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Hypervalence at tin(IV) by transannular bonding of sulfur in an eight-membered ring: The case of dibenzostannocines $[\{S(C_6H_4S)_2\}Sn]$

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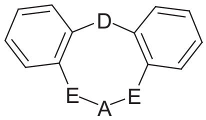
ABSTRACT

Treatment of Ph_2SnCl_2 with $S(C_6H_4SH)_2$ in benzene leaded to the formation of $[\{S(C_6H_4S)_2\}SnPhCl]$ (**1**); the same reaction with 1,4-diazabicyclo-[2.2.2]-octane leaded $[\{S(C_6H_4S)_2\}SnPh_2]$ (**4**). The compounds $[\{S(C_6H_4S)_2\}SnPhHal]$ (Hal = Br, 2; I, 3) have been synthesized by halogen exchange from **1** and the corresponding potassium halide. The compound $[\{S(C_6H_4S)_2\}SnCl_2]$ (**5**) was obtained from $S(C_6H_4SH)_2$ and $SnCl_4$. The reaction of 1 with $NaS_2CNEt_2\cdot 3H_2O$ yielded $[\{S(C_6H_4S)_2\}SnPh\{S_2CNEt_2\}]$ (**6**). X-ray structure determinations of dibenzostannocines **1**–**6** revealed that the tin atom acts as an acceptor atom displaying an intramolecular transannular interaction with the sulfur (thioether-like) atom. The local geometry of the Sn atom in the compounds **1**–**5** is described as distorted trigonal bipyramidal with a TBP character spanning from 81% to 73%. In **6** the tin atom is six-coordinate with a distorted octahedral geometry.

1. Introduction

It is well known that heavier group 14 elements have the ability to expand their coordination numbers above four, accommodating formally more than eight electrons in their valence shell and to form so-called hypervalent compounds [1–3]. To promote this hypervalent bonding situation, some ligands capable of yielding compounds containing five-membered chelate rings by means of a D···A donor–acceptor intramolecular bond have been used in order to increase the coordination number of an acceptor atom A. These compounds comprise the metallatranes [1] and metallocanes [4] which contain ethylene units quite flexible in the ring. When these ethylene units are replaced by less flexible groups as benzene rings, compounds of the type I containing p-block elements can be synthesized; they also display the same donor–acceptor interaction (some examples are with D = S, SO_2; E = O and A = Si, P [5–8]; with D = S, Se; E = O and A = Ge [9–11]). We have also studied these type of compounds with D = S, O; E = S and A = Ge, [12,13] shown by X-ray diffraction and theoretical methods the different degrees and nature of the D···Ge interaction, observing the strongest interaction when the exocyclic ligands are halides.



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Herein, we report a structural study of organotin compounds with tin(IV) as acceptor atom, an easy-to-follow nucleus by ^{119}Sn NMR spectroscopy, where the coordination number has been varied in function of the nature of the different exocyclic ligands. After the description of the synthesis of dibenzostannocines, Mass spectrometry, NMR spectroscopy and X-ray crystallographic data are presented and discussed.

2. Experimental

2.1. Materials and methods

All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. Melting points were determined on a Mel-Temp II instrument and are uncorrected. Spectra were recorded with the following instruments: Electron-impact mass spectra (EI-MS) were measured on either Finnigan MAT 8230 or Varian MAT CH5 instrument. Elemental analyses were recorded on a Perkin–Elmer Series II

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CHNS/O Analyzer. IR spectra were recorded in the 4000–400 cm^{-1} range on a Perkin–Elmer System 2000 FT-IR spectrometer, as KBr pellets. ^{1}H, $^{13}C\{^{1}H\}$ and $^{119}Sn\{^{1}H\}$ NMR spectra were recorded on a Jeol Eclipse 400 spectrometer operating at 399.78, 100.53, and 149.03 MHz, respectively; the spectra were acquired at room temperature (25 °C) unless otherwise specified. The chemical shifts are reported in ppm with respect to the references and stated relative to external tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR, and Me_4Sn for ^{119}Sn NMR spectroscopy. $S(C_6H_4SH)_2$ was synthesized according to literature methods [14]. Ph_2SnCl_2, $SnCl_4$, 1,4-diazabicyclo-[2.2.2]-octane (DABCO), KBr, KI, $NaS_2CNEt_2\cdot 3H_2O$ and HBr were purchased from Aldrich and Fluka and used as supplied.

2.2. Synthesis of the dibenzostannocine compounds *[{S(C₆H₄S)₂}SnL¹L²]*

2.2.1. Synthesis of *[{S(C₆H₄S)₂}SnPhCl]* (**1**)

Ph_2SnCl_2 (1.38 g, 4.0 mmol) in benzene (25 mL) was added to a solution of $S(C_6H_4SH)_2$ (1.00 g, 4.0 mmol) in benzene (25 mL) at 5 °C. The yellow mixture was stirred and refluxed for 24 h. The mixture was allowed to cool to room temperature. Colorless crystals of **1** were obtained by slow evaporation. The crystals were separated by suction and washed with hexanes (40 mL). Yield: 1.75 g (91%), m.p. 228 °C. *Anal.* Calc. for $[\{S(C_6H_4S)_2\}SnPhCl]$ (479.65): C, 45.07; H, 2.73. Found: C, 44.86; H, 2.81%. EI-MS: *m/z* (%) = 480 (10) $[M^+]$, 445 (10) $[M^+-Cl]$, 367 (10) $[S(C_6H_4S)_2Sn-1]$, 216 (base peak) $[S(C_6H_4S)^+]$. ^{1}H NMR ($CDCl_3$): $\delta = 7.84$ [m, $^{3}J(^{1}H-^{119}Sn) = 94$ Hz, 2H, H^5], 7.69 (dd, $^{3}J_{H^1-H^2} = 7.68$ Hz, $^{4}J_{H^1-H^3} = 1.44$ Hz, 2H, H^1), 7.48 (dd, $^{3}J_{H^4-H^3} = 7.68$ Hz, $^{4}J_{H^4-H^2} = 1.44$ Hz, 2H, H^4), 7.45 (m, 3H, H^6 and H^7), 7.29 (ddd, $^{3}J_{H^2-H^1} = {}^{3}J_{H^2-H^3} = 7.68$ Hz, $^{4}J_{H^2-H^4} = 1.44$ Hz, 2H, H^2), 7.17 (ddd, $^{3}J_{H^3-H^2} = {}^{3}J_{H^3-H^4} = 7.68$ Hz, $^{4}J_{H^3-H^1} = 1.44$ Hz, 2H, H^3) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 60 °C): $\delta = 141.6$ [$^{3}J(^{13}C-^{119}Sn) = 27$ Hz, C1a], 141.2 [C5a], 134.6 [$^{2}J(^{13}C-^{119}Sn) = 64$ Hz, C5], 133.6 [C4], 132.3 [$^{3}J(^{13}C-^{119}Sn) = 45$ Hz, C1], 131.2 [C7], 130.7 [C1a], 130.4 [C2], 129.5 [$^{3}J(^{13}C-^{119}Sn) = 96$ Hz, C6], 126.9 [C3] ppm. $^{119}Sn\{^{1}H\}$ NMR ($CDCl_3$): $\delta = -63.4$ ppm. IR (KBr): $\upsilon = 3049, 1567, 1444, 1430, 1255, 1037, 752, 727, 688$ cm^{-1}.

