The synthesis and characterisation of *C*-triorganometallated (metal = Sn, Si) bis-(thienyl)- and bis-(pyrazolyl)alkanes, including the crystal structure of [(Ph₃Sn)C₃N₂]₂CH₂

$$[(Ph_3Sn)C_3N_2]_2CH_2$$

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Abstract

C-organostannyl- and organosilyl-derivatives of 2-(thien-2-ylmethyl)thiophene and 1-[(1*H*-pyrazol-1-yl)methyl]-1*H*-pyrazole have been synthesised and characterised spectroscopically. Lithiation and subsequent substitution by R₃M takes place at the 5,5′ positions for both bis-heterocycles, and this is confirmed by the X-ray structure of 1,1′-[5,5′-(Ph₃Sn)C₃N₂]₂CH₂. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

We have been interested in developing organotin derivatives of *N*-containing heterocycles for their elaboration into more complex, poly-heterocylic species [1]. In this paper, we turn our attention to the synthesis of *C*-organometallic derivatives of the bis-heterocyles **1**–**3**. Organo-Group 14 derivatives of thiophene have attracted attention as precursors for the formation of conducting polymers by electropolymerisation methods [2]. Dipyrazolylmethane has been polymerised to a variety of poly-azamacrocyles [3,4] capable of coordinating alkali metal cations [5].
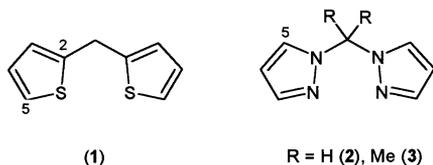
The thiophene ring system is known to be readily lithiated at the 2(5)-position by reaction with *n*-butyl lithium in ether or tetrahydrofuran [6] and this generality applies for both substituted and unsubstituted derivatives. The resulting species can subsequently be quenched with a trialkylstannyl or trialkylsilyl halide to yield the corresponding 2(5)-substituted tetralkyl-tin or -silicon derivatives [7]. This reactivity extends to ring-substituted thiophenes, including the readily prepared 2-(thien-2-ylmethyl)thiophene (**1**) which is lithiated at the 5,5′-positions [8].

Pyrazole derivatives have a well established and wide-ranging coordination chemistry [9], and organotin chloride adducts of bis-(pyrazol-1-yl)methanes have been reported [10–12]. Studies of geminal bis-(pyrazol-1-yl)alkanes such as **2** and **3** indicate that lithiation with a single equivalent of *n*-butyl lithium at −78°C followed by reaction with an electrophile such as CH₃I or PhCOCl gives the 5-substituted product and contrasts with the analogous reaction at room temperature where substitution occurs at the bridgehead carbon [13]. Subsequent work has confirmed the presence of two deprotonation sites of differing natures, the bridge position responding to soft electrophiles (e.g. MeI, MeSSMe) while ring-lithiated sites are preferred by hard electrophiles [e.g. Me₃SiCl, (H₂CO)ₙ] [14].

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2. Experimental

Infrared spectra (cm^{-1}) were recorded as KBr discs or liquid films between KBr plates using a Nicolet 510P FT-IR spectrophotometer, and elemental analyses were performed using a Carlo–Erba Strumentazione E.A. model 1106 microanalyser operating at 500°C. ^{1}H and ^{13}C NMR (δ ppm; J Hz) spectra were recorded on a JEOL JNM-GX270 FT spectrometer and ^{29}Si, ^{119}Sn NMR spectra were recorded on a JEOL JNM-EX400 FT machine, all using saturated CDCl$_3$ solutions unless indicated otherwise with Me$_4$Si or Me$_4$Sn as appropriate reference. Details of our Mössbauer spectrometer and related procedures are given elsewhere [15]. Dry solvents were obtained by distillation under inert atmosphere from the following drying agents: sodium-benzophenone (toluene, ether, THF), calcium hydride (CH$_2$Cl$_2$), sodium (hexane). Standard Schlenk techniques were used throughout. Starting materials were commercially obtained and used without further purification.

