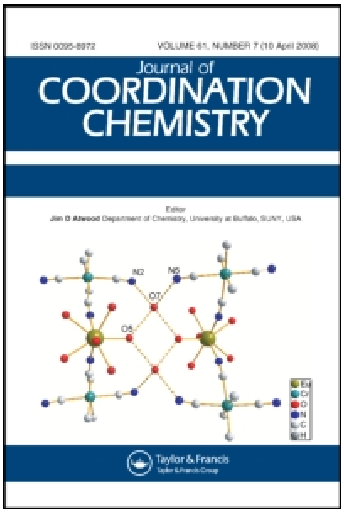

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Synthesis and spectroscopic characterization of new organotin(IV) complexes with bis(3,5-dimethylpyrazol-1-yl)dithioacetate

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Synthesis and spectroscopic characterization of new organotin(IV) complexes with bis(3,5-dimethylpyrazol-1-yl)dithioacetate

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New organotin(IV) derivatives containing the anionic ligand bis(3,5-dimethylpyrazolyl)dithioacetate $[L_2CS_2]^-$ have been synthesized by reaction of SnR_nX_{4-n} ($R = Me$, Ph, ^{n}Bu or Cy; $n = 1$–3) acceptors and $Li[L_2CS_2]$. Mononuclear complexes of the type $[L_2CS_2]R_nSnCl_{4-n-1}\}$ have been obtained and fully characterized by elemental analyses and FT-IR in the solid state, and by NMR (^{1}H and ^{119}Sn) spectroscopy, conductivity measurements and electrospray ionization mass spectrometry (ESI-MS) in solution. ESI-MS spectra of methanol solutions of diorganotin derivatives, recorded with fragmentor potentials of 0, 50, 100 and 150 V, show the occurrence at 150 V of peaks attributable to the loss of the CS_2 group from the ligands and the formation of stable tetraorganodistannoxane species.

Keywords: Organotin(IV); Bis(3,5-dimethylpyrazolyl)dithioacetate; Pyrazole; Tin-119 NMR; Electrospray ionization mass spectroscopy

1. Introduction

Since the first report of Trofimenko [1], poly(pyrazolyl)borates, or scorpionate ligands, have been used extensively as anionic σ-donor ligands in a wide variety of metal complexes [2]. Modifications of poly(pyrazolyl)borates can be made by replacement of the bridging boron atom with carbon, silicon or phosphorus. Other important variations can be effected by changing the substituents on the heterocyclic ring or by replacing the pyrazolyl with triazolyl, imidazolyl and methimazolyl moieties [3]. Otero *et al.* [4] introduced for the first time the bis(3,5-dimethylpyrazol-1-yl)acetate, a scorpionate ligand with a carboxylate and two pyrazole donor groups.

The bis(3,5-dimethylpyrazol-1-yl)dithioacetates [5,6] are analogues of bis(pyrazolyl)-acetates but with a soft dithiocarboxylate fragment on the central carbon. They can be

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easily deprotonated and can act in the anionic form like poly(pyrazolyl)borates. A series of titanium complexes of the bis(pyrazolyl)dithioacetate, $[LCS_2]^-$, has been prepared by reaction of $TiCl_4(THF)_2$ with lithium bis(pyrazolyl)dithioacetate, $Li[LCS_2]$, where a κ^3-N,N,S coordination is proposed; $[TiCl_2(\kappa^2\text{-}LCS_2)_2]$ is an exception where each $[LCS_2]^-$ ligand is coordinated to the titanium atom through a κ^2-S,S coordination mode [5].

To date, some organometallic alkynylcarbyne tungsten [7], alkylzinc [8] and tricarbonyl complexes of manganese and rhenium [9] have been reported for bis(pyrazolyl)-acetates but no organometallic derivatives have been synthesized involving bis(pyrazolyl)dithioacetate. For this reason we have decided to extend the coordination chemistry of bis(3,5-dimethylpyrazolyl)dithioacetate toward organotin(IV) acceptors. Our interest in the coordination chemistry of tin and organotin acceptors with poly (azolyl)alkanes [10], β-diketones [11] and poly(azolyl)borates [12] is long-standing. An additional reason for this study is based on the biological activity, use in antifouling paints and antitumor activity displayed by many organotin(IV) derivatives containing mixed N,X-ligands (X = O, S, P, etc.) [13–15]. In addition, many tri- and diorganotin(IV) compounds have been used as reagents or catalysts in organic reactions [16,17]. Another important industrial use of organotin compounds is in the stabilization of PVC [18]. Aside from these applications, organotin compounds are also of interest in view of the considerable structural diversity that they possess. This aspect has attracted the attention of a number of groups and a multitude of structural types has been discovered [19].

2. Experimental

2.1. *General*

All syntheses were carried out under a nitrogen atmosphere. All solvents were distilled and degassed with dry nitrogen prior to use. The samples for microanalysis were dried *in vacuo* to constant weight (20°C, *ca* 0.1 Torr). Elemental analyses (C, H, N, S) were performed with a Fisons Instruments 1108 CHNS-O apparatus. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument. ^1H and ^{119}Sn NMR spectra were recorded on a Varian VXR-300 spectrometer operating at room temperature (300 MHz for ^1H and 111.9 MHz for ^{119}Sn). Melting points were recorded on an SMP3 Stuart Scientific instrument. Electrospray ionization mass spectrometry (ESI-MS) was obtained in positive- or negative-ion mode on an HP Series 1100 MSD spectrometer, using acetone as the mobile phase. The compounds were added to reagent-grade methanol to give solutions of approximate concentration 1 mM. These solutions were injected (1 μL) into the spectrometer via an HP 1090 Series II HPLC pump fitted with an autosampler. The pump delivered the solutions to the mass spectrometer source at a flow rate of 300 $\mu L\,min^{-1}$, and nitrogen was used as both drying and nebulizing gas. Capillary voltages were typically 4000 and 3500 V for the positive- and negative-ion modes, respectively. Mass spectra were acquired by scanning from m/z 50 to 1500, with a fragmentor potential of 30 V; for derivatives **2**, $[(LCS_2)SnMe_2Cl]$, and **9**, $[(LCS_2)SnPh_2Cl]$, the mass spectra were also obtained with potentials of 0, 50, 100, 150, 200, 250, 300, 350 and 400 V. Confirmation of all major species in the ESI-MS study was aided by comparison of observed and predicted isotope distribution patterns, the latter calculated using the IsoPro program [20].