2.2.2. Synthesis of *[{S(C₆H₄S)₂}SnPhBr]* (**2**)

Compound 1 (0.4 g, 0.83 mmol), KBr (0.5 g, 4.2 mmol), and HBr 48% (2 mL) were suspended in benzene (25 mL) and refluxed for 16 h. The water was removed by means of a Dean–Stark trap. The white suspension obtained was filtered and dried by means of a column filled with Celite and anhydrous Na_2SO_4. After evaporation, the residue was redissolved in chloroform (50 mL); the solution was slowly evaporated with a dinitrogen gas flow to dryness, providing colorless crystals of **2**, which were washed with hexanes (40 mL) and filtered by suction. Yield: 300 mg (68%), m.p. 202 °C. *Anal.* Calc. for $[\{S(C_6H_4S)_2\}SnPhBr]$ (524.10): C, 41.25; H, 2.50. Found: C, 40.69; H, 2.41%. EI-MS: *m/z* (%) = 524 (13) $[M^+]$, 445 (50) $[M^+-Br]$, 367 (5) $[S(C_6H_4S)_2Sn-1]$, 216 (base peak) $[S(C_6H_4S)^+]$. ^{1}H NMR ($CDCl_3$): $\delta = 7.82$ [m, $^{3}J(^{1}H-^{119}Sn) = 96$ Hz, 2H, H^5], 7.68 (dd, $^{3}J_{H^1-H^2} = 7.52$ Hz, $^{4}J_{H^1-H^3} = 1.44$ Hz, 2H, H^1), 7.45 (dd, $^{3}J_{H^4-H^3} = 7.52$ Hz, $^{4}J_{H^4-H^2} = 1.44$ Hz, 2H, H^4), 7.44 (m, 3H, H^6 and H^7), 7.28 (ddd, $^{3}J_{H^2-H^1} = {}^{3}J_{H^2-H^3} = 7.52$ Hz, $^{4}J_{H^2-H^4} = 1.44$ Hz, 2H, H^2), 7.17 (ddd, $^{3}J_{H^3-H^2} = {}^{3}J_{H^3-H^4} = 7.52$ Hz, $^{4}J_{H^3-H^1} = 1.44$ Hz, 2H, H^3) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 141.3 [C5a], 141.1 [$^{3}J(^{13}C-^{119}Sn) = 27$ Hz, C4a], 134.6 [$^{2}J(^{13}C-^{119}Sn) = 65$ Hz, C5], 133.7 [C4], 132.2 [$^{3}J(^{13}C-^{119}Sn) = 40$ Hz, C1], 131.3 [C7], 130.6 [C1a], 130.4 [C2], 129.5 [$^{3}J(^{13}C-^{119}Sn) = 90$ Hz, C6], 127.0 [C3] ppm. $^{119}Sn\{^{1}H\}$ NMR ($CDCl_3$): $\delta = -95.1$ ppm. IR (KBr): $\upsilon = 3050, 1568, 1445, 1442, 1249, 1081, 1039, 862, 735, 730, 710, 692$ cm^{-1}.

2.2.3. Synthesis of *[{S(C₆H₄S)₂}SnPhI]* (**3**)

Compound 1 (0.4 g, 0.83 mmol) and KI (0.7 g, 4.2 mmol) were suspended in benzene (25 mL) and refluxed for 16 h. The yellow suspension obtained was dried by means of a column filled with Celite and anhydrous Na_2SO_4. After evaporation, the residue was redissolved in chloroform (50 mL); the solution was slowly evaporated with a dinitrogen gas flow to dryness, providing yellow-pale crystals of **3**, which were washed with hexanes (40 mL) and filtered by suction. Yield: 380 mg (80%), m.p. 178 °C. *Anal.* Calc. for $[\{S(C_6H_4S)_2\}SnPhI]$ (571.11): C, 37.85; H, 2.29. EI-MS: *m/z* (%) = 444 (95) $[M^+-I-1]$, 368 (5) $[S(C_6H_4S)_2Sn]$, 216 (base peak) $[S(C_6H_4S)^+]$. Found: C, 38.15; H, 2.21. ^{1}H NMR ($CDCl_3$): $\delta = 7.77$ [m, $^{3}J(^{1}H-^{119}Sn) = 93$ Hz, 2H, H^5], 7.68 (dd, $^{3}J_{H^1-H^2} = 7.68$ Hz, $^{4}J_{H^1-H^3} = 1.48$ Hz, 2H, H^1), 7.43 (dd, $^{3}J_{H^4-H^3} = 7.68$ Hz, $^{4}J_{H^4-H^2} = 1.48$ Hz, 2H, H^4), 7.42 (m, 3H, H^6 and H^7), 7.28 (ddd, $^{3}J_{H^2-H^1} = {}^{3}J_{H^2-H^3} = 7.68$ Hz, $^{4}J_{H^2-H^4} = 1.48$ Hz, 2H, H^2), 7.17 (ddd, $^{3}J_{H^3-H^2} = {}^{3}J_{H^3-H^4} = 7.68$ Hz, $^{4}J_{H^3-H^1} = 1.48$ Hz, 2H, H^3) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): $\delta = 141.2$ [$^{3}J(^{13}C-^{119}Sn) = 31$ Hz, C4a], 140.9 [C5a], 134.2 [$^{2}J(^{13}C-^{119}Sn) = 65$ Hz, C5], 133.8 [C4], 131.9 [$^{2}J(^{13}C-^{119}Sn) = 40$ Hz, C1], 131.2 [C7], 131.0 [C1a], 130.3 [C2], 129.4 [$^{3}J(^{13}C-^{119}Sn) = 92$ Hz, C6], 127.1 [C3] ppm. $^{119}Sn\{^{1}H\}$ NMR ($CDCl_3$): $\delta = -180.8$ ppm. IR (KBr): $\upsilon = 3043, 1570, 1443, 1430, 1251, 1105, 1037, 800, 752, 727, 687, 653$ cm^{-1}.

2.2.4. Synthesis of *[{S(C₆H₄S)₂}SnPh₂]* (**4**)

A solution of $S(C_6H_4SH)_2$ (0.5 g, 2.0 mmol) and DABCO (0.225 g, 2.0 mmol) in chloroform (25 mL) at 0 °C was stirred for 1 h; afterward a solution of Ph_2SnCl_2 (0.69 g, 2.0 mmol) in chloroform (25 mL) was added. The mixture was refluxed for 24 h. Then, the solution was dried by means of a column filled with Celite and anhydrous Na_2SO_4. The solution was slowly evaporated with a dinitrogen gas flow to dryness, providing colorless crystals of **4**, which were washed with hexanes (20 mL) and filtered by suction. Yield: 0.93 g (90%), m.p. 132 °C. *Anal.* Calc. for $[\{S(C_6H_4S)_2\}SnPh_2]$ (521.30): C, 55.29; H, 3.48. Found: C, 55.99; H, 3.61%. EI-MS *m/z* (%): 522 (10) $[M^+]$, 445 (85) $[M^+-Ph]$, 368 (5) $[S(C_6H_4S)_2Sn]$, 216 (base peak) $[S(C_6H_4S)^+]$. ^{1}H NMR ($CDCl_3$): $\delta = 7.71$ (dd, $^{3}J_{H^1-H^2} = 7.72$ Hz, $^{4}J_{H^1-H^3} = 1.48$ Hz, 2H, H^1), 7.65 (m, 2H, H^5), 7.42 (dd, $^{3}J_{H^4-H^3} = 7.72$ Hz, $^{4}J_{H^4-H^2} = 1.48$ Hz, 2H, H^4), 7.37 (m, 3H, H^6 and H^7), 7.22 (ddd, $^{3}J_{H^2-H^1} = {}^{3}J_{H^2-H^3} = 7.72$ Hz, $^{4}J_{H^2-H^4} = 1.48$ Hz, 2H, H^2), 7.11 (ddd, $^{3}J_{H^3-H^2} = {}^{3}J_{H^3-H^4} = 7.72$ Hz, $^{4}J_{H^3-H^1} = 1.48$ Hz, 2H, H^3) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): $\delta = 142.4$ [C5a], 140.5 [$^{3}J(^{13}C-^{119}Sn) = 24$ Hz, C4a], 135.5 [$^{2}J(^{13}C-^{119}Sn) = 50$ Hz, C5], 134.8 [C1a], 133.8 [C4], 133.3 [$^{3}J(^{13}C-^{119}Sn) = 28$ Hz, C1], 129.9 [$^{4}J(^{13}C-^{119}Sn) = 15$ Hz, C7], 129.0 [C2], 128.9 [$^{3}J(^{13}C-^{119}Sn) = 65.4$ Hz, C6], 126.6 [C6] ppm. $^{119}Sn\{^{1}H\}$ NMR ($CDCl_3$): $\delta = -18.4$ ppm. IR (KBr): $\upsilon = 3060, 1569, 1441, 1427, 1245, 1101, 1066, 1039, 747, 724, 691$ cm^{-1}.

