

Formation of 3-Sulfanylcoumarins by SnPh_3OH -Promoted Cyclization of 3-Aryl-2-Sulfanylpropenoic Acids

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Reaction of SnPh_3OH with 3-(2-hydroxyphenyl)sulfanylpropenoic acid [$\text{H}_2(\text{o-hpspa})$] yielded $[\text{SnPh}_3(\text{SC})]$, where SC is deprotonated 3-sulfanylcoumarin (3-sulfanyl-2H-1-benzopyran-2-one, HSC), by a cyclization process. Similarly, when 3-(2-hydroxy-5-bromophenyl)- and 3-(2-hydroxy-3,5-dibromophenyl)-2-sulfanylpropenoic acids were treated with the same tin hydroxide, the cyclization resulted in $[\text{SnPh}_3(\text{BrSC})]$ and $[\text{SnPh}_3(\text{Br}_2\text{SC})]$, where BrSC and Br_2SC are the new ligands formed from the deprotonation of 3-sulfanyl-6-bromocoumarin and 3-sulfanyl-6,8-dibromocoumarin, respectively.

The new compounds were characterized by elemental analysis, multinuclear NMR (^1H , ^{13}C and ^{119}Sn) and vibrational spectroscopy, and mass spectrometry. Single-crystal X-ray structures of these complexes all showed that the tin atom is surrounded by three phenyl C atoms and the S and O atoms of the bidentate ligand in a distorted trigonal-bipyramidal environment.

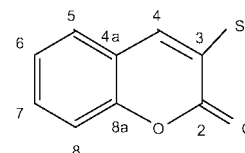
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Introduction

In previous work,^[1] treatment of 3-(phenyl)-2-sulfanylpropenoic acid (H_2pspa) with SnPh_3OH in the presence of diisopropylamine afforded the compound $[\text{Q}][\text{SnPh}_3(\text{pspa})]$ (Q = diisopropylammonium), which showed antibacterial activity against *Staphylococcus aureus* and, although minor, against *Escherichia coli*. In an effort to synthesize a more soluble product with similar activity we have now prepared the 3-(2-hydroxyphenyl)-2-sulfanylpropenoic acid [$\text{H}_2(\text{o-hpspa})$]. However, reaction of this compound with SnPh_3OH yielded the unexpected complex $[\text{SnPh}_3(\text{SC})]$, where SC is deprotonated 3-sulfanylcoumarin. Formation of the same product in the absence of diisopropylamine showed that the amine played no role in the reaction.

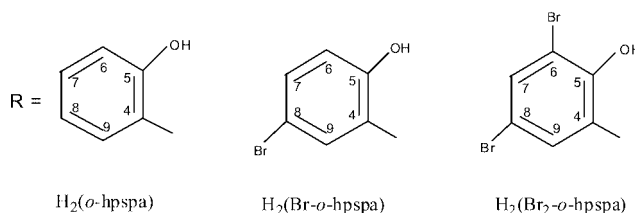
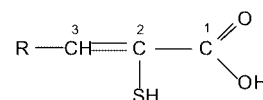
Coumarin (1,2-benzopyrone, Scheme 1) is a natural product present in plants with widespread use in foodstuffs and cosmetic products. Furthermore, this substance is used in medicine as an anticoagulant. Coumarin derivatives (in par-

ticular those substituted at positions 3 or 4 of the pyrone cycle), have bacteriostatic and rodenticide applications.^[2–4]



Scheme 1.

The synthesis of 3-sulfanylcoumarin had been previously carried out by Shi et al.^[5] by reacting 5-(*o*-hydroxybenzylidene)rhodanine with hydrazine hydrate in EtOH at 80 °C. In this paper, we describe the formation of tin(IV) complexes containing this deprotonated species as well as its 6-

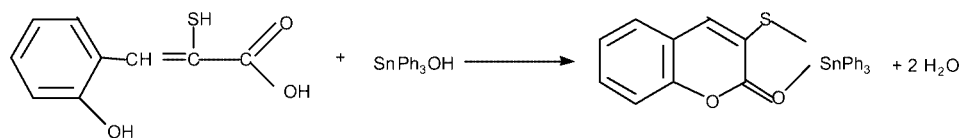


Scheme 2.