2.2. *Syntheses*

All reagents were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received. The ligand Li[LCS$_2$] was prepared according to a literature method [5].

2.2.1. Synthesis of [(LCS$_2$)Sn(CH$_3$)Cl$_2$] (1). To a CH$_2$Cl$_2$ solution (50 cm^3) of (CH$_3$)SnCl$_3$ (0.240 g, 1.0 mmol), Li[LCS$_2$] (0.286 g, 1.0 mmol) was added. The mixture was stirred for 4 h at room temperature, then solvent was removed on a rotary evaporator and chloroform added (20 cm^3). LiCl was removed by filtration and the filtrate reduced to half volume. Diethylether (40 cm^3) was added to give a colorless precipitate, which was filtered off, washed with *n*-hexane (10 cm^3) and dried to constant weight under reduced pressure. Yield: 55%. Mp: 200°C dec. IR (nujol mull, cm^{-1}): 3137w, 3114w (CH), 1557s (C=N, C=C), 1042m ($\nu_{asym}CS_2^-$), 808m ($\nu_{sym}CS_2^-$), 542s (Sn–C), 430m (Sn–S), 302m (Sn–N), 291s, 270s (Sn–Cl). ^{1}H NMR (DMSO, 293 K): δ 0.82 (s, 3H, Sn–C*H*$_3$, $^2J(^{119}\text{Sn}–^1\text{H}) = 117$ Hz, $^2J(^{117}\text{Sn}–^1\text{H}) = 111$ Hz), 2.08 (s, 6H, 3- or 5-C*H*$_3$), 2.46 (s, 6H, 3- or 5-C*H*$_3$), 5.90 (s, 2H, 4-C*H*), 7.45 (sbr, 1H, C*H*). ^{119}Sn NMR (DMSO, 293 K): δ–429.6 (s). Anal. Calcd. for C$_{13}$H$_{18}$Cl$_2$N$_4$S$_2$Sn(%): C, 32.26; H, 3.75; N, 11.58; S, 13.25. Found: C, 32.09; H, 3.81; N, 11.49; S, 13.01.

2.2.2. Synthesis of [(LCS$_2$)Sn(CH$_3$)$_2$Cl] (2). Compound **2** was prepared similarly to compound **1**, by using (CH$_3$)$_2$SnCl$_2$ (0.220 g, 1.0 mmol) and Li[LCS$_2$] (0.286 g, 1.0 mmol) in dichloromethane solution (30 cm^3). Recrystallization from diethylether gave complex **2** as a microcrystalline solid (85% yield). Mp: 155–158°C dec. IR (nujol mull, cm^{-1}): 3130w, 3096w (CH), 1558s (C=N, C=C), 1038m ($\nu_{asym}CS_2^-$), 810m ($\nu_{sym}CS_2^-$), 550s, 520s (Sn–C), 402w (Sn–S), 306w (Sn–N), 250s, 243s (Sn–Cl). ^{1}H NMR (CDCl$_3$, 293 K): δ 1.04 (s, 6H, Sn–C*H*$_3$, $^2J(^{119}\text{Sn}–^1\text{H}) = 75$ Hz, $^2J(^{117}\text{Sn}–^1\text{H}) = 72$ Hz), 2.19 (s, 6H, 3- or 5-C*H*$_3$), 2.45 (s, 6H, 3- or 5-C*H*$_3$), 6.05 (s, 2H, 4-C*H*), 7.05 (s, 1H, C*H*). ^{1}H NMR (CDCl$_3$, 218 K): δ 1.16 (sbr, 6H, Sn–C*H*$_3$), 2.15 (s, 3H, 3- or 5-C*H*$_3$), 2.20 (s, 3H, 3- or 5-C*H*$_3$), 2.25 (s, 3H, 3- or 5-C*H*$_3$), 2.45 (s, 3H, 3- or 5-C*H*$_3$), 5.95 (s, 1H, 4-C*H*), 6.09 (s, 1H, 4-C*H*), 7.05 (s, 1H, C*H*). ^{119}Sn NMR (CDCl$_3$, 293 K): δ –188.6 (s). ESI-MS (acetone) *m*/*z* (%): (–) 463 (100) [(LCS$_2$)SnMe$_2$Cl – H$^+$]$^-$. ESI-MS (acetone) *m*/*z* (%): (+) 428 (100) [(LCS$_2$)(SnMe$_2$)]$^+$, 873 (20) [(LCS$_2$)$_2$(SnMe$_2$)$_2$(OH)]$^+$. Anal. Calcd. for C$_{14}$H$_{21}$ClN$_4$S$_2$Sn(%): C, 36.27; H, 4.57; N, 12.08; S, 13.83. Found: C, 36.45; H, 4.48; N, 12.23; S, 13.51.