2.1. Synthesis of 2-(thien-2-ylmethyl)thiophene (1)

Thiophene (20.2 g, 24.0 mmol) was stirred at room temperature with 1,3,5-trioxane (3.6 g, 4.0 mmol). HCl (37%) (20 ml) was added to this and stirring continued for a further 24 h resulting in a dark brown oil which was extracted with diethyl ether (80 ml) and separated from the aqueous layer to produce a brown ethereal solution. This was washed consecutively with dilute sodium carbonate solution and distilled water before being dried over magnesium sulfate. Removal of the ether in vacuo yielded a brown oil which was distilled at reduced pressure to give a single fraction (1) as a colourless oil which crystallised on exposure to the atmosphere (10.6 g, 48%), b.p. 120°C/0.05 mmHg, m.p. 45°C. *Anal.* Found: C, 59.9; H, 4.44. Calc. for C$_9$H$_8$S$_2$: C, 60.0; H, 4.45%. ^{1}H NMR (δ ppm): 4.32 (s, 2H, CH$_2$); 6.85 (m, 2H, 4,3′-C$_4$H$_3$S); 6.91 (dd, 2H, [$J = 3.4$, 4.2 Hz], 3,4′-C$_4$H$_3$S); 7.13 (dd, 2H, [$J = 2.7$, 4.0 Hz], 3,5′-C$_4$H$_3$S). ^{13}C NMR (δ ppm): 30.1 (CH$_2$); 124.1 (2,5′-C$_4$H$_3$S); 125.2 (4,3′-C$_4$H$_3$S); 126.8 (3,4′-C$_4$H$_3$S); 143.1 (5,2′-C$_4$H$_3$S).

2.2. Synthesis of 1-[(1H-pyrazol-1-yl)methyl]-1H-pyrazole (2)

A solution of pyrazole (7.5 g, 110.0 mmol) in THF (100 ml) was added dropwise to potassium metal (3.9 g, 100.0 mmol) suspended in THF (200 ml) and stirred under nitrogen. The reaction mixture was stirred and refluxed for 4 h resulting in a fine white suspension. Di-iodomethane (13.4 g, 50.0 mmol) in THF (20 ml) was then added and the reaction refluxed and stirred for a further 3 and 24 h, respectively. This white

suspension was then filtered and the colourless filtrate evaporated to produce a yellow oil. Trituration with heptane gave a cream-coloured solid which, after several recrystallisations from heptane, yielded **2** as white needles (4.12 g, 51%), m.p. 108°C. *Anal.* Found: C, 56.7; H, 5.44; N, 37.7. Calc. for C$_7$H$_8$N$_4$: C, 56.5; H, 5.26; N, 37.8%. ^{1}H NMR (δ ppm): 6.23 (d, 2H, [$J = 4.0$ Hz], 4,4′-C$_3$H$_3$N$_2$); 6.25 (s, 2H, CH$_2$); 7.50 (d, 2H, [$J = 1.6$ Hz], 3,3′-C$_3$H$_3$N$_2$); 7.60 (d, 2H, [$J = 2.3$ Hz], 5,5′C$_3$H$_3$N$_2$). ^{13}C NMR (δ ppm): 65.0 (CH$_2$); 106.9 (4,4′-C$_3$H$_3$N$_2$); 129.5 (5,5′-C$_3$H$_3$N$_2$); 140.6 (3,3′-C$_3$H$_3$N$_2$). IR (KBr, cm^{-1}): 3129, 3107, 1514, 1435, 1375, 1291, 1271, 1205, 1093, 1051, 951, 783, 763, 720, 653, 613.