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Scheme 3.

bromo- and 6,8-dibromo derivatives which resulted from the cyclization of 2-sulfanylpropenoic acids (Scheme 2), together with their structural study by means of X-ray diffraction and characterisation by vibrational and NMR spectroscopy. We chose Br-substituted derivatives in an effort to examine the influence of relatively bulky and electronegative atoms in the aromatic moiety of the acids on the cyclization process.

Results and Discussion

Synthesis of [SnPh₃(L)] (L = SC, BrSC, Br₂SC)

The reaction of the complex formation is shown in Scheme 3.

In the Experimental Section we describe the reactions carried out with excess SnPh₃OH. Besides these conditions, the reaction was also explored in a 1:1 mol ratio of reactants in the presence and absence of diisopropylamine in EtOH solution. In all cases, the solid isolated was determined to be the same sulfanylcoumarin derivative.

The reactions of H₂(Br₂-*o*-hpspa) with Zn(OAc)₂, Cd(OAc)₂, Pb(OAc)₂ and SnR₂O (R = Me, Et, Bu, Ph) were also explored. In all cases, the solids isolated have stoichiometries corresponding to the 3-aryl-2-sulfanylpropenoic acid derivatives. For example, the reaction of H₂(Br₂-*o*-hpspa) with SnMe₂O afforded a solid with the analytical data C 26.4, H 1.9, S 6.3%; [SnMe₂(Br₂-*o*-hpspa)] requires C 26.4, H 2.0, S 6.4%, while [SnMe₂(SC)₂] requires C 29.3, H 1.5, S 7.8%. Further work to elucidate the role of the metal in the cyclization process is in progress. In order to explore the behaviour of [SnPh₃(SC)] in acidic medium, HOCCF_{3(aq.)} was used as a proton source; no formation of free sulfanylcoumarin was detected.

Crystal Structures

[SnPh₃(SC)]

Tin Coordination Sphere

Figure 1 shows the structure of the compound and the numbering scheme, and Table 1 lists the significant bond lengths and angles. The tin atom is coordinated to three phenyl C atoms and to the S and O donor atoms of the SC ligand, which results a distorted trigonal-bipyramidal environment in which O(1) and C(11) are apical. The equatorial C atoms are closer to Sn than the apical carbon, as expected in this type of polyhedron; i.e. for the apical C atom: Sn–C(11) = 2.154(3) Å, for the equatorial C atoms: Sn–C(21) = 2.137(3), Sn–C(31) = 2.131(3) Å – all three are

within the range of 2.12–2.18 Å reported for other triphenyltin compounds.^[6] On the other hand, the Sn–S bond length [2.4691(10) Å] is slightly greater than the sum of the covalent radii of tin and sulphur atoms (2.42 Å),^[7] but within the range reported for triphenyltin thiolates (2.405–2.481 Å).^[6,8–10] The most remarkable bond length around the tin atom is the long (even for an apical position) Sn–O distance [2.589(2) Å], which is greater than the sum of their covalent radii (2.13 Å),^[7] though smaller than the sum of their van der Waals radii (3.70 Å)^[7] and in the range that has confidently been reported to indicate Sn–O bonding.^[11] This long bond length denotes a weak interaction between these atoms and is in line with the short C–O distance of 1.215(4) Å, indicating that the C=O bond is only slightly altered upon coordination [*d*(C=O) = 1.20 Å].^[7]

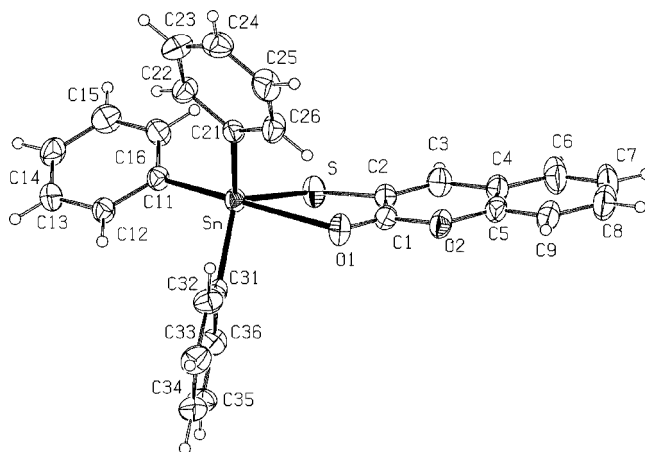


Figure 1. Displacement ellipsoid plot for [SnPh₃(SC)] with the atom numbering scheme. Ellipsoids at 30% probability.