2.2.5. Synthesis of *[{S(C₆H₄S)₂}SnCl₂]* (**5**)

To a solution of $SnCl_4$ (0.52 g, 2.0 mmol) in benzene (25 mL) was added $S(C_6H_4SH)_2$ (0.5 g, 2.0 mmol) in benzene (25 mL) at 5 °C. The mixture was stirred and refluxed for 6 h. The yellow solution was dried by means of a column filled with Celite and anhydrous Na_2SO_4. The solution was slowly evaporated with a dinitrogen gas flow to dryness, providing crystals of **5**, which were washed with hexanes (40 mL) and filtered by suction. Yield: 0.34 g (43%), m.p. 112 °C. *Anal.* Calc. for $[\{S(C_6H_4S)_2\}SnCl_2]$ (438.00): C, 32.91; H, 1.84. Found: C, 32.35; H, 1.90%. EI-MS: *m/z* (%) = 438 (5) $[M^+]$, 400 (8) $[M^+-Cl]$, 368 (8) $[S(C_6H_4S)_2Sn]$, 216 (base peak) $[S(C_6H_4S)^+]$. ^{1}H NMR ($CDCl_3$): $\delta = 7.71$ (dd, $^{3}J_{H^1-H^2} = 7.72$ Hz, $^{4}J_{H^1-H^3} = 1.48$ Hz, 2H, H^1), 7.54 (dd, $^{3}J_{H^4-H^3} = 7.72$ Hz, $^{4}J_{H^4-H^2} = 1.48$ Hz, 2H, H^4), 7.34 (ddd, $^{3}J_{H^2-H^1} = {}^{3}J_{H^2-H^3} = 7.72$ Hz, $^{4}J_{H^2-H^4} = 1.48$ Hz, 2H, H^2), 7.27 (ddd, $^{3}J_{H^3-H^2} = {}^{3}J_{H^3-H^4} = 7.72$ Hz, $^{4}J_{H^3-H^1} = 1.48$ Hz, 2H, H^3) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): $\delta = 139.1$ [$^{3}J(^{13}C-^{119}Sn) = 35$ Hz, C4a], 133.6 [C4], 131.8 [$^{3}J(^{13}C-^{119}Sn) = 69$ Hz, C1], 131.1

[C2], 130.0 [$^{2}J(^{119}\mathrm{Sn}-^{13}\mathrm{C}) = 40$ Hz, C1a], 127.8 [C3] ppm. $^{119}\mathrm{Sn}\{^{1}\mathrm{H}\}$ NMR ($CDCl_3$): $\delta = -142.8$ ppm. IR (KBr): $\upsilon = 3047$, 1569, 1441, 1245, 1101, 1039, 747 cm^{-1}.

2.2.6. Synthesis of [{$S(C_6H_4S)_2$}SnPh{S_2CNEt_2}] (**6**)

Compound 1 (0.1 g, 0.20 mmol) and $NaS_2CNEt_2\cdot 3H_2O$ (0.125 g, 0.60 mmol) were suspended in benzene (25 mL) and refluxed for 16 h. The yellow suspension obtained was dried by means of a column filled with Celite and anhydrous Na_2SO_4. After evaporation, the residue was redissolved in chloroform (40 mL); the solution was slowly evaporated with a dinitrogen gas flow to provide yellow crystals of **6**, which were washed with hexanes (40 mL) and filtered by suction. Yield: 90 mg (80%), m.p. 140 °C. *Anal.* Calc. for [{$S(C_6H_4S)_2$}SnPh{S_2CNEt_2}] (592.47): C, 46.63; H, 3.91. Found: C, 46.78; H, 3.94%. ^{1}H NMR ($CDCl_3$): $\delta = 7.89$ [m, $^{3}J(^{1}\mathrm{H}-^{119}\mathrm{Sn}) = 94$ Hz, 2H, H^5], 7.62 (dd, $^{3}J_{\mathrm{H}^{1}-\mathrm{H}^{2}} = 7.72$ Hz, $^{4}J_{\mathrm{H}^{1}-\mathrm{H}^{3}} = 1.48$ Hz, 2H, H^1), 7.48 (dd, $^{3}J_{\mathrm{H}^{4}-\mathrm{H}^{3}} = 7.72$ Hz, $^{4}J_{\mathrm{H}^{4}-\mathrm{H}^{2}} = 1.48$ Hz, 2H, H^4), 7.35 (m, 3H, H^6 and H^7), 7.21 (ddd, $^{3}J_{\mathrm{H}^{2}-\mathrm{H}^{1}} = {}^{3}J_{\mathrm{H}^{2}-\mathrm{H}^{3}} = 7.72$ Hz, $^{4}J_{\mathrm{H}^{2}-\mathrm{H}^{4}} = 1.48$ Hz, 2H, H^2), 7.07 (ddd, $^{3}J_{\mathrm{H}^{3}-\mathrm{H}^{2}} = {}^{3}J_{\mathrm{H}^{3}-\mathrm{H}^{4}} = 7.72$ Hz, $^{4}J_{\mathrm{H}^{3}-\mathrm{H}^{1}} = 1.48$ Hz, 2H, H^3), 3.65 (c, $^{3}J_{\mathrm{H-H}} = 7.14$ Hz, 4H, CH_2), 1.24 (t, $^{3}J_{\mathrm{H-H}} = 7.14$ Hz, 6H, CH_3) ppm. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($CDCl_3$, 60 °C): $\delta = 197.7$ [C=N], 150.2 [C5a], 145.2 [$^{3}J(^{113}\mathrm{C}-^{119}\mathrm{Sn}) = 20$ Hz, C4a], 135.0 [C1a], 133.8 [$^{2}J(^{13}\mathrm{C}-^{119}\mathrm{Sn}) = 30$ Hz, C5], 133.3 [C4], 132.9 [$^{3}J(^{13}\mathrm{C}-^{119}\mathrm{Sn}) = 40$ Hz, C1], 129.3 [C7], 128.5 [$^{3}J(^{13}\mathrm{C}-^{119}\mathrm{Sn}) = 40.0$ Hz, C6], 125.4 [C3], 51.3 [CH_2], 12.0 [CH_3] ppm. $^{119}\mathrm{Sn}\{^{1}\mathrm{H}\}$ NMR ($CDCl_3$): $\delta = -322.6$ ppm. IR (KBr): $\upsilon = 3043$, 2929, 2869, 1570, 1443, 1430, 1251, 1105, 1037, 800, 752, 727, 687, 653 cm^{-1}.

2.3. X-ray crystallography

Suitable single crystals of compounds **1**, **2**, 3 and **5** were grown by slow evaporation from a benzene solution. Compounds **4** and **6** were grown by slow evaporation from a chloroform solution. X-ray diffraction data on **1**–**6** were collected at room temperature on a CCD SMART 6000 diffractometer through the use of Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator). Data were integrated, scaled, sorted and averaged using the SMART software package. The structures were solved by direct methods, using SHELXTL NT Version 5.1 and refined by full-matrix least squares against F^2 [15]. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using the program SADABS [16]. The displacement parameters of non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were kept fixed with a common isotropic displacement parameter. Selected crystallographic data are given in Table 1.