2.3. Synthesis of 1-[1-methyl-1-(1H-pyrazol-1-yl)-ethyl]-1H-pyrazole (3)

A mixture of pyrazole (13.6 g, 200.0 mmol) and 2,2-dimethoxypropane (10.4 g, 100 mmol) was heated with *p*-toluenesulphonic acid (0.1 g, 0.6 mmol) so that methanol distilled out slowly. After ca. 8 ml (200 mmol) had been collected, the melt was poured into cold heptane (40 ml) and cooled. Recrystallisation of the resulting solid three times from heptane yielded **3** as a crystalline solid (8.2 g, 47%), m.p. 82°C. *Anal.* Found: C, 60.8; H, 6.03; N, 31.4. Calc. for C$_9$H$_{12}$N$_4$: C, 61.3; H, 6.86; N, 31.7%. ^{1}H NMR (δ ppm): 2.24 (s, 6H, CH$_3$); 6.21 (dd, 2H, [$J = 2.0$, 2.3 Hz], 4,4′-C$_3$H$_3$N$_2$); 7.37 (d, 2H, [$J = 2.3$ Hz], 3,3′-C$_3$H$_3$N$_2$); 7.54 (d, 2H, [$J = 1.9$ Hz], 5,5′-C$_3$H$_3$N$_2$). ^{13}C NMR (δ ppm): 27.8 (CH$_3$); 80.4 (C(CH$_3$)$_2$); 106.0 (4,4′-C$_3$H$_3$N$_2$); 126.8 (5,5′-C$_3$H$_3$N$_2$); 139.4 (3,3′-C$_3$H$_3$N$_2$). IR (KBr, cm^{-1}): 3112, 2998, 1510, 1422, 1387, 1313, 1259, 1210, 1169, 1148, 1097, 1082, 1045, 955, 770, 706, 686, 653, 632.

2.4. Synthesis of 2-tributylstannyl-5-[(5-tributylstannyl-thien-2-yl)methyl]thiophene (4)

Compound **1** (2.2 g, 12 mmol) was stirred in diethyl ether (80 ml) under nitrogen. BuLi (1.6 M) in hexane (17 ml, 27 mmol) was added over a period of 30 min at room temperature causing the formation of a dark brown solution. After stirring for a further 1 h, tributyltin chloride (8.0 g, 24.5 mmol) in diethyl ether (20 ml) was added dropwise resulting in a light brown suspension. This was stirred for a further 2 h before filtration under nitrogen and solvent evaporation to yield a dark brown oil. Distillation on a Kühgelrohr apparatus gave two fractions, unreacted tributyltin chloride (0.74 g) and **4** as a colourless oil (accompanied by a large amount of thermal decomposition) (3.1 g, 33%), b.p. 190–200°C/1 mmHg. *Anal.* Found: C, 52.3; H, 8.21. Calc. for C$_{33}$H$_{60}$S$_2$Sn$_2$: C, 52.3; H, 7.92%. ^{1}H NMR (δ ppm): 0.91 (m, 18H, CH$_3$); 1.12 (m, 12H, CH$_2$(CH$_2$)$_2$CH$_3$); 1.34 (m, 12H, CH$_2$(CH$_2$)$_2$CH$_3$); 1.62

(m, 12H, $CH_2(CH_2)_2CH_3$); 5.30 (s, 2H, CH_2); 7.21–7.30 (m, 2H, 4,3'-C_4H_2S); 7.66 (d, 2H, [$J = 3.3$ Hz], 3,4'-C_4H_2S), $^3J(3,4'$-$C_4^1H_2S$–$^{117,119}Sn) = 14.8$ Hz (unresolved). ^{13}C NMR (δ ppm): 10.8 (CH_3); 13.6 ($CH_2(CH_2)_2CH_3$); 27.2 ($CH_2(CH_2)_2CH_3$); 28.9 ($CH_2(CH_2)_2CH_3$); 30.1 (CH_2); 127.8 (4,3'-C_4H_2S); 135.1 (3,4'-C_4H_2S); 135.2 (2,5'-C_4H_2S); 148.9 (5,2'-C_4H_2S); $^1J(^{13}C$–$^{117,119}Sn) = 344.5, 356.9$ Hz; $^2J(^{13}C$–$^{117,119}Sn) = 20.9$ Hz (unresolved); $^3J(^{13}C$–$^{117,119}Sn) = 47.4$ Hz (unresolved). ^{119}Sn NMR (δ ppm): -39.4. ^{119m}Sn Mössbauer (mm s^{-1}): I.S. = 1.21; Q.S. = 0.61. IR (liq. film, cm^{-1}): 2959, 2926, 2872, 1464,1418, 1377, 1340, 1211, 1074, 961, 939, 875, 769, 698, 594.