The bond angles around the metal atom are indicative of the distortion from the regular trigonal-bipyramidal geometry. Thus, for instance, C(11)–Sn–S = 95.36(9)°, C(31)–Sn–C(11) = 105.09(12)° and C(21)–Sn–C(11) = 105.23(12)° (instead of 90°); C(31)–Sn–C(21) = 113.77(13)°, C(31)–Sn–S = 115.41(9)° and C(21)–Sn–S = 118.47(9)° (instead of 120°). The bond angles involving the two donor atoms of the sulfanylcoumarin ligand have values quite different from that expected for a regular polyhedron, namely: C(31)–Sn–O(11) = 78.01(10)°, C(21)–Sn–O(11) = 83.50(11)° and, specially, S–Sn–O(1) = 73.08(6)°, which are considerably narrower than the theoretical 90° angle because of the bite of the SC ligand. Nevertheless, according to Addison's τ -criterion,^[12] (τ = 0.83) we can state that the coordination polyhedron is much closer to a trigonal bipyramid (τ = 1) than to a square pyramid (τ = 0).

The general features of the tin kernel are similar to those found in triphenyltin sulfanylcarboxylates,^[1] in which an

Table 1. Selected bond lengths [Å] and angles [°] for the prepared complexes with estimated standard deviations in parentheses.

	[SnPh ₃ (SC)]	[SnPh ₃ (BrSC)]·EtOH	[SnPh ₃ (Br ₂ SC)]
Sn–C(31)	2.131(3)	2.124(4)	2.143(7)
Sn–C(21)	2.137(3)	2.123(4)	2.129(7)
Sn–C(11)	2.154(3)	2.146(4)	2.170(7)
Sn–S	2.4691(10)	2.4540(10)	2.470(2)
Sn–O(1)	2.589(2)	2.784(3)	2.666(5)
S–C(2)	1.758(3)	1.751(4)	1.750(7)
O(1)–C(1)	1.215(4)	1.205(4)	1.200(8)
C(31)–Sn–C(21)	113.77(13)	118.56(14)	119.7(3)
C(31)–Sn–C(11)	105.09(12)	106.26(14)	103.9(3)
C(21)–Sn–C(11)	105.23(12)	108.64(14)	105.9(3)
C(31)–Sn–S	115.41(9)	112.17(11)	115.8(2)
C(21)–Sn–S	118.47(9)	115.47(10)	112.78(18)
C(11)–Sn–S	95.36(9)	91.76(10)	94.25(19)
C(31)–Sn–O(1)	78.01(10)	77.56(12)	81.9(2)
C(21)–Sn–O(1)	83.50(11)	83.74(12)	80.5(2)
C(11)–Sn–O(1)	168.04(11)	161.95(11)	167.0(2)
S–Sn–O(1)	73.08(6)	70.73(6)	72.77(12)
C(2)–S–Sn	105.87(13)	108.49(12)	107.4(2)
C(1)–O(1)–Sn	116.7(2)	113.3(2)	115.7(5)

SCCO donor fragment is also present; the main difference lies in the Sn–O bond length, which is longer in this case.

The SC Ligand

The C–C (1.44–1.46 Å) and C–O [1.354(4), 1.382(4) Å] bond lengths are as expected for a single bond between sp² carbon atoms, except for the C(12)–C(13) [1.345(5) Å] and C(1)–O(1) [1.215(4) Å] lengths which indicate some double bond character.

[SnPh₃(BrSC)]·EtOH and [SnPh₃(Br₂SC)]

The type of coordination and the bond lengths involving the tin atom are similar to those discussed above for [SnPh₃(SC)]. As seen in Table 1, the bond lengths around the metal atom are almost identical in all three compounds. The only noticeable difference in the metrical data of these complexes is the Sn–O bond length. Even though the Sn–O bond lengths are quite different [2.589(2), 2.784(3) and 2.666(5) Å], we can conclude that the presence of one or two Br atoms on the phenyl ring of the SC ligand does not induce any significant change in the molecular structure of the complex.