2.2.3. Synthesis of (LCS$_2$)Sn(CH$_3$)$_3$ (3). Compound **3** was prepared similarly to compound **1**, by using (CH$_3$)$_3$SnCl (0.199 g, 1.0 mmol) and Li[LCS$_2$] (0.286 g, 1.0 mmol) in dichloromethane solution (30 cm^3). Recrystallization from diethylether/*n*-hexane gave complex **3** as a microcrystalline solid (45% yield). Mp: 155°C dec. IR (nujol mull, cm^{-1}): 3116w, 3104w (CH), 1563s (C=N, C=C), 1079m ($\nu_{asym}CS_2^-$), 871m, 859m ($\nu_{sym}CS_2^-$), 545m (Sn–C), 368w (Sn–S). ^{1}H NMR (CDCl$_3$, 293 K): δ 0.63 (s, 9H, Sn–C*H*$_3$, $^2J(^{119}\text{Sn}–^1\text{H}) = 57$ Hz, $^2J(^{117}\text{Sn}–^1\text{H}) = 55$ Hz), 2.02 (s, 6H, 3- or 5-C*H*$_3$), 2.43 (s, 6H, 3- or 5-C*H*$_3$), 5.85 (s, 2H, 4-C*H*), 7.09 (sbr, 1H, C*H*). ^{119}Sn NMR (CDCl$_3$, 293 K): δ 79.8 (s). ESI-MS (acetone) *m*/*z* (%): (–) 235 (60) [Sn(CH$_3$)$_3$Cl$_2$]$^-$, 279 (100) [LCS$_2$]$^-$, 463 (20) [(LCS$_2$)Sn(CH$_3$)$_2$Cl – H$^+$]$^-$, 442 (60)

$[(LCS_2)Sn(CH_3)_3-H^+]^-$. ESI-MS (acetone) m/z (%): (+) 164 (20) $[Sn(CH_3)_3]^+$, 444 (60) $[(LCS_2)Sn(CH_3)_3+H^+]^+$. Anal. Calcd. for $C_{15}H_{24}N_4S_2Sn$(%): C, 40.65; H, 5.46; N, 12.64; S, 14.47. Found: C, 40.41; H, 5.36; N, 12.50; S, 14.29.

2.2.4. Synthesis of $[(LCS_2)Sn(C_4H_9)Cl_2]$ (4). Compound **4** was prepared similarly to compound **1**, by using $(C_4H_9)SnCl_3$ (0.282 g, 1.0 mmol) and $Li[LCS_2]$ (0.286 g, 1.0 mmol) in dichloromethane solution (30 cm^3). Recrystallization from diethylether gave complex **4** as a microcrystalline solid (69% yield). Mp: 150°C dec. IR (nujol mull, cm^{-1}): 3078w, 3013w (CH), 1558s (C=N, C=C), 1039s ($\nu_{asym}CS_2^-$), 813s ($\nu_{sym}CS_2^-$), 601m (Sn–C), 413m (Sn–S), 298sh (Sn–N), 286s (Sn–Cl). ^{1}H NMR ($CDCl_3$): δ 0.94 (t, 3H, $CH_3(CH_2)_3Sn$), 1.43 (mc, 2H, $CH_3(CH_2)_3Sn$), 1.80 (mc, 2H, $CH_3(CH_2)_3Sn$), 2.03 (mc, 2H, $CH_3(CH_2)_3Sn$), 2.47 (s, 6H, 3- or 5-CH_3), 2.64 (s, 6H, 3- or 5-CH_3), 6.16 (s, 2H, 4-CH), 7.35 (s, 1H, CH). ^{119}Sn NMR ($CDCl_3$, 293 K): δ −448.1 (s). ESI-MS (acetone) m/z (%): (−) 525 (100) $[(LCS_2)Sn(C_4H_9)Cl_2-H^+]^-$. ESI-MS (acetone) m/z (%): (+) 268 (40) $[(C_4H_9)_2SnCl]^+$, 491 (60) $[(LCS_2)Sn(C_4H_9)Cl]^+$, 527 (100) $[(LCS_2)Sn(C_4H_9)Cl_2+H^+]^+$, 773 (40) $[(LCS_2)\{Sn(C_4H_9)Cl_2\}_2]^+$. Anal. Calcd. for $C_{16}H_{24}Cl_2N_4S_2Sn$(%): C, 36.53; H, 4.60; N, 10.65; S, 12.19. Found: C, 36.42; H, 4.70; N, 10.53; S, 11.98.

2.2.5. Synthesis of $[(LCS_2)Sn(C_4H_9)_2Cl]$ (5). Compound **5** was prepared similarly to compound **1**, by using $(C_4H_9)_2SnCl_2$ (0.304 g, 1.0 mmol) and $Li[LCS_2]$ (0.286 g, 1.0 mmol) in dichloromethane solution (30 cm^3). Recrystallization from dichloromethane gave complex **5** as a microcrystalline solid (53% yield). Mp: 82–85°C dec. IR (nujol mull, cm^{-1}): 3122w (CH), 1551m (C=N, C=C), 1034m ($\nu_{asym}CS_2^-$), 860m, 825m ($\nu_{sym}CS_2^-$), 599m, 587m (Sn–C), 404w (Sn–S), 326w, 301s (Sn–N), 240sbr (Sn–Cl). ^{1}H NMR ($CDCl_3$, 293 K): δ 0.86 (t, 6H, $CH_3(CH_2)_3Sn$), 1.40 (mc, 4H, $CH_3(CH_2)_3Sn$), 1.68 (mc, 4H, $CH_3(CH_2)_3Sn$), 1.76 (mc, 4H, $CH_3(CH_2)_3Sn$), 2.18 (s, 6H, 3- or 5-CH_3), 2.48 (sbr, 6H, 3- or 5-CH_3), 5.97 (s, 2H, 4-CH), 7.12 (s, 1H, CH). ^{1}H NMR ($CDCl_3$, 218 K): δ 0.88 (br, 6H, $CH_3(CH_2)_3Sn$), 1.36 (br, 4H, $CH_3(CH_2)_3Sn$), 1.61 (br, 4H, $CH_3(CH_2)_3Sn$), 1.78 (br, 4H, $CH_3(CH_2)_3Sn$), 2.22 (s, 3H, 3- or 5-CH_3), 2.28 (s, 3H, 3- or 5-CH_3), 2.44 (s, 3H, 3- or 5-CH_3), 2.49 (s, 3H, 3- or 5-CH_3), 6.02 (s, 1H, 4-CH), 6.10 (s, 1H, 4-CH), 7.02 (s, 1H, CH). ^{119}Sn NMR ($CDCl_3$, 293 K): δ −183.1 (s). ESI-MS (acetone) m/z (%): (−) 547 (100) $[(LCS_2)Sn(C_4H_9)_2Cl-H^+]^-$. ESI-MS (acetone) m/z (%): (+) 512 (100) $[(LCS_2)Sn(C_4H_9)_2]^+$. Anal. Calcd. for $C_{20}H_{33}ClN_4S_2Sn$(%): C, 43.85; H, 6.07; N, 10.23; S, 11.71. Found: C, 43.55; H, 6.23; N, 10.33; S, 11.44.