3. Results and discussion

3.1. Synthesis

Treatment of Ph_2SnCl_2 in benzene at reflux with the ligand $S(C_6H_4SH)_2$ yielded the corresponding organotin compound [{$S(C_6H_4S)_2$}SnPhCl] (**1**) (see Scheme 1); the Sn–Ph cleavage reaction was favored by the HCl formed in the reaction. The same reaction in chloroform in presence of the base 1,4-diazabicyclo-[2.2.2]-octane (DABCO) yielded the corresponding diphenylated compound [{$S(C_6H_4S)_2$}$SnPh_2$] (**4**). The addition of the base DABCO avoided the Sn–C cleavage reaction by trapping the HCl formed. Treatment of $S(C_6H_4SH)_2$ with $SnCl_4$ in hot benzene yielded [{$S(C_6H_4S)_2$}$SnCl_2$] (**5**). [{$S(C_6H_4S)_2$}SnPhBr] (**2**) was synthesized from **1** by treatment with an excess of KBr in a refluxing HBr/benzene mixture, giving **2** as colorless crystals. The compounds [{$S(C_6H_4S)_2$}SnPhI] (**3**) and [{$S(C_6H_4S)_2$}SnPh{S_2CNEt_2}] (**6**) were obtained by the reaction of **1** with an excess of KI and $NaS_2CNEt_2\cdot 3H_2O$, respectively (see Section 2 for details).

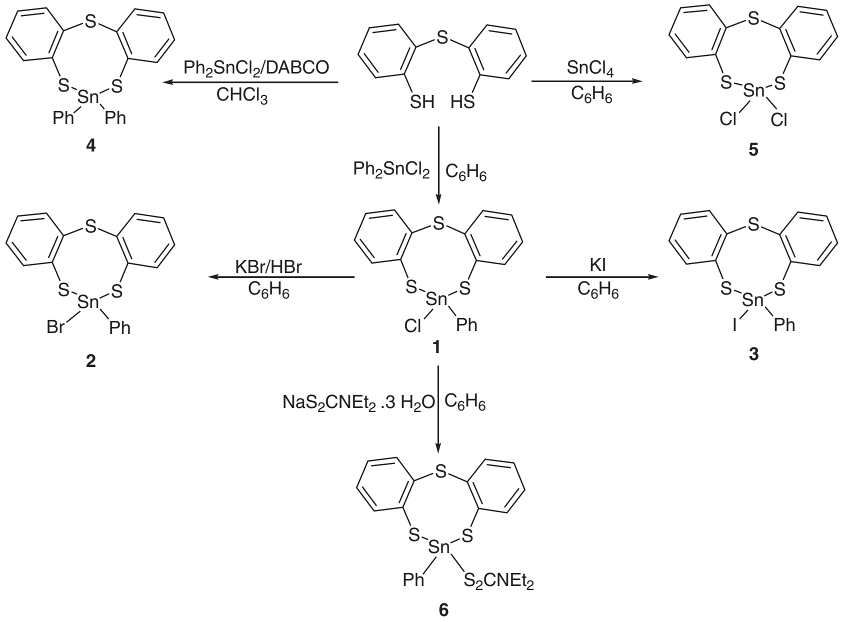
All compounds are air-stable, soluble in benzene, toluene, dichloromethane and chloroform, and insoluble in pentane, hexane and isopropanol.

3.2. Mass spectra

Electron-impact mass spectra for **1**–**5** were obtained at 70 eV. Spectra for **1**, **2**, 4 and **5** exhibit a low intensity ion with the appropriate isotopic ratio representing the molecular ion (M^+). In the compounds **1**–**4** was observed a peak at 445 *m*/*z* corresponding to the fragment M–L [L = Cl (**1**), Br (**2**), I (**3**), Ph (**4**)] and assigned in all cases to the [{$S(C_6H_4S)_2$}SnPh]$^+$ fragment, confirming the binding of tin to the sulfur atoms. In **5** was observed a low intensity

Table 1
Selected crystallographic data for dibenzostannocines **1**–**6**.

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{18}H_{13}ClS_3Sn$	$C_{18}H_{13}BrS_3Sn$	$C_{18}H_{13}IS_3Sn$	$C_{24}H_{18}S_3Sn$	$C_{12}H_8Cl_2S_3Sn$	$C_{23}H_{23}NS_5Sn$
Molecular weight (g/mol)	479.60	524.06	571.05	521.25	437.95	592.41
Crystal size (mm)	0.45 × 0.30 × 0.15	0.5 × 0.30 × 0.12	0.25 × 0.17 × 0.07	0.60 × 0.30 × 0.14	0.56 × 0.30 × 0.09	0.50 × 0.40 × 0.35
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
ρ_{calc} (mg m^{-3})	1.714	1.833	1.936	1.588	1.881	1.549
Z	4	4	4	2	4	4
a (Å)	9.9842(7)	9.9795(9)	10.0005(5)	9.9619(8)	10.7133(13)	10.2910(5)
b (Å)	10.3455(7)	10.5556(8)	10.8314(5)	10.3246(9)	12.1698(15)	15.7117(8)
c (Å)	18.2982(12)	18.3338(16)	18.3957(9)	11.2615(10)	12.2679(15)	17.1812(9)
α (°)	90	90	90	73.151(2)	88.048(3)	70.9350(10)
β (°)	100.469(2)	100.496(2)	100.4690(10)	79.617(2)	89.735(3)	76.2620(10)
γ (°)	90	90	90	88.713(2)	75.314(3)	80.6230(10)
V ($Å^3$)	1858.6(2)	1899.0(3)	1959.44(16)	1089.85(16)	1546.3(3)	2539.5(2)
μ (mm^{-1})	1.851	3.775	3.195	1.467	2.381	1.428
$F(0\,0\,0)$	944	1016	1088	520	848	1192
GOF	0.919	0.864	1.021	0.997	0.993	1.107
Absorption correction	SADABS	SADABS	SADABS	SADABS	SADABS	SADABS
Reflections collected	12,114	12,275	12,772	7279	9943	18,784
Unique reflections	3666	3711	3849	4256	6119	9943
R_{int}	0.0683	0.0606	0.0356	0.0200	0.0479	0.0273
R_1, wR_2 [$I > 2\sigma(I)$]	0.0357, 0.0735	0.0383, 0.0776	0.0328, 0.0849	0.0294, 0.0695	0.0591, 0.1631	0.0405, 0.1269
R_1, wR_2 (all data)	0.0561, 0.0793	0.0784, 0.1089	0.0463, 0.0911	0.0388, 0.0726	0.0989, 0.1843	0.0539, 0.1645
Large residuals (e $Å^{-3}$)	0.828/−0.606	0.655/−0.777	0.414/−1.204	0.320/−0.463	1.225/−0.874	0.673/−1.072



Scheme 1. Synthesis of compounds [{S(C$_6$H$_4$S)$_2$}SnL^{1}L^2].

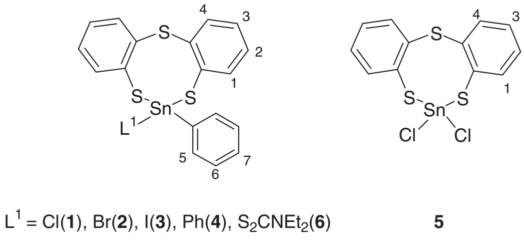
peak at 403 *m*/*z* assignable to the loss of a chloro ligand. In all compounds was observed a peak at 368 *m*/*z* corresponding to the tricyclic moiety {S(C$_6$H$_4$S)$_2$}Sn. For **1**, **2**, 4 and **5** was observed a base peak at 216 *m*/*z* assigned to the thianthrenic fragment S(C$_6$H$_4$)$_2$S; in **3** the base peak was assigned to the loss of the iodo ligand. In all compounds a peak was also observed at 184 *m*/*z* attributable to the dibenzothiophene fragment. No more peaks could be assigned.