Spectroscopic Studies

The vibrational patterns of the complexes have been analysed in light of their structural study by X-ray diffraction. Thus, the position of $\nu(\text{C}=\text{O})$ is consistent with the weak Sn–O bond, which is close to that found in inclusion complexes^[13] in which a coumarin ligand is hydrogen-bonded via this group. The band at 360 cm^{−1}, present in both IR and Raman spectra and attributable to $\nu(\text{Sn}–\text{S})$, is consistent with the coordination via the S atom, and $\nu_{\text{asym}}(\text{Sn}–\text{C})$ and $\nu_{\text{sym}}(\text{Sn}–\text{C})$ vibrations are located at positions typical of a non-planar SnC₃ framework.^[1,14]

The ¹H NMR spectra agree with the evolution associated with the cyclization and deprotonation processes. For in-

stance, carboxylic acid signal found in the spectra of the parent sulfanylpropenoic acids (between 13 and 11 ppm) is absent in the spectra of the tin derivatives due to cyclization. In addition, no signal attributable to the SH proton is observed in the spectra of any of these complexes. The ¹³C NMR spectra for these complexes are consistent with those for other 3-substituted, 6-bromo-3-substituted or 6,8-dibromo-3-substituted coumarins.^[15]

The ¹¹⁹Sn NMR spectra show a singlet at about −101 ppm. This value for the chemical shift falls in the range proposed for a tetra-coordinated tin centre,^[16,17] which seems to indicate the loss of the five-coordinate nature upon dissolution. This signal slightly shifts upfield as the temperature increases from 230 to 330 K, but no splitting occurs.

Experimental Section

Methods and Materials: Triphenyltin(IV) hydroxide, rhodanine and diisopropylamine (Aldrich-Chemie) were used as supplied. Elemental analyses were performed with a Carlo Erba 1108 apparatus. Melting points were determined using a Gallenkamp MFB-595 apparatus. The IR spectra were recorded on a Bruker IFS 66v FT-IR spectrometer, and the Raman spectra were recorded with the same spectrometer using an FRA-106 accessory. NMR spectra were recorded at room temperature in CDCl₃. ¹H and ¹³C NMR spectra were obtained with a Bruker AMX300 spectrometer operating at 300.14 and 75.48 MHz, respectively (referenced to SiMe₄). ¹¹⁹Sn NMR spectra were recorded with a Bruker AMX500 apparatus operating at 186.50 MHz (referenced to SnMe₄). Downfield shifts were taken to be positive. Mass spectra were recorded with a Kratos MS50TC spectrometer connected to a DS90 data system and operating under EI (70 eV, 250 °C) and FAB conditions (Xe, 8 eV) using as liquid matrix 3-nitrobenzyl alcohol. Crystallographic data were recorded at room temperature on a Bruker CCD Smart apparatus using Mo-K α radiation (λ = 0.71073 Å). An absorption correction was made by means of the SADABS program,^[18] and the structure solution was carried out using the SHELXS-97 program.^[19a] Least-squares full-matrix refinements on *F*² were performed using the program SHELXL97.^[19a] Reflection data for [SnPh₃(BrSC)] were corrected for the diffuse scattering as a result of disordered ethanol molecules by means of the program SQUEEZE,^[19b] and the illustrations were obtained with the PLATON package.^[19c] Crystal data, details of data collections and refinements are given in Table 2. The molecular structures of the complexes are depicted in Figure 1 and Figures S1 and S2 (Supporting Information) and show ellipsoids at 30% probability level. CCDC reference numbers 265333–265335 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of the Compounds: 3-Aryl-2-sulfanylpropenoic acids were prepared^[20] by condensation of the appropriate benzaldehyde with rhodanine, subsequent hydrolysis in NaOH (1 M) and subsequent acidification with aqueous HCl (1 M).

H₂(*o*-hpspa): From 2-hydroxybenzaldehyde (2.50 g, 10 mmol) as starting material. Colour: yellow. Yield: 1.14 g, 58%. Mp: 140 °C. IR and (Raman): 1682 vs $\nu(\text{C}=\text{O})$, 1452 s $\delta(\text{OH})$, 1264 s $\nu(\text{C}–\text{O})$, 2568 m (2568 m) $\nu(\text{S}–\text{H})$ cm^{−1}. EI (main signals): *m/z* (%) = 196 (16) [M⁺], 178 (40) [M⁺ – H₂O], 150 (100) [M⁺ – H₂O – CO], 133

Table 2. Crystal data and structure refinement for [SnPh₃(SC)], [SnPh₃(BrSC)]·EtOH and [SnPh₃(Br₂SC)].