2.2.6. Synthesis of $[(LCS_2)Sn(C_4H_9)_3]$ (6). Compound **6** was prepared similarly to compound **1**, by using $(C_4H_9)_3SnCl$ (0.325 g, 1.0 mmol) and $Li[LCS_2]$ (0.286 g, 1.0 mmol) in dichloromethane solution (30 cm^3) at 243 K. Purification from petroleum ether gave complex **6** as microcrystalline solid (42% yield). Mp: 110°C dec. IR (nujol mull, cm^{-1}): 3185w (CH), 1563s (C=N, C=C), 1076m, 1035m ($\nu_{asym}CS_2^-$), 872m, 858m ($\nu_{sym}CS_2^-$), 589br (Sn–C), 419w (Sn–S). ^{1}H NMR ($CDCl_3$, 293 K): δ 0.89 (t, 9H, $CH_3(CH_2)_3Sn$), 1.29 (mc, 6H, $CH_3(CH_2)_3Sn$), 1.59 (mc, 6H, $CH_3(CH_2)_3Sn$), 1.70 (mc, 6H, $CH_3(CH_2)_3Sn$), 2.06 (s, 6H, 3- or 5-CH_3), 2.43 (sbr, 6H, 3- or 5-CH_3), 5.85 (s, 2H, 4-CH), 7.10 (s, 1H, CH). ^{119}Sn NMR ($CDCl_3$, 293 K): 70 (br). ESI-MS (acetone) m/z (%): (−) 279 (100) $[LCS_2]^-$, 547 (40) $[(LCS_2)Sn(C_4H_9)_2Cl-H^+]^-$, 568 (60) $[(LCS_2)Sn(C_4H_9)_3-H^+]^-$, 791 (30) $[(LCS_2)_2Sn(C_4H_9)_2-H^+]^-$. ESI-MS (acetone) *m*/*z* (%): (+) 512 (50) $[(LCS_2)Sn(C_4H_9)_2]^+$, 570 (60) $[(LCS_2)Sn(C_4H_9)_3+H^+]^+$, 593 (100) $[(LCS_2)_2Sn(C_4H_9)_3+Na^+]^+$. Anal. Calcd. for $C_{24}H_{42}N_4S_2Sn$(%): C, 50.62; H, 7.43; N, 9.84; S, 11.26. Found: C, 50.02; H, 7.53; N, 9.96; S, 10.86.

2.2.7. Synthesis of $[(LCS_2)Sn(C_6H_{11})_3]$ (7). Compound **7** was prepared similarly to compound **1**, by using $(C_6H_{11})_3SnCl$ (0.404 g, 1.0 mmol) and $Li[LCS_2]$ (0.286 g, 1.0 mmol) in THF solution (30 cm^3) at 243 K. Purification from petroleum ether gave complex **7** as microcrystalline solid (48% yield). Mp: 170°C dec. IR (nujol mull, cm^{-1}): 3114w (CH), 1560s (C=N, C=C), 1080m, 1039m ($\nu_{asym}CS_2^-$), 871m ($\nu_{sym}CS_2^-$), 490s (Sn–C), 418m (Sn–S). ^{1}H NMR ($CDCl_3$, 293 K): δ 1.30–2.00 (m, 33H, Sn–C_6H_{11}), 2.15 (s, 6H, 3- or 5-C*H*$_3$), 2.23 (sbr, 6H, 3- or 5-C*H*$_3$), 5.92 (s, 2H, 4-C*H*), 7.12 (s, 1H, C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): δ 23.2 (s). ESI-MS (acetone) *m*/*z* (%): (–) 279 (40) $[LCS_2]^-$, 439 (60) $[Sn(C_6H_{11})_3Cl_2]^-$, 599 (100) $[(LCS_2)Sn(C_6H_{11})_2Cl-H^+]^-$, 842 (15) $[\{Sn(C_6H_{11})_3\}_2Cl_3]^-$, 1049 (80) $[(LCS_2)\{Sn(C_6H_{11})_3\}_2Cl-H^+]^-$. ESI-MS (acetone) *m*/*z* (%): (+) 648 (90) $[(LCS_2)Sn(C_6H_{11})_3+H^+]^+$, 772 (60) $[\{Sn(C_6H_{11})_3\}_2Cl]^+$. Anal. Calcd. for $C_{30}H_{48}N_4S_2Sn$(%): C, 55.65; H, 7.47; N, 8.65; S, 9.90. Found: C, 55.46; H, 7.65; N, 8.35; S, 9.57.

2.2.8. Synthesis of $[(LCS_2)Sn(C_6H_5)Cl_2]$ (8). Compound **8** was prepared similarly to compound **1**, by using $(C_6H_5)SnCl_3$ (0.302 g, 1.0 mmol) and $Li[LCS_2]$ (0.286 g, 1.0 mmol) in dichloromethane solution (30 cm^3). Recrystallization from petroleum ether gave complex **8** as a microcrystalline solid (78% yield). Mp: 200°C dec. IR (nujol mull, cm^{-1}): 3139w, 3071w (CH), 1560s (C=N, C=C), 1053s, 1044s ($\nu_{asym}CS_2^-$), 804s ($\nu_{sym}CS_2^-$), 430m (Sn–S), 300w (Sn–N), 295s (Sn–Cl), 266m (Sn–C). ^{1}H NMR ($CDCl_3$): δ 2.00 (s, 6H, 3- or 5-C*H*$_3$), 2.55 (s, 6H, 3- or 5-C*H*$_3$), 6.11 (s, 2H, 4-C*H*), 7.28–7.60 (m, 5H, C_6H_5), 7.45 (s, 1H, C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): δ –508.6 (s). ESI-MS (acetone) *m*/*z* (%): (–) 545 (60) $[(LCS_2)Sn(C_6H_5)Cl_2-H^+]^-$. Anal. Calcd. for $C_{18}H_{20}Cl_2N_4S_2Sn$(%): C, 39.59; H, 3.69; N, 10.26; S, 11.74. Found: C, 39.32; H, 3.74; N, 10.51; S, 11.90.