3.3. NMR spectra

NMR spectra of compounds **1**–**6** were recorded in the non-coordinating solvent CDCl$_3$, at room temperature unless otherwise specified. The assignments of these compounds were performed by 1D (^{1}H, ^{13}C and ^{119}Sn) and 2D ^{1}H–^{1}H COSY, ^{1}H–^{13}C HETCOR and COLOC as well as ^{1}H–^{119}Sn HETCOR spectroscopy. The numbering scheme for the assignment of the ^{1}H and ^{13}C{^{1}H} NMR signals are shown in Scheme 2, and the ^{1}H, ^{13}C{^{1}H} and ^{119}Sn{^{1}H} NMR chemical shifts are shown in Tables 2–4, respectively.

3.3.1. ^{1}H NMR spectra

The ^{1}H NMR spectra of **1**–**6** show four signals in an ABCD pattern, typical of *ortho*-substituted benzenic rings. In solution, the two S(C$_6$H$_4$S)Sn halves are equivalent. The protons H-5 in **1**, **2**, 3 and **6** show coupling with the ^{119}Sn isotope [$^3J(^1\text{H}–^{119}\text{Sn})$ ranging from 93 to 96 Hz]; in **4** the coupling constant was not observed. For **6** the ethyl groups displayed only two signals at 1.24 (CH$_3$) and 3.65 (CH$_2$) ppm.



Scheme 2. Labeling of compounds [{S(C$_6$H$_4$S)$_2$}SnL^{1}L^2].

Table 2
^{1}H NMR chemical shifts (δ values, ppm) for dibenzostannocines **1**–**6**.

	L^1	H-1	H-2	H-3	H-4	H-5	H-6	H-7
1	Cl	7.69	7.29	7.17	7.48	7.84	7.45	7.45
2	Br	7.68	7.28	7.17	7.48	7.82	7.44	7.44
3	I	7.68	7.28	7.17	7.43	7.77	7.42	7.42
4	Ph	7.71	7.22	7.11	7.42	7.65	7.37	7.37
5	Cl	7.71	7.34	7.27	7.54	–	–	–
6	S$_2$CNEt$_2$	7.62	7.21	7.07	7.48	7.89	7.35	7.35

3.3.2. ^{13}C{^{1}H} NMR spectra

Proton decoupled ^{13}C spectra of compounds **2**, 3 and **4** display the expected ten signals in the aromatic region while **1** and **6** just display nine signals at room temperature; the missing signals could be observed at higher temperatures. The spectrum of compound **5** displays the expected six signals. The ethyl groups of the dithiocarbamate moiety in **6** are equivalents; the methyl group is observed at 12.0 ppm and the methylene at 51.3 ppm, whereas the C=N group is observed at 197.1 ppm. A noteworthy observation is that the magnitude of the $^3J(^{13}\text{C}–^{119}\text{Sn})$ coupling constant involving the *ortho*-carbon C-1 in the dibenzostannocine moiety is dependent of the nature of the exocyclic ligands binded to the tin atom; the highest value is observed in **5** (69 Hz, two chloro ligands), whereas the lowest value is observed in **4** (28 Hz, two phenyl groups).

3.3.3. ^{119}Sn{^{1}H} NMR spectroscopy

The ^{119}Sn NMR spectra were obtained in the non-coordinating solvent CDCl$_3$. ^{119}Sn spectra of the compounds **1**–**6** showed a sharp signal indicating the existence of a single tin compound (see Table 4). In seminal papers, has been noted that the ^{119}Sn chemical shifts, δ^{119}Sn), move to lower frequencies as the coordination number increases, although the δ^{119}Sn) ranges are somewhat dependent on the nature of the substituents [17,18]. In this work, all tin compounds contain the potentially tridentate {S(C$_6$H$_4$S)$_2$}$^{2-}$ moiety, so they can be compared when the pendant exocyclic ligands L^1 and L^2 are changed. For example, **4** has two phenyl groups attached to the tin atom; it is well known that organic fragments usually diminishes the acceptor abilities of a central atom. Hence, is plau-

Table 3
$^{13}C\{^1H\}$ NMR chemical shifts (δ values, ppm) and coupling constants [$^nJ(^{13}C-^{119}Sn)$, ^nJ in Hz] for dibenzostannocines **1**–**6**.

	L^1	C-1	C-2	C-3	C-4	C-1a	C-4a	C-5	C-5a	C-6	C-7
1	Cl	132.4 ^3J = 45	130.4	127	133.6	[a]	140.9 ^3J = 27	134.7 ^2J = 64	141.2	129.6 ^3J = 96	131.3
1[b]	Cl	132.3 ^3J = 45	130.3	126.9	133.6	130.7	141.6 ^3J = 27	134.6 ^2J = 64	141.2	129.5 ^3J = 96	131.2
2	Br	132.2 ^3J = 40	130.4	127	133.7	130.6	141.1 ^3J = 27	134.6 ^2J = 65	141.3	129.5 ^3J = 90	131.3
3	I	131.9 ^3J = 40	130.3	127.1	133.8	131	141.2 ^3J = 31	134.2 ^2J = 65	140.9	129.3 ^3J = 92	131.2
4	Ph	133.3 ^3J = 28	129	126.6	133.8	134.8	140.5 ^3J = 24	135.5 ^2J = 50	142.4	128.9 ^3J = 65	129.9 ^4J = 15
5	Cl	131.8 ^3J = 69	131.1	127.8	133.6	130	139.1 ^3J = 35	–	–	–	–
6	S_2CNEt_2	133.9 ^3J = 40	129.2	125.5	132.9	134.9	145 ^3J = 20	133.8 ^2J = 30	[a]	128.6 ^3J = 40	129.4
6[b]	S_2CNEt_2	132.9 ^3J = 40	129	125.4	133.3	135	145.2 ^3J = 20	133.8 ^2J = 30	150.2	128.5 ^3J = 40	129.3

[a] Not observed at room temperature.

[b] At 60 °C.

Table 4
$^{119}Sn\{^1H\}$ NMR data (ppm) for **1**–**6** compounds in chloroform solution (25 °C) and coordination number assigned in solution (CN).

	1	**2**	**3**	**4**	**5**	**6**
$\delta(^{119}Sn)$	−63.4	−95.1	−180.8	−18.4	−142.8	−322.6
$\Delta\delta$[a]	45.0	76.7	162.4	–	124.4	304.2
CN	4	5	5	4	5	6

[a] $\Delta\delta$: chemical shift variation.

sible to propose that **4** might show the lowest coordination number in the series (CN = 4). Respect to the $\delta(^{119}Sn)$ of the monohalogenate tin compounds **1**, 2 and **3**, they were observed at low frequencies according to the electronegativity of the halogen substituents; by quoting the Otera's ranges [17], only **2** and **3** would display a coordination number of **5**. On the other hand, the $\delta(^{119}Sn)$ of the compounds **4**, 1 and **5** were observed at lower frequencies as the number of the chloro ligands increases, respectively. Moreover, in **5** the presence of two chloro ligands should increase the Lewis acidity on the tin atom, enhancing the increase of the coordination number [19].

When the monodentate chloro ligand in **1** is replaced by a dithiocarbamate bidentate ligand, the $\delta(^{119}Sn)$ experiences a low-frequency shift, with a variation of the chemical shift ($\Delta\delta$) of **6** compared with **4** of 304.2 ppm; the $\Delta\delta$ values obtained in a same fashion suggest higher coordination numbers than four in solution for the compounds **2**, **3**, 5 and **6**.

3.4. X-ray structures of compounds *1*–*6*

The solid-state structures of **1**–**6** were determined by single-crystal X-ray diffraction analyses. The structures are depicted in Fig. 1. Selected bond lengths, angles and torsion angles are given in Table 5. The unit cells of the compounds **5** and **6** have two crystallographically independent molecules (**5a**, 5b and **6a**, 6b, respectively).

The analog organotin compounds [$\{S(C_6H_4S)_2\}SnPhHal$] (Hal = Cl, 1; Br, 2; I, 3) are isomorphic and isostructural with very small differences in the lattice constants; the smallest volume is observed in the chloro organotin compound **10** and goes up as the halogen size increases.