Compound	[SnPh ₃ (SC)]	[SnPh ₃ (BrSC)]·EtOH	[SnPh ₃ (Br ₂ SC)]
Empirical formula	C ₂₇ H ₂₀ O ₂ SSn	C ₂₉ H ₂₅ BrO ₃ SSn	C ₂₇ H ₁₈ Br ₂ O ₂ SSn
Molecular weight	527.18	652.15	684.98
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1̄	<i>C</i> 2/ <i>c</i>
<i>a</i> [Å]	9.5474(3)	9.4458(10)	16.3047(16)
<i>b</i> [Å]	24.5775(8)	9.8333(11)	10.0204(10)
<i>c</i> [Å]	10.2597(3)	15.8031(17)	31.026(3)
β [°]	108.6187(10)	99.854(2)	91.607(2)
Volume [Å ³]	2281.45(12)	1397.2(3)	5067.1(9)
<i>Z</i>	4	2	8
Density calcd. [g cm ⁻³]	1.535	1.550	1.796
Absorption coefficient [mm ⁻¹]	1.233	2.446	4.267
<i>F</i> (000)	1056	648	2656
Crystal size [mm]	0.20 × 0.25 × 0.25	0.43 × 0.32 × 0.14	0.28 × 0.21 × 0.15
θ range for data collection	1.66–28.27	2.14–28.03	2.39–27.99
Limiting indices	–12 ≤ <i>h</i> ≤ 12, –30 ≤ <i>k</i> ≤ 32, –13 ≤ <i>l</i> ≤ 7	–12 ≤ <i>h</i> ≤ 12, –12 ≤ <i>k</i> ≤ 10, –20 ≤ <i>l</i> ≤ 20	–21 ≤ <i>h</i> ≤ 20, –13 ≤ <i>k</i> ≤ 13, –24 ≤ <i>l</i> ≤ 40
Reflections collected	15526	8621	14715
Reflections unique, <i>R</i>	5592 [<i>R</i> (int) = 0.0512]	6006 [<i>R</i> (int) = 0.0253]	5803 [<i>R</i> (int) = 0.0448]
Absorption correction	semi-empirical	semi-empirical	semi-empirical
Data/restrictions/parameters	5592/0/280	6006/0/283	5803/0/293
Goodness-of-fit on <i>F</i> ²	1.013	0.849	1.116
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0435 <i>wR</i> ₂ = 0.0671	<i>R</i> ₁ = 0.0359 <i>wR</i> ₂ = 0.0696	<i>R</i> ₁ = 0.0581 <i>wR</i> ₂ = 0.1211
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0892 <i>wR</i> ₂ = 0.0788	<i>R</i> ₁ = 0.0573 <i>wR</i> ₂ = 0.0743	<i>R</i> ₁ = 0.1101 <i>wR</i> ₂ = 0.1307
Largest diff. peak and hole [e Å ⁻³]	0.476 and –0.447	0.577 and –0.730	2.850 and –3.077

(5) [M⁺ – COOH], 121 (67) [M⁺ – H₂O – CO – CHO], 90 (41) [M⁺ – H₂O – 2CO – S], 77 (28) [M⁺ – H₂O – 2CO – S – CH]. The MS (FAB) spectrum shows the same signals. ¹H NMR: δ = 12.84 [br. s, 1 H, C(1)OH], 7.71 [s, 1 H, C(3)H], 10.07 [s, 1 H, C(5)OH], 6.86 [d, 1 H, C(6)H], 7.27 [1 H, C(7)H], 6.88 [d, 1 H, C(8)H], 7.67 [d, 1 H, C(9)H] ppm. ¹³C NMR: δ = 168.7 C(1), 139.0 C(2), 132.2 C(3), 120.9 C(4), 153.7 C(5), 116.1 C(6), 131.0 C(7), 123.2 C(8), 129.6 C(9) ppm. C₉H₈O₃S: calcd. C 55.1, H 4.1, S 16.3%; found C 55.6, H 3.9, S 16.1%.

