ^{31}P MAS NMR spectra were obtained using the same spectrometer equipped with a 6 mm rotor or with a Bruker Avance 300 spectrometer equipped with a 4 mm rotor. A ^{119}Sn rotor synchronized Hahn echo was also recorded on a Bruker ASX 100 spectrometer equipped with a 4 mm probe. ^{19}F MAS NMR was performed on a Bruker ASX 300 spectrometer equipped with a 4 mm probe. ^{119}Sn, ^{31}P and ^{19}F solid-state chemical shifts are referenced to Me_4Sn, 85% H_3PO_4 and $CFCl_3$, using secondary external references: *c*-Hex_4Sn (δ −97.35), $NH_4(H_2PO_4)$ (δ 0.95) and C_6F_6 (δ −164.9). The ES mass spectra were obtained with a Platform II single quadrupole mass spectrometer (Micromass, Altrincham, UK) using an acetonitrile mobile phase. Acetonitrile solutions (0.1 mM) were injected directly into the spectrometer via a Rheodyne injector equipped with a 50 µl loop. A Harvard 22 syringe pump delivered the solutions to the vaporization nozzle of the ES ion source at a flow rate of 10 µl min^{-1}. Nitrogen was used as both a drying gas and for nebulization, with flow rates of approximately 200 ml min^{-1} and 20 ml min^{-1} respectively. Pressure in the mass analyser region was usually about 4×10^{-5} mbar. IR spectra of KBr pellets of the samples were collected using a BioRad FTIR spectrometer. The conductivity measurement was performed using a CDM80 conductivity meter equipped with CDC104 conductivity cell (Radiometer Copenhagen, Denmark) at 25 °C. Microanalyses were carried out by CMAS, Belmont, Australia.

Synthesis of $[Ph_3SnOPPh_2OSnPh_3](O_3SCF_3)$ (4)

Triflic acid (150 mg, 1.00 mmol) was added slowly via syringe to a suspension of $Ph_3SnOSnPh_3$ (716 mg, 1.00 mmol) in acetonitrile (30 ml) to give a clear solution after 5 min stirring at room temperature. Solid Ph_2PO_2H (218 mg, 1.00 mmol) was added in small portions that dissolved immediately. The mixture was stirred for 30 min at 60 °C before the solvent was removed in vacuum. The residue was recrystallized from hexane–CH_2Cl_2, providing colourless crystals of **4** (989 mg, 0.927 mmol, 93%, m.p. 226 °C). ^{31}P NMR (MeCN-d_3) δ: 26.2 ($^2J(^{31}P–O–^{119/117}Sn) = 140$ Hz). ^{119}Sn NMR (MeCN-d_3) δ: −212.0 ($^2J(^{119}Sn–O–\ ^{31}P) = 145$ Hz). Conductivity measurement: 384 µS cm^{-1}; $c = 3.3$ mmol l^{-1}. IR (KBr, cm^{-1}): 3070 m, 3051 m, 3029 m, 1481 m, 1431 s, 1300 s, 1262 m, 1218 vs, 1184 m, 1129 s, 1113 vs, 1078 m, 1038 sh, 1024vs, 996 m, 729 s, 693 s, 632 m, 560 m, 539 m, 452 m. Anal. Found: C, 55.15; H, 3.73. Calc. for $C_{49}H_{40}F_3O_5PSSn_2$ (1066.36): C, 55.19; H, 3.78%.

Synthesis of $[(Ph_3SnF)_2(Ph_3SnO_2PPh_2)]$ (3)

A solution of $Bu_4N[Ph_3SnF_2]$ (315 mg, 0.500 mmol) in THF (15 ml) was quickly added to a magnetically stirred solution of **4** (533 mg, 0.500 mmol) in THF (15 ml) at room temperature. Immediately, a colourless precipitate was formed that, after 30 min of stirring, was filtered and washed with THF (2×10 ml). Air drying for 1 h gave **3** (620 mg, 0.475 mmol, 95%, m.p. 327 °C dec.). Anal. Found: C, 60.79; H, 4.25. Calc. for $C_{66}H_{55}F_2O_2PSn_3$ (1305.34): C, 60.73; H, 4.25%.

Crystallography

Single crystals of $[Ph_3SnOPPh_2OSnPh_3](O_3SCF_3)$ (**4**) suitable for X-ray crystallography were obtained by slow evaporation of a CH_2Cl_2–hexane solution of the compound. Crystal data and structure solution at $T = 293(2)$ K: $C_{49}H_{40}F_3O_5PSSn_2$, $M = 1066.36$, orthorhombic, *Pbca*, crystal dimensions: $0.30 \times 0.35 \times 0.45$ mm^3, $a = 20.319(2)$, $b = 19.014(2)$, $c = 23.236(3)$ Å, $V = 8977.2(18)$ Å^3, $Z = 8$, $D_{calcd} = 1.578$ Mg m^{-3}, $\mu = 1.254$ mm^{-1}. Intensity data were collected on Bruker SMART Apex CCD diffractometer fitted with Mo Kα radiation (graphite crystal monochromator, $\lambda = 0.71073$ Å) to a maximum of $\theta_{max} = 27.6°$ via ω scans. Data were reduced and corrected for absorption using the programs SAINT and SADABS.[28] The structure was solved by direct methods and difference Fourier synthesis using SHELX-97 implemented in the program WinGX 2002.[29] The weighting scheme employed was of the type $w = [\sigma^2(F_o^2) + (0.0427P)^2]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. $R_1 = 0.029$ for 8543 [$I > 2\sigma(I)$] reflections and $wR_2 = 0.077$ for 10 319 independent reflections. CCDC deposition number: 227 967.

Acknowledgements

We are grateful to the French Embassy in Yarralumla, ACT 2600, Australia, for a travel grant (F. R.) and to the ARC for a Linkage Grant (D. D.). Dr Jonathan White (The University of Melbourne) is thanked for the X-ray crystallography data collection.

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