In all compounds, the Sn–S(thiolate-like) distances are in good agreement with those reported for eight-membered heterocycles and several other compounds with tin–sulfur bonds [20–31].

The Sn–Hal distances in **1**, **2**, 3 and **5** are only 0.5–4.0% longer than the accepted Sn–Hal bond length (2.33 in $SnCl_4$, 2.46 in $SnBr_4$ and 2.69 Å in SnI_4) [32]. The Sn–Cl distance in **1** is shorter than the reported for the analog stannocane [2.453(1) Å in $S(CH_2CH_2S)_2SnPhCl$] [25]. There are two different Sn–Cl distances in **5** and are similar to those found for $S(CH_2CH_2S)_2SnCl_2$ [2.392(3) and 2.348(3) Å], a compound where has been described a trigonal bipyramidal (TBP) local geometry for the tin atom; where the longest distance corresponds to the chloro ligand in an axial position [21]. The Sn–Br distance in **2** is similar to other one observed for stannocanes with bromo ligands in axial position [24]. The Sn–I in **3** is shorter than the observed for stannocanes with tin bonded to an iodo ligand in axial position [2.804(2) Å $S(CH_2CH_2S)_2SnI_2$] [24]. The Sn–C distances are in good agreement with other organotin compounds [23,24,33–35]. In particular the compounds **4** and **5** display two different tin-exocyclic ligand bond lengths, indicating the different environment of these ligands (*vide infra*).

In addition to the expected covalent bonding of the two sulfur atoms (thiolate-like) and the two exocyclic L^1 and L^2 ligands to tin, a relatively transannular short distance involving the sulfur donor (thioether-like) and tin atoms is observed in all compounds (see Table 5). The S···Sn distances are 12–30% longer than the covalent radii sum of Sn and S [$\Sigma r_{cov}(Sn, S) = 2.43$ Å] [36] but significantly shorter than the van der Waals radii sum [$\Sigma r_{vdW}(Sn, S) = 3.96$ Å] [37]. The magnitude of these distances is consistent with the existence of a secondary bonding [38]. These S···Sn distances in **1** and **5** are similar to those observed in the corresponding stannocanes and similar compounds containing tin–chloro exocyclic bonds [2.866(2) Å in $S(CH_2CH_2S)_2SnPhCl$, 2.760(3) Å in $S(CH_2CH_2S)_2SnCl_2$, 2.863(1) Å in $S(CH_2CH_2S)_2SnMeCl$ and 2.785(1) Å in $S(CH_2CH_2S)_2Sn(^nBu)Cl$] [21,23,25,29]. As has been mentioned for **5**, there are two different Sn–Cl bond distances, being the *trans* distance to the interaction the longest. For **2** the S···Sn distance is similar to that observed in $S(CH_2CH_2S)_2SnMeBr$ [2.835(2) Å] [23] but longer than that found in $S(CH_2CH_2S)_2SnBr_2$ [2.767(2) Å] [24]. For **3** the distance S···Sn is longer than the found in $S(CH_2CH_2S)_2SnI_2$ [2.779(2) Å] [24], whereas in **4** the distance S···Sn is shorter than the observed in the stannocanes $S(CH_2CH_2S)_2SnPh_2$ and $S(CH_2CH_2S)_2SnMe_2$ [3.246(1) and 3.514(1) Å, respectively] [23,26]. Furthermore, in **4** the longer Sn–Ph bond distance is observed for the phenyl group *trans* to the interaction, as observed for the compound **5**. If the four covalent bonds and the transannular interaction S···Sn observed in compounds **1**–**5** are taken into account, the tin atom has expanded its coordination number from four to five, and the local coordination geometry is in the pathway from tetrahedral to trigonal bipyramidal. In order to evaluate the geometry displacement at the tin

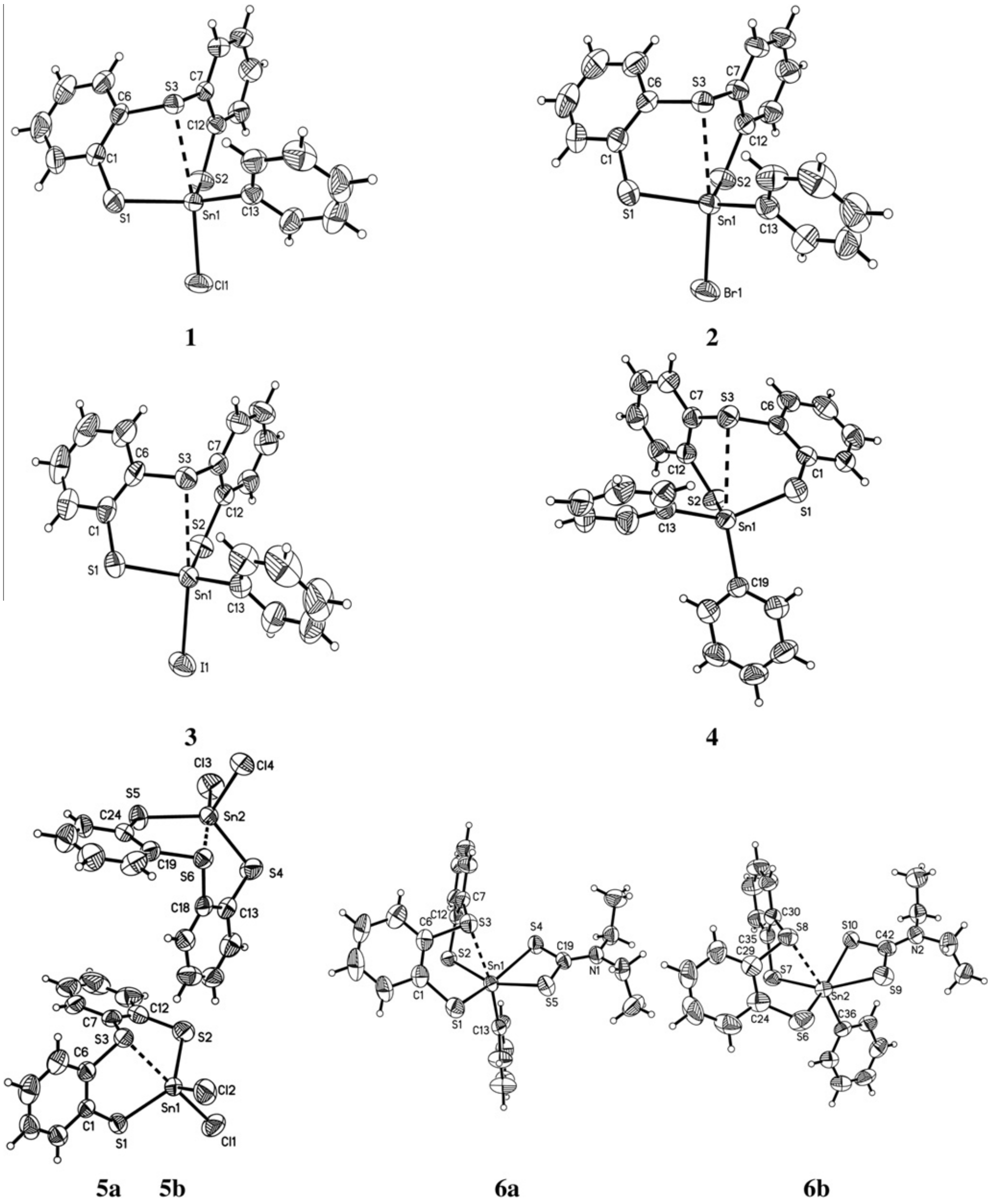


Fig. 1. ORTEP diagrams of [{S(C_6H_4S)$_2$}SnPhCl] (**1**), [{S(C_6H_4S)$_2$}SnPhBr] (**2**), [{S(C_6H_4S)$_2$}SnPhI] (**3**), [{S(C_6H_4S)$_2$}SnPh$_2$] (**4**), [{S(C_6H_4S)$_2$}SnCl$_2$] (**5**) and [{S(C_6H_4S)$_2$}SnPh{S_2CNEt_2}] (**6**) (50% probability ellipsoids).

atom and the magnitude of the interaction, we have used the Holmes approach [39–41] and the Pauling type Bond Order based on interatomic distances [42,23], respectively. These results are presented in Table 6. As in the lighter dibenzogermocines [12], the TBP% and the BO in the **1**–**5** tin compounds are strongly dependent of the number and nature of the electronegative ligands attached to the tin acceptor atom.