H₂(Br-*o*-hpspa): From 5-bromo-2-hydroxybenzaldehyde (3.16 g, 10 mmol) as starting material. Colour: yellow. Yield: 2.56 g, 93%. Mp: 133 °C. IR and (Raman): 1677 vs ν (C=O), 1414 m δ (OH), 1278 vs ν (C–O), 2566 w (2575 m) ν (S–H) cm⁻¹. EI (main signals): *m/z* (%) = 275 (36) [M⁺ – H], 256 (100) [M⁺ – H – H₂O], 228 (97) [M⁺ – H₂O – CO], 230 (95) [M⁺ – COOH], 168 (26) [M⁺ – H₂O – 2CO – SH], 150 (44) [M⁺ – COOH – Br], 120 (54) [M⁺ – H₂O – CO – CHO – Br], 149 (98) [M⁺ – H₂O – CO – Br]. The FAB spectrum shows the same signals. ¹H NMR: δ = 9.84 [s, 1 H, C(3)H], 10.88 [s, 1 H, C(5)OH], 6.90 [d, 1 H, C(6)H], 7.94 [dd, 1 H, C(7)H], 7.66 [d, 1 H, C(9)H] ppm. ¹³C NMR: δ = 166.6 C(1)OH, 118.2 C(2)SH, 119.8 C(4), 160.1 C(5), 111.3 C(6), 139.6 C(7), 113.0 C(8), 135.5 C(9) ppm. C₉H₇BrO₃S: calcd. C 39.3, H 2.5, S 11.6%; found C 39.9, H 2.3, S 11.2%.

H₂(Br₂-*o*-hpspa): From 3,5-dibromo-2-hydroxybenzaldehyde (3.79 g, 10 mmol) as starting material. Colour: beige. Yield: 3.36 g, 95%. Mp: 120 °C. IR and (Raman): 1682 vs ν (C=O), 1448 s δ (OH), 1276 vs ν (C–O), 2565 m (2565 w) ν (S–H) cm⁻¹. EI (main signals): *m/z* (%) = 354 (25) [M⁺], 336 (80) [M⁺ – H₂O], 308 (100) [M⁺ – H₂O – CO], 279 (24) [M⁺ – H₂O – CO – CHO], 227 (46) [M⁺ – H₂O – CO – BrH], 167 (24) [M⁺ – H₂O – 2CO – SH – Br], 148 (21) [M⁺ – H₂O – CO – 2Br], 119 (52) [M⁺ – H – H₂O – 2CO – 2Br]. The FAB spectrum shows the same signals. ¹H NMR: δ = 9.81 [s, 1 H, C(3)H], 11.50 [s, 1 H, C(5)H], 7.94 [s, 1 H, C(7)H], 7.67 [d, 1 H, C(9)OH] ppm. ¹³C NMR: δ = 157.6 C(1)OH, 118.3 C(2)SH, 122.0 C(4), 160.1 C(5), 111.3 C(6), 142.4 C(7), 111.8 C(8), 135.3 C(9)

ppm. C₉H₆Br₂O₃S: calcd. C 30.5, H 1.7, S 9.0%; found C 30.7, H 1.6, S 8.8%.

[SnPh₃(SC)]: A solution of SnPh₃OH (0.40 g, 1.0 mmol) in 10 mL of an ethanol/acetone mixture (1:1 v/v) was treated with a solution of H₂(*o*-hpspa) (0.10 g, 0.5 mmol) in 10 mL of the same solvent. After stirring and refluxing for 5 h, a beige solid was formed. Yield: 0.32 g, 60%. Mp: 135 °C. IR and (Raman): 1676 s ν (C=O), 269 s ν_{asym} (Sn–C), 232 s ν_{sym} (Sn–C) 361 sh (360 w) ν (Sn–S) cm⁻¹. EI (main signals): *m/z* (%) = 528 (3) [M⁺], 351 (35) [SnPh₃], 197 (8) [SnPh], 120 (6) [Sn]. Besides these signals, the EI spectrum shows signals for H₂(*o*-hpspa) and its fragments, and the FAB spectrum shows the same metallated signals. ¹H NMR: δ = 7.91 [s, C(4)H], 7.37–7.22 [m, C(5)H–C(8)H], 7.74–7.72 (m, Ph_o), 7.41–7.38 (m, Ph_{m,p}) ppm. ¹³C NMR: δ = 162.8 C(2), 139.3 C(3), 126.5 C(4), 130.1 C(4a), 151.8 C(8a), 116.4 C(8), 126.5 C(7), 120.0 C(6), 124.9 C(5), 140.6 C_i, 136.7 C_o, 128.7 C_m, 129.3 C_p ppm. ¹¹⁹Sn NMR: δ = –100.9 (s) ppm. C₂₇H₂₀O₂SSn: calcd. C 61.5, H 3.8, S 6.1%; found C 61.4, H 3.9, S 6.0%. From the mother liquor of the reaction flask, suitable crystals for X-ray diffraction were isolated.