2.2.9. Synthesis of $[(LCS_2)Sn(C_6H_5)_2Cl]$ (9). Compound **9** was prepared similarly to compound **1**, by using $(C_6H_5)_2SnCl_2$ (0.344 g, 1.0 mmol) and $Li[LCS_2]$ (0.286 g, 1.0 mmol) in dichloromethane solution (30 cm^3). Recrystallization from petroleum ether gave complex **9** as a microcrystalline solid (52% yield). Mp: 160°C dec. IR (nujol mull, cm^{-1}): 3130w, 3121w (CH), 1554m (C=N, C=C), 1032m ($\nu_{asym}CS_2^-$), 814m ($\nu_{sym}CS_2^-$), 418w (Sn–S), 303m (Sn–N), 266s (Sn–Cl), 253s, 229s (Sn–C). ^{1}H NMR ($CDCl_3$, 293 K): δ 2.13 (s, 6H, 3- or 5-C*H*$_3$), 2.42 (s, 6H, 3- or 5-C*H*$_3$), 5.84 (s, 2H, 4-C*H*), 7.25–7.70 (m, 11H, C*H* and C_6H_5). ^{1}H NMR ($CDCl_3$, 218 K): δ 1.70 (s, 3H, 3- or 5-C*H*$_3$), 1.94 (s, 3H, 3- or 5-C*H*$_3$), 2.39 (s, 3H, 3- or 5-C*H*$_3$), 2.75 (s, 3H, 3- or 5-C*H*$_3$), 5.42 (s, 1H, 4-C*H*), 5.86 (s, 1H, 4-C*H*), 7.36 (s, 1H, C*H*), 7.20–7.51 (m, 10H, C_6H_5). ^{119}Sn NMR ($CDCl_3$, 293 K): δ –302.1 (s). ESI-MS (acetone) *m*/*z* (%): (–) 587 (100) $[(LCS_2)Sn(C_6H_5)_2Cl-H^+]^-$. ESI-MS (acetone) *m*/*z* (%): (+) 552 (100) $[(LCS_2)Sn(C_6H_5)_2]^+$. Anal. Calcd. for $C_{24}H_{25}ClN_4S_2Sn$(%): C, 49.05; H, 4.29; N, 9.53; S, 10.91. Found: C, 48.91; H, 4.37; N, 9.40; S, 10.76.

2.2.10. Synthesis of $[(LCS_2)Sn(C_6H_5)_3]$ (10). Compound **10** was prepared similarly to compound **1**, by using $(C_6H_5)_3SnCl$ (0.385 g, 1.0 mmol) and $Li[LCS_2]$ (0.286 g, 1.0 mmol) in dichloromethane solution (30 cm^3). Recrystallization from petroleum ether gave complex **10** as a microcrystalline solid (54% yield). Mp: 70°C dec. IR (nujol mull, cm^{-1}): 3130w (CH), 1560s (C=N, C=C), 1073m ($\nu_{asym}CS_2^-$), 851m ($\nu_{sym}CS_2^-$), 421w (Sn–S), 303s, 269sbr (Sn–C). ^1H NMR ($CDCl_3$, 293 K): δ 1.70 (s, 6H, 3- or 5-CH_3), 2.18 (s, 6H, 3- or 5-CH_3), 5.82 (s, 2H, 4-C*H*), 7.30–7.68 (m, 16H, C*H* and C_6H_5). ^{119}Sn NMR ($CDCl_3$, 293 K): δ –112.9(s). ESI-MS (acetone) *m*/*z* (%): (–) 279 (20) $[LCS_2]^-$, 587 (60) $[(LCS_2)Sn(C_6H_5)_2Cl-H^+]^-$, 628 (100) $[(LCS_2)Sn(C_6H_5)_3-H^+]^-$. ESI-MS (acetone) *m*/*z* (%): (+) 350 (100) $[Sn(C_6H_5)_3]^+$, 552 (40) $[(LCS_2)Sn(C_6H_5)_2]^+$, 630 (60) $[(LCS_2)Sn(C_6H_5)_3+H^+]^+$. Anal. Calcd. for $C_{30}H_{30}N_4S_2Sn$(%): C, 57.25; H, 4.80; N, 8.90; S, 10.19. Found: C, 56.91; H, 4.97; N, 8.40; S, 9.96.

3. Results and discussion

Complexes **1**–**10** have been synthesized by metathetic reaction of $Li[LCS_2]$ with SnR_nX_{4-n} in CH_2Cl_2 or THF (equation (1)).

$$Li[LCS_2] + SnR_nCl_{4-n} \rightarrow \underset{\mathbf{1-10}}{[LCS_2]R_nSnCl_{4-n-1}]} + LiCl \tag{1}$$

1: $R = CH_3$, $n = 1$; **2**: $R = CH_3$, $n = 2$; **3**: $R = CH_3$, $n = 3$; **4**: $R = {}^nBu$, $n = 1$; **5**: $R = {}^nBu$, $n = 2$; **6**: $R = {}^nBu$, $n = 3$; **7**: $R = Cy$, $n = 3$; **8**: $R = Ph$, $n = 1$; **9**: $R = Ph$, $n = 2$; **10**: $R = Ph$, $n = 3$.