In the dibenzostannocines **1**–**5**, the local geometry at the tin atom is best described as trigonal bipyramidal, where the halogen (for **1**, **2**, 3 and **5**) or carbon (for **4**) and the sulfur (thioether-like) atoms are in the axial positions, meanwhile the two thiolate-like sulfur and carbon for **1**, **2**, 3 and **4** or chloro for **5** atoms are occupying equatorial positions.

From the TBP% character and BO calculated data, can be observed that the interaction between the sulfur (thioether-like) atom and the tin atom decreases in the order of the *trans* substituents Cl > Br > I > Ph, with the shortest S···Sn distance of 2.735(2) Å in the case of the dichlorocompound **5**. The longest distance of 3.1615(9) Å in the case of the diphenylated compound **4** is consistent with the ^{119}Sn NMR data, where a coordination number of four in solution was proposed. In addition, the tin atom displays a more pronounced Lewis acidity that the germanium atom when are compared dibenzostannocines respect to dibenzogermocines [12] [{S(C_6H_4S)$_2$}A] (A = Sn, Ge), with higher TBP% and BO values.

In order to expand the coordination number of the tin atom in the dibenzostannocines, we synthesized the compound **6** containing a dithiocarbamate ligand with a high bidentate character. In solution, the ^{119}Sn NMR signal is observed at low frequencies indicating the expansion of the tin coordination number from four to six (Table 4). This chemical shift in solution can be explained by means of the presence of a transannular interaction S···Sn and a bidentate coordination mode of the dithiocarbamate ligand, beside to the four expected covalent bonds. This was confirmed in the solid state. The compound **6** displays in the unit cell two crystallographically independent molecules that are practically superimposable. In fact a computer fitting of molecules **6a** and **6b** shows as the only difference between the conformers the orientation of the phenyl group. The S···Sn distance observed in com-

Table 5
Selected bond lengths (Å), angles, and torsion angles (°) for dibenzostannocines [{S(C_6H_4S)$_2$}SnL^{1}L^2].

	1	**2**	**3**	**4**	**5a**	**5b**	**6a**	**6b**
L^1	Cl1	Br1	I1	C19	Cl1	Cl3	C13	C36
L^2	C13	C13	C13	C13	Cl2	Cl4	S4, S5	S9, S10
S^a	S3	S3	S3	S3	S3	S6	S3	S8
S···Sn	2.827(1)	2.834(2)	2.840(1)	3.1615(9)	2.735(2)	2.725(2)	2.824(1)	2.872(1)
Sn–S(L)^b	2.407(1)	2.416(2)	2.415(1)	2.4373(9)	2.394(2)	2.398(3)	2.500(1)	2.4750(16)
Sn–S(L)^b	2.404(1)	2.409(2)	2.405(1)	2.4254(9)	2.399(3)	2.396(2)	2.496(1)	2.5021(14)
Sn–L^1	2.397(1)	2.5475(8)	2.7417(5)	2.151(3)	2.361(3)	2.359(3)	2.152(5)	2.163(5)
Sn–L^2	2.118(4)	2.121(7)	2.130(5)	2.138(3)	2.341(3)	2.348(3)	2.592(1), 2.559(1)	2.611(2), 2.558(1)
S(L)–Sn–S(L)^b	112.75(4)	112.25(7)	111.55(5)	111.00(3)	122.4(1)	127.5(1)	102.66(5)	102.58(6)
S···Sn–L^1	166.93(4)	167.92(5)	168.98(3)	164.65(8)	176.3(1)	175.3(1)	171.0(1)	172.5(2)
S···Sn–L^2	91.6(1)	90.7(2)	89.7(1)	83.96(8)	86.0(1)	88.1(1)	89.11(4), 84.93(4)	92.04(5), 83.75(5)
L^1–Sn–S(L)^b	98.48(4)	98.81(5)	99.35(3)	104.3(1)	97.4(1)	98.4(1)	101.5(1)	101.9(2)
L^1–Sn–S(L)^b	91.52(4)	91.87(5)	92.57(3)	99.08(9)	97.8(1)	95.0(1)	97.1(1)	99.8(1)
L^1–Sn–L^2	101.0(1)	100.9(2)	100.9(1)	111.3(1)	97.4(1)	96.6(1)	101.1(1), 99.3(1)	94.5(2), 102.0(2)
S(dtc)–Sn–S(dtc)^c	–	–	–	–	–	–	69.80(4)	69.60(5)
C–S–C	101.9(2)	102.0(3)	102.7(2)	102.8(1)	106.2(5)	103.8(4)	101.2(2)	101.7(3)
S(L)–Sn–S(L)–C^d	98.4(1)	98.3(2)	98.9(2)	92.6(1)	−96.4(3)	85.4(3)	108.3(2)	106.6(2)
S(L)–Sn–S(L)–C^d	−31.8(2)	−33.3(3)	−34.2(2)	−9.9(1)	36.4(5)	−37.4(4)	−31.4(2)	−28.6(2)
C–C–S–C^e	130.1(3)	128.9(6)	127.5(4)	132.0(2)	−135.4(8)	136.4(7)	132.8(4)	131.8(4)
C–C–S–C^e	−73.6(4)	−74.8(6)	−75.5(4)	−65.2(3)	81.3(9)	−87.3(8)	−69.8(4)	−65.0(5)

[a] S = sulfur thioether-like donor atom.
[b] S(L) = each sulfur thiolate-like atoms in the S(C_6H_4S)$_2^{2-}$ moiety.
[c] S(dtc) = each sulfur of the dithiocarbamate ligand.
[d] Each torsion angle in the central eight-membered ring containing both sulfur thiolate-like, tin and one benzenic carbon atoms.
[e] Each torsion angle in the central eight-membered ring containing the sulfur thioether-like donor atom and three benzenic carbon atoms.

Table 6
Comparison of S···Sn–L^1 geometrical bond parameters in dibenzostannocines [{S(C_6H_4S)$_2$}SnL^{1}L^2] **1**–**5**; bond lengths (Å), bond angles (°), TBP% and Bond Order.

	L^1	L^2	S···Sn	S···Sn–L^1	TBP%	Δd^a	BO^{b}S···Sn
1	Cl	Ph	2.827(1)	166.9(4)	74.1	0.397	0.275
2	Br	Ph	2.834(2)	167.9(5)	73.6	0.404	0.269
3	I	Ph	2.840(1)	169.0(3)	73.2	0.410	0.264
4	Ph	Ph	3.162(9)	164.6(8)	52.2	0.732	0.093
5a	Cl	Cl	2.725(2)	176.3(1)	80.7	0.295	0.384
5b	Cl	Cl	2.735(2)	175.3(1)	80.1	0.305	0.372

[a] Bond widening, $\Delta d = (d_{exp} - \Sigma r_{cov})$, according to standard bond distances d(Sn, S) 2.43 Å.
[b] Mode of calculation BO = 10 − (1.41 Δd).

pound **6** is shorter than the observed in stannocanes containing an hexacoordinate tin atom [3.074(3) and 3.241(3) Å in {S(CH_2CH_2S)$_2$}Sn] [28]. In both conformers the diethyldithiocarbamate ligand is symmetrically coordinated to the tin atom; the Sn–S(dtc) distances are slightly different, see Table 5, with bite angles of 69.80(4)° and 69.60(5)°. Hence, the geometry of the coordination sphere of the tin atom can be described as distorted octahedral. The tridentate ligand {S(C_6H_4S)$_2$}$^{2-}$ is occupying a *fac* position into the octahedron. It is interesting to note the geometrical change in the position of the phenyl group; in the parent compound **1** as well as in the other halocompounds **2** and **3**, the phenyl group is in a *cis* position respect to the transannular interaction S···Sn whereas in the dithiocarbamate compound **6** is in a *trans* position, showing the higher electronic requirements of the Ph group as compared with the dithiocarbamate ligand when they are coordinated to the tin included in the dibenzostannocine moiety.