[SnPh₃(BrSC)]: A solution of SnPh₃OH (0.29 g, 0.8 mmol) in 10 mL of an ethanol/acetone mixture (1:1 v/v) was treated with a solution of H₂(Br-*o*-hpspa) (0.10 g, 0.4 mmol) in 10 mL of the same solvent. After refluxing for 5 h, a brown solid was formed. Yield: 0.19 g, 40%. Mp: 145 °C. IR (Raman): 1686 s ν (C=O), 261 s ν_{asym} (Sn–C), 233 s (235 w) ν_{sym} (Sn–C), 359 w (354 w) ν (Sn–S) cm⁻¹. EI (main signals): *m/z* (%) = 607 (2) [M⁺ + H], 351 (65) [SnPh₃], 307 (7) [HSSnPh₂], 197 (80) [SnPh], 121 (9) [SnH], 120 (34) [Sn]. Besides these signals, the EI spectrum shows signals for H₂(Br-*o*-hpspa) and its fragments, and the FAB spectrum shows the same metallated signals. ¹H NMR: δ = 7.81 [s, 1 H, C(4)H], 7.71 [d, 1 H, C(5)H], 7.46 [dd, 1 H, C(7)H], 7.41 [d, 1 H, C(8)H], 7.70 (d, 6 H, Ph_o), 7.40 (q, 9 H, Ph_{m,p}) ppm. ¹³C NMR: δ = 162.1 C(2), 119.8 C(3), 121.5 C(4a), 150.6 C(8a), 118.1 C(8), 128.3 C(7), 117.5 C(6), 132.7 C(5), 140.2 C_i, 136.6 C_o, 128.7 C_m, 129.5 C_p ppm. ¹¹⁹Sn NMR: δ = –98.1 (s) ppm. C₂₇H₁₉BrO₂SSn: calcd. C 53.5, H

3.1, S 5.3%; found C 52.6, H 3.3, S 4.6%. From the mother liquor, crystals of the ethanol solvate suitable for X-ray diffraction were isolated.

[SnPh₃(Br₂SC)]: A solution of SnPh₃OH (0.20 g, 0.6 mmol) in 10 mL of an ethanol/acetone mixture (1:1 v/v) was treated with a solution of H₂(Br₂-o-hpspa) (0.10 g, 0.3 mmol) in 10 mL of the same solvent. After refluxing for 5 h, a white solid was formed. Yield: 0.22 g, 54%. Mp: 162 °C. IR (Raman): 1699 s ν (C=O), 273 w ν_{asym} (Sn–C), 258 s (255 w) ν_{sym} (Sn–C), 361 w ν (Sn–S) cm^{−1}. EI (main signals): *m/z* (%) = 609 (31) [M⁺ + H – Ph], 351 (72) [SnPh₃], 308 (17) [SnPh₂S + 2H], 197 (93) [SnPh], 120 (43) [Sn]. Besides these signals, the EI spectrum shows signals for H₂(Br₂-o-hpspa) and its fragments, whilst the FAB spectrum shows the signals for the same metallated fragments as well as another signal at 685 (3) [M⁺]. ¹H NMR: δ = 7.74 [s, 1 H, C(4)H], 7.42 [d, 1 H, C(7)H], 7.41 [d, 1 H, C(5)H], 7.69 (d, 6 H, Ph_o), 7.40 (q, 9 H, Ph_{m,p}) ppm. ¹³C NMR: δ = 161.3 C(2), 122.2 C(3), 127.5 C(4a), 147.6 C(8a), 117.4 C(8), 137.3 C(7), 110.77 C(6), 135.4 C(5), 139.8 C_b, 136.6 C_o, 128.7 C_m, 129.6 C_p ppm. ¹¹⁹Sn NMR: δ = −94.0 (s) ppm. C₂₇H₁₈Br₂O₂SSn: calcd. C 47.3, H 2.6, S 4.7%; found C 46.7, H 2.3, S 4.8%. From the mother liquor, suitable crystals for X-ray diffraction were isolated.

Supporting Information (see footnote on the first page of this article): Figures S1 and S2 showing the molecular structures and numbering schemes of the two complexes are provided.

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