2.5. Synthesis of 2-triphenylstannyl-5-[(5-triphenyl-stannylthien-2-yl)methyl]thiophene (5)

Compound **1** (2.0 g, 11.1 mmol) was stirred in diethyl ether (80 ml) under nitrogen. BuLi (1.6 M) in hexanes (15 ml, 24 mmol) was added at room temperature over a period of 1 h resulting in a dark brown solution. To this was then added triphenyltin chloride (8.5 g, 22.0 mmol) in diethyl ether (80 ml) giving a brown suspension which was stirred for a further 2 h. This was then filtered and the solvent evaporated giving a sticky dark brown mass. Flash chromatography on silica gel using a gradient of hexane to CH_2Cl_2 yielded **5** as an amorphous, pale yellow solid (3.8 g, 40%). *Anal*. Found: C, 61.4; H, 4.35. Calc. for $C_{45}H_{36}S_2Sn_2$: C, 61.5; H, 4.15%. ^1H NMR (δ ppm): 4.35 (s, 2H, CH_2); 7.23–7.60 (m, 34H, o,m,p-C_6H_5, 3,4'-C_4H_2S, 4,3'-C_4H_2S). ^{13}C NMR (δ ppm): 30.2 (CH_2); 128.6 (4,3'-C_4H_2S); 128.7 (m-C_6H_5); 129.3 (p-C_6H_5); 131.5 (3,4'-C_4H_2S); 137.0 (o-C_6H_5); 137.5 (i-C_6H_5); 137.6 (2,5'-C_4H_2S); 150.0 (5,2'-C_4H_2S); $^2J(o$-$^{13}C_6H_5$–$^{117,119}Sn) = 36.3$ Hz (unresolved); $^3J(m$-$^{13}C_6H_5$–$^{117,119}Sn) = 56.2$ Hz (unresolved); $^2J(3,4'$-$^{13}C_4H_2S$–$^{117,119}Sn) = 39.6$ Hz (unresolved). ^{119}Sn NMR (δ ppm): -137.4. ^{119m}Sn Mössbauer (mm s^{-1}): I.S. = 1.16; Q.S. = 0.00. IR (KBr, cm^{-1}): 3061, 1480, 1428, 1383, 1332, 1302, 1259, 1074, 1022, 997, 731, 698, 657, 455, 446.

2.6. Synthesis of 2-trimethylsilyl-5-[(5-trimethyl-silylthien-2-yl)methyl]thiophene (6)

Compound **1** (2.0 g, 11.1 mmol) in diethyl ether (100 ml) was treated with 1.6 M BuLi (15 ml, 24 mmol) at room temperature giving a dark brown solution which was stirred for a further 1 h. Trimethylsilyl chloride (2.4 g, 22.1 mmol) was then added via a syringe and the resulting cream-coloured precipitate stirred for 2 h. Filtration under nitrogen and in vacuo removal of solvent gave a brown oil which was vacuum distilled on a Kügelrohr apparatus to give **6** as a colourless oil (1.4 g, 39%), b.p. 180°C/0.5 mmHg. *Anal*. Found: C, 56.6;