Derivatives **1**–**10** are reasonably stable in air, but prolonged warming and/or storage under reduced pressure induces some decomposition via decarbonylation with release of CS_2 and formation of a mixture of pyrazole-containing metal complexes and other unidentified products. Compound **1** shows good solubility only in DMSO solution. Derivatives **2**–**10** are stable in alcohols, acetonitrile, acetone and chlorinated solvents, and are nonelectrolytes in CH_2Cl_2 solution.

All complexes were characterized by analytical and spectroscopic data. The infrared spectra carried out on the solid samples (nujol mull) showed all expected bands for the ligands and the tin moieties: weak absorptions near 3100 cm^{-1} are due to pz ring C–H stretching and medium to strong absorptions in the range 1550–1565 cm^{-1} are related to ring "breathing" vibrations.

The presence of the CS_2 group is detected by an intense absorption in the ranges 1032–1080 and 804–872 cm^{-1}, due to asymmetric and symmetric CS_2^- stretching modes, respectively, a red shift with respect to free neutral ligands ($\nu_{asym}CS_2^- = 1078\,cm^{-1}$ and $\nu_{sym}CS_2^- = 831\,cm^{-1}$) being observed upon complex formation. This is in accordance with electronic donation from the ligand to tin, with consequent decreasing C=S bond order. These values fit those reported for analogous Ti complexes [5].

In the far-IR region medium to strong absorptions appear upon coordination, due to Sn–S, Sn–N, Sn–R and Sn–Cl stretching modes [21]. Frequencies of the Sn–Cl mode undergo a decrease on passing from mono- to dialkyl or diphenyl derivatives. Sn–Cl stretching frequencies in the dichloride and monochloride tin(IV) derivatives appear as strong or medium broad bands in the range 270–291 and 240–250 cm^{-1}, respectively, for the alkyl derivatives **1**, **2**, **4** and **5**, and at 295 and 266 cm^{-1} for the phenyl derivatives **8** and **9**. These trends can be easily explained on the basis of the higher inductive effect of chlorine with respect to alkyls or phenyls, which strengthens the Sn–S bond. The absence of Sn–Cl stretching vibrations in the spectra of derivatives **3**, **6**, **7** and

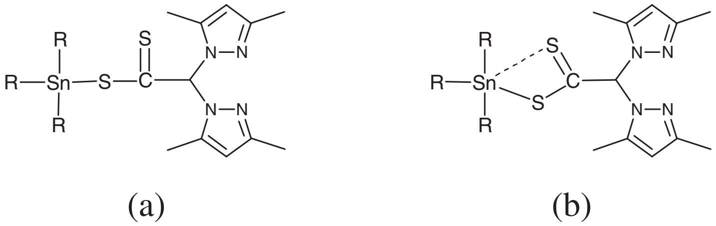

Figure 1. Hypothesized structures in solution for four-coordinate (a) or five-coordinate (b) triorganotin derivatives.

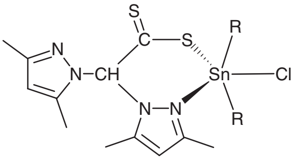

Figure 2. Hypothesized structure in solution for five-coordinate diorganotin derivatives.

10 confirms the substitution of chloride in the tin core by the $[LCS_2]^-$ ligand. In the far-IR spectra the Sn–C stretching frequencies appear as strong or medium broad bands in the range 490–601 cm^{-1} for alkyl derivatives **1**–**7**, and in the range 229–269 cm^{-1} for phenyl complexes **8**–**10**; these absorptions agree well with trends previously observed in similar *N*-donor complexes [22].

In IR spectra of **1**–**10** one absorption assigned to Sn–S is always detected between 368 and 430 cm^{-1}. Sn–N stretching frequencies in the mono- and dichloride tin(IV) derivatives appear as medium or weak bands in the range 326–298 cm^{-1}. The absence of Sn–N stretching vibrations in the spectra of triorganotin derivatives **3**, **6**, **7** and **10** may be due to a four-coordinate configuration around tin, with the ligand acting as a monodentate (κ^1-S [23]; figure 1a) or a five-coordinate arrangement with the ligand acting as an "anisobidentate" (κ^2-S,S′ [24]; figure 1b).

In the ^{1}H NMR spectra of complexes **1**–**10** in $CDCl_3$ solution (see Experimental section), the signals due to the pyrazolyl rings are always deshielded with respect to those in the spectra of the free donor, confirming the existence of the complexes in solution. Room-temperature ^{1}H NMR spectra of derivatives **1**–**10** exhibit only one set of signals for the protons of the pyrazolyl rings of the $[LCS_2]^-$ ligand, resulting from dynamic exchange processes. This is common in complexes of corresponding poly(pyrazolyl)borates [25], suggesting highly fluxional species or complete dissociation and reassociation of the pyrazolyl nitrogens, which occurs rapidly even at lower temperatures. On cooling solutions of mono- and triorganotin derivatives to 223 K, no additional signals due to the pyrazole ring appeared. For diorganotin(IV) derivatives **2**, **5** and **9** it was possible to slow down the rate of the dynamic process responsible for the spectra obtained at room temperature, and at 218 K static spectra were obtained; the resonances due to the pyrazole protons split into two set of signals, one of them being assignable to the free pyrazole ring. This pattern indicates that the two pyrazolyl rings are magnetically different according to the hypothesized five-coordinate tin core (figure 2).

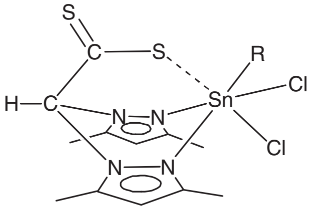

Figure 3. Hypothesized structure in solution for six-coordinate monoorganotin species.