With respect to the eight-membered ring conformation in the dibenzostannocines **1**–**6** it can be described as twist-boat (C_1 symmetry), description based on the non equivalence of the torsion angles, see Table 5.

4. Conclusion

In order to study the phenomena of hypervalence in eight-membered ring compounds we have synthesized and structurally characterized six new dibenzostannocines of the type [{S(C_6H_4S)$_2$}SnL^{1}L^2] by using the {S(C_6H_4S)$_2$}$^{2-}$ potentially tridentate ligand. In this study, the nature of the substituents L^1 (Cl, Br, I and Ph) and L^2 (Cl and Ph) is a determinant factor in the enhancing of the intramolecular interaction between the sulfur and the tin atoms; the S···Sn distance is shorter when the substituents are highly electronegative atoms such as the halogen ligands and is longer when the substituents are less electronegative such as the phenyl group. In the solid state, the dibenzostannocines with two chloro ligands display the highest TBP% character and BO while the lowest values are observed in the dibenzostannocines with two phenyl ligands. Lastly, the insertion of the dithiocarbamate ligand prompts the increase of the coordination number of the tin atom, remaining the interaction S···Sn.

5. Supplementary data

CCDC 756927, 756928, 756929, 756930, 756931, and 756932 contains the supplementary crystallographic data for **1**, **2**, **3**, **4**, **5** and **6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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References

[1] Y.I. Baukov, S.N. Tandura, Hypervalent compounds of organic germanium, tin and lead derivatives, in: Zvi Rappoport (Ed.), The Chemistry of Organic Germanium Tin and Lead Compounds, vol 2, John Wiley and Sons, England, 2002.
[2] T. Munguia, M. López Cardoso, F. Cervantes Lee, K.H. Panell, Inorg. Chem. 46 (2007) 1305.
[3] K. Tani, S. Kato, T. Kanda, S. Inagaki, Org. Lett. 3 (2001) 655.
[4] R. Cea Olivares, V. García Montalvo, M.M. Moya Cabrera, Coord. Chem. Rev. 249 (2005) 859 (and references therein cited).
[5] N.V. Timosheva, T.K. Prakasha, A. Chandrasekaran, R.O. Day, R.R. Holmes, Inorg. Chem. 35 (1996) 3614.
[6] T.K. Prakasha, S. Srinivasan, A. Chandrasekaran, R.O. Day, R.R. Holmes, J. Am. Chem. Soc. 117 (1995) 10003.

[7] A. Chandrasekaran, R.O. Day, R.R. Holmes, Inorg. Chem. 36 (1997) 2578.
[8] A. Chandrasekaran, P. Sood, R.O. Day, R.R. Holmes, Inorg. Chem. 38 (1999) 3952.
[9] S.D. Pastor, V. Huang, D. NabiRahni, Inorg. Chem. 36 (1997) 5966.
[10] T. Thompson, S.D. Pastor, G. Rihs, Inorg. Chem. 38 (1999) 4163.
[11] M.Y. Chiang, J.W. Lin, W.F. Zeng, Acta Crystallogr., Sect. C 61 (2005) m84.
[12] S. González-Montiel, N. Andrade-López, V. García-Montalvo, J.A. Cogordan, J.G. Alvarado-Rodríguez, Eur. J. Inorg. Chem. (2006) 4752.
[13] B. Flores Chávez, J.G. Alvarado-Rodríguez, N. Andrade-López, V. García-Montalvo, E. Aquino-Torres, Polyhedron 28 (2009) 782.
[14] D. Sellmann, D. Haussinger, Eur. J. Inorg. Chem. (1999) 1715.
[15] G.M. Sheldrick, SHELXTL 5.10, Bruker AXS, Inc., Madison, WI, USA, 1998.
[16] G.M. Sheldrick, SADABS Area-Detector Absorption Correction, Siemens Industrial Automation, Inc., Madison, WI, 1996.
[17] J. Otera, J. Organomet. Chem. 221 (1981) 57.
[18] J. Holecek, M. Nadvornik, K. Handlir, J. Organomet. Chem. 241 (1983) 177.
[19] B. Wrackmeyer, Modern Magnetic Resonance, Part 1, in: A. Graham Webb (Ed.), Springer, Netherlands, 2008, p. 461.
[20] M. Draeger, J. Organomet. Chem. 251 (1983) 209.
[21] M. Draeger, R. Engler, Chem. Ber. 108 (1975) 17.
[22] M. Draeger, Chem. Ber. 114 (1981) 2051.
[23] U. Kolb, M. Beuter, M. Gerner, M. Draeger, Organometallics 13 (1994) 4413.
[24] U. Kolb, M. Beuter, M. Draeger, Inorg. Chem. 33 (1994) 4522.
[25] M. Draeger, Z. Anorg. Allg. Chem. 527 (1985) 169.
[26] M. Draeger, H.J. Guttmann, J. Organomet. Chem. 212 (1981) 171.
[27] J.J. Zhang, W.X. Du, S.M. Hu, S.Q. Xia, L.S. Wang, X.T. Wu, Inorg. Chem. Commun. 6 (2003) 387.
[28] R. Cea-Olivares, V. Lomeli, S. Hernández-Ortega, S.I. Haiduc, Polyhedron 14 (1995) 747.
[29] P.G. García, R. Cruz-Almanza, R.A. Toscano, R. Cea-Olivares, J. Organomet. Chem. 598 (2000) 160.
[30] A.L. Beauchamp, S. Latour, M.J. Olivier, J.D. Wuest, J. Am. Chem. Soc. 105 (1983) 7778.
[31] P. García y García, A.M. Cotero-Villegas, M. López-Cardoso, V. García-Montalvo, R.A. Toscano, A. Gómez-Ortíz, R. Ferrari Zijlstra, R. Cea-Olivares, J. Organomet. Chem. 587 (1999) 214.
[32] J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry: Principles of Structure and Reactivity, fourth ed., Harper Collins College Publishers, USA, 1993. p. A30.
[33] P.T. Greene, R.F. Bryan, J. Chem. Soc. A (1971) 2549.
[34] J.S. Tse, F.L. Lee, E.J. Gabe, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 42 (1986) 1876.
[35] M. Charisse, B. Mathiasch, M. Draeger, U. Russo, Polyhedron 14 (1995) 2429.
[36] W.W. Porterfield, Inorganic Chemistry: A Unified Approach, second ed., Academic Press, Inc., USA, 1993. p. 214.
[37] A. Bondi, J. Phys. Chem. 68 (1964) 441.
[38] N.W. Alcock, Adv. Inorg. Chem. Radiochem. 15 (1972) 1.
[39] A. Chandrasekaran, P. Sood, R.O. Day, R.R. Holmes, Inorg. Chem. 38 (1999) 3369.
[40] N.V. Timosheva, A. Chandrasekaran, R.O. Day, R.R. Holmes, Inorg. Chem. 37 (1998) 3862.
[41] D.J. Sherlock, A. Chandrasekaran, R.O. Day, R.R. Holmes, Inorg. Chem. 36 (1997) 5082.
[42] L. Pauling, The Nature of the Chemical Bond, third ed., Cornell University Press, Ithaca, NY, 1960. p. 239.