H, 7.88. Calc. for $C_{15}H_{24}S_2Si_2$: C, 55.6; H, 7.41%. ^1H NMR (δ ppm): 0.48 (s, 18H, CH_3); 4.58 (s, 2H, CH_2); 7.09–7.13 (m, 2H, 4,3'-C_4H_2S); 7.26 (m, 2H, 3,4'-C_4H_2S). ^{13}C NMR (δ ppm): -0.03 (CH_3); 30.2 (CH_2); 126.7 (4,3'-C_4H_2S); 126.8 (3,4'-C_4H_2S); 134.0 (2,5'-C_4H_2S); 148.5 (5,2'-C_4H_2S). ^{29}Si NMR (δ ppm): -6.8. IR (liq. film, cm^{-1}): 2953, 2897, 1464, 1262, 1250, 1214, 1157, 1097, 1042, 1033, 993, 839, 805, 757, 705.

2.7. Synthesis of 2-triphenylsilyl-5-[(5-triphenyl-silylthien-2-yl)methyl]thiophene (7)

Compound **1** (2 g, 11.1 mmol), stirred in diethyl ether (150 ml) under nitrogen, was treated with 1.6 M BuLi (15 ml, 24 mmol) at room temperature giving a dark brown solution. After stirring for 1 h, triphenylsilyl chloride (6.55 g, 22.1 mmol) in diethyl ether (75 ml) was added dropwise giving a dark brown suspension. This was stirred for a further 1 h before filtration and evaporation of the solvent. The resulting brown tar was chromatographed on silica gel using 40–60° petroleum ether as eluant to give **7** as an off-white amorphous solid (2.2 g, 30%). *Anal*. Found: C, 77.1; H, 5.17. Calc. for $C_{45}H_{36}S_2Si_2$: C, 77.5; H, 5.17%. ^1H NMR (δ ppm): 4.31 (s, 2H, CH_2); 7.23–7.50 (m, 34H, o,m,p-C_6H_5, 3,4'-C_4H_2S, 4,3'-C_4H_2S). ^{13}C NMR (δ ppm): 34.0 (CH_2); 127.1 (4,3'-C_4H_2S); 127.9 (m-C_6H_5); 129.8 (p-C_6H_5); 134.1 (i-C_6H_5); 135.0 (3,4'-C_4H_2S); 136.1 (o-C_6H_5); 138.6 (2,5'-C_4H_2S); 150.3 (5,2'-C_4H_2S). ^{29}Si NMR (δ ppm): -19.2.

2.8. Synthesis of 5-trimethylstannyl-1-[(5-trimethyl-stannyl-1H-pyrazol-1-yl)methyl]-1H-pyrazole (8)

To **2** (1.0 g, 6.75 mmol) in THF (50 ml) under nitrogen at -78°C was added 1.6 M BuLi in hexanes (9 ml, 14.4 mmol) and the resulting yellow solution stirred for 2 h. Trimethyltin chloride (2.7 g, 13.5 mmol) in THF (20 ml) was then added at 0°C and the resulting solution stirred for 2 h. In vacuo removal of the solvent gave a sticky white solid which was extracted with 40–60° petrol/diethyl ether (1:1) and filtered to remove LiCl. Evaporation of the filtrate gave a white solid and two successive recrystallisations from 40–60° petrol/diethyl ether (1:1) yielded **8** as a colourless crystalline solid (1.58 g, 49%), m.p. 88°C. *Anal*. Found: C, 33.1; H, 5.21; N, 11.9. Calc. for $C_{13}H_{24}N_4Sn_2$: C, 33.0; H, 5.11; N, 11.8%. ^1H NMR (δ ppm): 0.44 (s, 18H, CH_3); 6.34 (d, 4H, CH_2, [$J = 1.6$ Hz], 4,4'-$C_3H_2N_2$); 7.54 (d, 2H, [$J = 1.8$ Hz], 3,3'-$C_3H_2N_2$); $^2J(C^1H_3$–$^{117,119}Sn) = 55.7, 58.4$ Hz. ^{13}C NMR (δ ppm): -7.7 (CH_3); 67.3 (CH_2); 115.9 (4,4'-$C_3H_2N_2$); 139.7 (3,3'-$C_3H_2N_2$); 142.9 (5,5'-$C_3H_2N_2$); $^1J(^{13}CH_3$–$^{117,119}Sn) = 364.7, 382.3$ Hz; $^2J(4,4'$-$^{13}C_3H_2N_2$–$^{117,119}Sn) = 50.6$ Hz (unresolved); $^3J(3,3'$-$^{13}C_3H_2N_2$–$^{117,119}Sn) = 44.0$ Hz (unresolved).