The tin–hydrogen $^{2}J(^{119,117}Sn,^{1}H)$ coupling constants in various cases can be correlated with the percentage of s-character that the Sn atom presents in the Sn–C bond and hence $^{2}J(^{119,117}Sn,^{1}H)$ may give information about the coordination number of tin [26]. In compound **1** it is found that $^{2}J(^{119}Sn,^{1}H)$ has a value of 117 Hz and $^{2}J(^{117}Sn,^{1}H)$ has a value of 111 Hz, not very different from those reported in the literature for six-coordinate organotin(IV) complexes [27,28]. Octahedral coordination around tin is confirmed by the presence of only one sharp signal in ^{119}Sn NMR spectra of **1** at δ −429.6 ppm, in the range typical for other six-coordinate tin(IV) species [29], as expected for the tripodal ligand (κ^3-N,N′,S; figure 3).

^{119}Sn chemical shifts of monoorganotin(IV) derivatives **4** and **8**, at −448.1 and −508.6 ppm, respectively, provide additional support for six-coordinate tin. Moreover, they show that a progressive decomposition process operates in solution; after some days the initial resonances decrease in intensity and new signals appear at −453.0 and −466.2 ppm for derivatives **1** and **4**, respectively, likely due to dissociation of the ligand and formation of solvated tin species.

^{119}Sn chemical shifts of derivatives **2**, **5** and **9**, at −188.6, −183.1 and −302.1 ppm, respectively, are in accordance with those of five-coordinate diorganotin(IV) halides involving S-, O- or N-donors [27,30,31]. In compound **2** $^{2}J(^{119}Sn,^{1}H)$ and $^{2}J(^{117}Sn,^{1}H)$ are 75 and 72 Hz, respectively, falling in the range for other pentacoordinate dimethyltin(IV) species [28]. On the basis of Lockart's equation [28] the Me–Sn–Me angle is estimated to be *ca* 125°, which suggests skewed pentacoordination around tin with an equatorial disposition of both Me groups (figure 2).

The triorganotin(IV) derivatives **3**, **6** and **7** give in ^{119}Sn NMR spectra a single resonance at 79.8 ppm, a very broad peak at *ca* 70 ppm, and a single resonance at 23.2 ppm, respectively, consistent with the range expected for tetrahedral triorganotin compounds [32,33] (figure 1a). Only complex **10** exhibits a resonance at −112.9 ppm, being in the range expected for an intermediate between four- and five-coordinate triorganotin(IV) species and corresponding to an anisobidentate ligand (figure 2).

It was previously observed [34] that ^{119}Sn chemical shifts for the complexes $[R_nSnCl_{4-n-1}(Tp^{\#})]$, plotted against n (where $n = 0$, 1, 2 and 3; R = Me or Ph), show linear correlations within each ligand series, with very similar slopes; the distance between each pair of lines has been empirically interpreted as being roughly proportional to the difference in donating power of each pair of ligands. In figure 4 a similar trend for the new organotin compounds is shown, extending the study to R = ^{n}Bu and to different coordination environments. For monoorganotin(IV) ^{119}Sn NMR resonances are comparable to values previously observed for other classical scorpionate

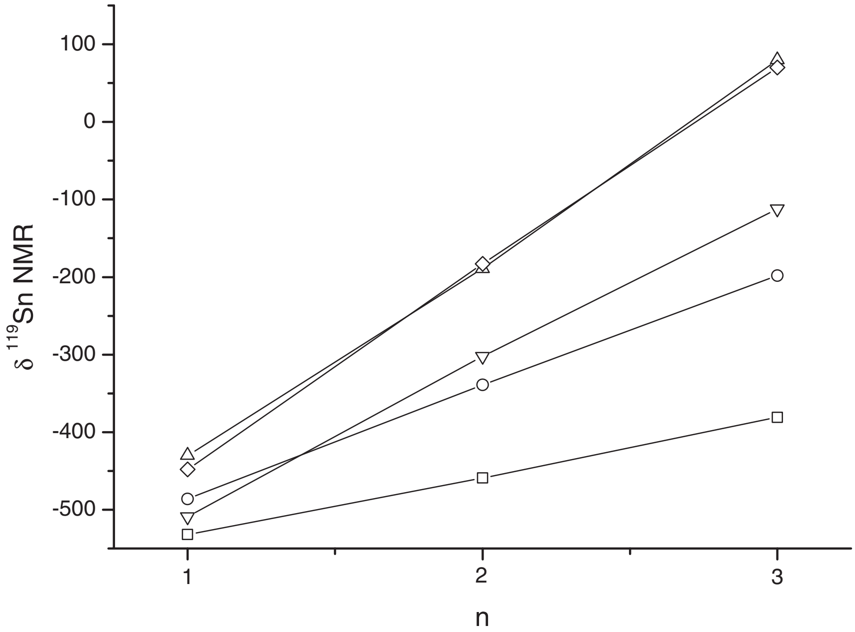

Figure 4. ^{119}Sn chemical shifts of $Cl_{4-n-1}R_nSnTp^{\#}$ where $Tp^{\#} = Tp$ or L_2CS_2: (□) $Cl_{4-n-1}(C_6H_5)_nSnTp$; (○) $Cl_{4-n-1}(CH_3)_nSnTp$; (Δ) $Cl_{4-n-1}(CH_3)_nSn(LCS_2)$; (∇) $Cl_{4-n-1}(C_6H_5)_nSn(LCS_2)$; (◇) $Cl_{4-n-1}(C_4H_9)_n Sn(LCS_2)$.

ligands, in accordance with six coordination around tin. For $[R_nSnCl_{4-n-1}(LCS_2)]$ derivatives where R = Me or ^{n}Bu, the ^{119}Sn chemical shift values plotted against n show linear correlations; the two lines almost overlap, with a similar slope to that for the Ph derivatives. The increase of the slope of the lines relative to (LCS_2) derivatives with respect to plots for corresponding Tp complexes is in accordance with the lowering of the coordination number in (LCS_2) derivatives.

Electrospray ionization is considered a ‘‘soft’’ ionization technique and is particularly suitable for the study of labile organotin systems in solution [35]. In the discussion of the mass spectra that follows, only the most abundant ions of the isotope cluster, based on ^{120}Sn (tin has 10 isotopes), are mentioned.