^{119}Sn NMR (δ ppm): -47.1. ^{119m}Sn Mössbauer (mm s^{-1}): I.S. = 1.20; Q.S. = 0.81. IR (KBr, cm^{-1}): 2980, 2915, 1435, 1379, 1348, 1321, 1257, 1190, 1177, 944, 925, 777, 745, 650.

2.9. Synthesis of 5-tributylstannyl-1-[(5-tributylstannyl-1H-pyrazol-1-yl)methyl]-1H-pyrazole (**9**)

To **2** (0.33 g, 2.25 mmol) under nitrogen in THF (30 ml) was added 1.6 M BuLi in hexanes (3 ml, 4.8 mmol) at -78°C. The resulting yellow solution was stirred for 1 h before addition of tributyltin chloride (1.45 g, 4.6 mmol) at 0°C. This gave a yellow solution which was stirred for 2 h before being heated to reflux for a further 1 h. In vacuo removal of solvent gave a brown oil containing some suspended solids. This was extracted with diethyl ether and filtered to remove LiCl. Evaporation of the filtrate gave a yellow oil which was chromatographed on silica gel using a gradient of 40–60° petrol/diethyl ether to yield **9** (0.95 g, 58%) as a yellow oil which turns brown on standing. *Anal.* Found: C, 50.2; H, 8.54; N, 7.7. Calc. for $C_{31}H_{60}N_4Sn_2$: C, 51.3; H, 8.33; N, 7.7%. ^{1}H NMR (δ ppm): 0.79 (t, 18H, [$J = 7.4$ Hz], CH$_3$); 1.18–1.30 (m, 24H, CH$_2$CH_2CH_2CH$_3$); 1.40–1.59 (m, 12H, CH_2CH$_2$-CH$_2$CH$_3$); 6.30 (d, 2H, [$J = 1.7$ Hz], 4,4'-$C_3H_2N_2$); 6.31 (s, 2H, CH$_2$); 7.50 (d, 2H, [$J = 1.8$ Hz], 3,3'-$C_3H_2N_2$). ^{13}C NMR (δ ppm): 13.4 (CH$_3$); 16.7 (CH$_2$(CH$_2$)$_2$CH$_3$); 27.7 ((CH$_2$)$_2$CH$_2$CH$_3$); 28.8 (CH$_2$CH$_2$CH$_2$CH$_3$); 67.6 (CH$_2$); 116.1 (4,4'-$C_3H_2N_2$); 139.5 (3,3'-$C_3H_2N_2$); 142.3 (5,5'-$C_3H_2N_2$); $^3J(^{13}C-^{117,119}Sn) = 22.1$ Hz (unresolved). ^{119}Sn NMR (δ ppm): -58.9. ^{119m}Sn Mössbauer (mm s^{-1}): I.S. = 1.31; Q.S. = 1.00. IR (liq. film, cm^{-1}): 2959, 2926, 2872, 2855, 1464, 1377, 1358, 1342, 1260, 1078, 1047, 875, 789, 752, 695, 673, 599.

2.10. Synthesis of 5-triphenylstannyl-1-[(5-triphenylstannyl-1H-pyrazol-1-yl)methyl]-1H-pyrazole (**10**)

To **2** (0.5 g, 3.4 mmol), stirred under nitrogen in THF (50 ml) at -78°C was added 1.6 M BuLi in hexanes (4.5 ml, 7.2 mmol) giving a yellow solution. This was stirred for 1 h before being allowed to warm to 0°C when triphenyltin chloride (2.62 g, 6.8 mmol) was added in THF (25 ml) resulting in a yellow solution. In vacuo removal of the solvent yielded a pale brown tar which was dissolved in toluene and reprecipitated by the addition of pentane. The resulting off-white solid was filtered and recrystallised from chloroform to yield **10** as a colourless crystalline solid (0.32 g, 12%), m.p. 154°C. *Anal.* Found: C, 60.7; H, 4.26; N, 6.7. Calc. for $C_{43}H_{36}N_4Sn_2$: C, 60.9; H, 4.26; N, 6.6%. ^{1}H NMR (δ ppm): 5.97 (s, 2H, CH$_2$); 6.25 (d, 2H, [$J = 1.8$ Hz], 4,4'-$C_3H_2N_2$); 7.08 (d, 2H, [$J = 1.9$ Hz], 3,3'-$C_3H_2N_2$); 7.22–7.25 (m, 18H, *m,p*-C$_6$H$_5$); 7.54

(dd, 12H, *o*-C$_6$H$_5$). ^{13}C NMR (δ ppm): 66.3 (CH$_2$); 117.5 (4,4'-$C_3H_2N_2$); 128.6 (*m*-C$_6$H$_5$); 129.2 (*p*-C$_6$H$_5$); 137.3 (*o*-C$_6$H$_5$); 137.8 (*i*-C$_6$H$_5$); 139.7 (5,5'-$C_3H_2N_2$); 140.2 (3,3'-$C_3H_2N_2$); $^2J(o$-$^{13}C_6H_5-^{117,119}$Sn) = 39.4 Hz (unresolved); $^3J(m$-$^{13}C_6H_5-^{117,119}$Sn) = 56.2 Hz (unresolved); $^4J(p$-$^{13}C_6H_5-^{117,119}$Sn) = 12.1 Hz (unresolved). ^{119}Sn NMR (δ ppm): -162.5; ^{119m}Sn Mössbauer (mm s^{-1}): I.S. = 1.23; Q.S. = 0.62. IR (KBr, cm^{-1}): 3092, 3065, 2990, 1429, 1352, 1257, 1074, 727, 698, 447.

2.11. Synthesis of 5-trimethylsilyl-1-[(5-trimethyl-silyl-1H-pyrazol-1-yl)methyl]-1H-pyrazole (**11**)

To a solution of **2** (1.0 g, 6.75 mmol) stirred under nitrogen in THF was added 1.6 M BuLi in hexanes (9 ml, 14.4 mmol) at -78°C. The resulting yellow solution was stirred at this temperature for a further 1 h before the temperature was allowed to rise to 0°C and the addition of trimethylsilyl chloride (1.46 g, 13.5 mmol). This resulted in an orange solution which was stirred at room temperature for a further 2 h. In vacuo removal of the solvent gave an orange oil. Extraction with diethyl ether followed by filtration and evaporation of the filtrate gave an off-white solid. This was recrystallised twice from 40–60° petroleum ether to yield **11** as colourless needles (0.81 g, 41%), m.p. 82°C. *Anal.* Found: C, 53.0; H, 8.22; N, 19.1. Calc. for $C_{13}H_{24}N_4Si_2$: C, 53.4; H, 8.22; N, 19.2%. ^{1}H NMR (δ ppm): 0.37 (s, 18H, CH$_3$); 6.40 (s, 2H, CH$_2$); 6.41 (d, 2H, [$J = 1.6$ Hz], 4,4'-$C_3H_2N_4$); 7.51 (d, 2H, [$J = 1.6$ Hz], 3,3'-$C_3H_2N_4$).