Peaks at m/z 279, due to the free ligand $[LCS_2]^-$, are present only in the anionic spectra of triorganotin derivatives **3**, **6**, **7** and **10**, due to the lower stability of triorganotin derivatives in acetone solutions. This instability is also demonstrated by the presence for all the triorganotin derivatives of minor peaks due to diorganotin complexes. Only the positive-ion spectrum of compound **10** is dominated by a fragment at m/z 350 (100), attributable to the species $[Sn(C_6H_5)_3]^+$. Different behavior is found in the positive-ion electrospray spectra of the others triorganotin derivatives **3**, **6** and **7**, which show only peaks due to species containing the triorganotin fragment.

The anionic spectra of monoorganotin derivatives **4** and **8** show a single molecular peak, at m/z 525 and 545, due to the mononuclear complexes $[(LCS_2)Sn(C_4H_9)Cl_2 - H^+]^-$ and $[(LCS_2)Sn(C_6H_5)Cl_2 - H^+]^-$, respectively, indicating the stability of monoorganotin complexes in acetone solution. A very simple fragmentation pattern was detected in the positive- and negative-ion spectra of diorganotin derivatives **2**, **5** and **9** dissolved in

Table 1. ESI-MS data at variable fragmentor potentials in methanol solution of derivatives $[(LCS_2)SnMe_2Cl]$, **2**, and $[(LCS_2)SnPh_2Cl]$, **9**.

	0 V	50 V	100 V	150 V
m/*z* (%) major peaks (−)				
2	463 (100) $[(LCS_2)SnMe_2Cl-H^+]^-$	463 (100) $[(LCS_2)SnMe_2Cl-H^+]^-$	463 (100) $[(LCS_2)SnMe_2Cl-H^+]^-$	
			218 (40) $[(OH)_2SnMe_2Cl]^-$	218 (100) $[(OH)_2SnMe_2Cl]^-$
9	587 (100) $[(LCS_2)SnPh_2Cl-H^+]^-$	587 (100) $[(LCS_2)SnPh_2Cl-H^+]^-$	587 (100) $[(LCS_2)SnPh_2Cl-H^+]^-$	587 (20) $[(LCS_2)SnPh_2Cl-H^+]^-$
			342 (20) $[(OH)_2SnPh_2Cl]^-$	342 (100) $[(OH)_2SnPh_2Cl]^-$
m/*z* (%) major peaks (+)				
2	428 (30) $[(LCS_2)(SnMe_2)]^+$	428 (100) $[(LCS_2)(SnMe_2)]^+$	428 (100) $[(LCS_2)(SnMe_2)]^+$	428 (30) $[(LCS_2)(SnMe_2)]^+$
	873 (100) $[(LCS_2)_2(SnMe_2)_2(OH)]^+$	873 (20) $[(LCS_2)_2(SnMe_2)_2(OH)]^+$	873 (20) $[(LCS_2)_2(SnMe_2)_2(OH)]^+$	
				203 (40) $[(LCS_2)-CS_2+H^+]^+$
				331 (40) $[(SnMe_2O)_2+H^+]^+$
				451 (100) $[(LCS_2)(SnMe_2O)_2+4H^+]^{2+}$
9	552 (70) $[(LCS_2)(SnPh_2)]^+$	552 (100) $[(LCS_2)(SnPh_2)]^+$	552 (100) $[(LCS_2)(SnPh_2)]^+$	552 (20) $[(LCS_2)(SnPh_2)]^+$
	1122 (100) $[(LCS_2)_2(SnPh_2)_2(OH)]^+$	1122 (20) $[(LCS_2)_2(SnPh_2)_2(OH)]^+$	1122 (20) $[(LCS_2)_2(SnPh_2)_2(OH)]^+$	1122 (10) $[(LCS_2)_2(SnPh_2)_2(OH)]^+$
	1158 (50) $[(LCS_2)_2(SnPh_2)_2Cl(H_2O)]^+$	1158 (10) $[(LCS_2)_2(SnPh_2)_2Cl(H_2O)]^+$	1158 (10) $[(LCS_2)_2(SnPh_2)_2Cl(H_2O)]^+$	1158 (10) $[(LCS_2)_2(SnPh_2)_2Cl(H_2O)]^+$
				203 (30) $[(LCS_2)-CS_2+H^+]^+$
				578 (100) $[(SnPh_2O)_2+H^+]^+$

acetone solution and detected at a fragmentation voltage of 30 V; in the positive-ion spectra significant fragments at *m*/*z* 428 (100%), 512 (100%) and 552 (100%) are attributable, respectively, to loss of chloride from [(LCS$_2$)SnR$_2$Cl], where R = Me, ^{n}Bu and Ph. Loss of only one proton was observed in the negative-ion spectra of all the diorganotin derivatives at *m*/*z* 463 (100%), 547 (100%) and 587 (100%). Mass spectra of derivatives [(LCS$_2$)SnMe$_2$Cl], **2**, and [(LCS$_2$)SnPh$_2$Cl], **9**, dissolved in methanol, were also acquired by scanning from *m*/*z* 50 to 1500, with fragmentor potentials of 0, 50, 100 and 150 V. The dependence of relative intensities (%) of major peaks on fragmentor potential is reported in table 1. The observed ESI-MS behavior is consistent with the fact that at 150 V fragmentation of the complexes occurs; in the positive-ion spectra *m*/*z* 203 peaks are attributable to the loss of CS$_2$ from the ligand and *m*/*z* 331, 451 and 578 peaks are attributable to the formation of stable tetraorganodistannoxane species [36], $[(\mathrm{SnMe_2O})_2 + \mathrm{H}^+]^+$, $[(\mathrm{SnPh_2O})_2 + \mathrm{H}^+]^+$ and $[(\mathrm{LCS_2})(\mathrm{SnMe_2O})_2 + 4\mathrm{H}^+]^{2+}$, respectively.

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