2.12. Synthesis of 5-trimethylstannyl-1-[1-methyl-1-(5-trimethylstannyl-1H-pyrazol-1-yl)ethyl]-1H-pyrazole (**12**)

To a solution of **3** (1.0 g, 5.7 mmol) in THF (20 ml) under nitrogen at -78°C was added 1.6 M BuLi in hexanes (8 ml, 12.8 mmol) and the resulting yellow suspension stirred for 1 h. The temperature was then allowed to rise to 0°C and trimethyltin chloride (2.26 g, 11.4 mmol) in THF (20 ml) was added to give a yellow solution which was stirred at room temperature overnight. In vacuo removal of the solvent gave a yellow oil containing some suspended solid and Mössbauer analysis of this revealed some unreacted trimethyltin chloride. Chromatography on silica gel employing CH$_2$Cl$_2$ yielded **12** as a moisture-sensitive, colourless oil (0.92 g, 32%). *Anal.* Found: C, 36.2; H, 5.94; N, 9.90. Calc. for $C_{15}H_{28}N_4Sn_2$: C, 35.9; H, 5.98; N, 11.2%. ^{1}H NMR (δ ppm): 0.00 (s, 18H, SnCH$_3$); 2.09 (s, 6H, C(CH$_3$)$_2$); 6.45 (d, 2H, [$J = 1.7$ Hz], 4,4'-$C_3H_2N_2$); 7.55 (d, 2H, [$J = 1.5$ Hz], 3,3'-$C_3H_2N_2$); $^2J(C^1H_3-^{117,119}$Sn) = 50.2, 57.3 Hz. ^{13}C NMR (δ ppm): -7.23 (SnCH$_3$); 31.5 (C(CH$_3$)$_2$); 80.4 (C(CH$_3$)$_2$); 118.6 (4,4'-$C_3H_2N_2$); 137.7 (3,3'-$C_3H_2N_2$); 141.0 (5,5'-

Table 1
Crystallographic data for **10**

Empirical formula	$C_{43}H_{36}N_4Sn_2$
Formula weight	846.14
Crystal habit	colourless block
Crystal size (mm)	$0.3 \times 0.3 \times 0.3$
Diffractometer	Enraf–Nonius CAD4
Radiation wavelength	0.71069 Å
Temperature (K)	293(2)
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.486(2)
b (Å)	13.446(2)
c (Å)	13.998(1)
α (°)	99.28(1)
β (°)	97.26(1)
γ (°)	101.90(1)
V (Å^3)	1879.7(5)
Z	2
D_{calc} (Mg m^{-3})	1.495
Absorption coefficient (mm^{-1})	1.364
Theta range for data collection (°)	2.01–23.97
Reflections collected	6232
Independent reflections	5869 [$R_{int} = 0.0121$]
Reflections observed ($>2\sigma$)	4623
Refinement method	Full-matrix least-squares on F
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0277$, $wR_2 = 0.0832$
R indices (all data)	$R_1 = 0.0427$, $wR_2 = 0.0926$

$C_3H_2N_2$); $^1J(^{13}CH_3–^{117,119}Sn) = 366.8$ Hz (unresolved). ^{119}Sn NMR (δ ppm): -35.7. ^{119m}Sn Mössbauer (mm s^{-1}): I.S. $= 1.22$; Q.S. $= 0.93$. IR (liq. film, cm^{-1}): 2980, 2919, 1415, 1388, 1369, 1305, 1259, 1199, 1170, 989, 924, 787, 736, 588.

2.13. Synthesis of 5-trimethylsilyl-1-[1-methyl-1-(5-trimethylsilyl-1H-pyrazol-1-yl)ethyl]-1H-pyrazole (13)

To a solution of **3** (1.0 g, 5.7 mmol) in THF (20 ml) under nitrogen at 0°C was added 1.6 M BuLi in hexanes (9 ml, 14.4 mmol). This produced a yellow suspen-sion which was stirred for 1 h before addition of trimethylsilyl chloride (1.24 g, 11.4 mmol) at 0°C. The resulting yellow solution was stirred for 2 h and the solvent evaporated. This gave a yellow oil containing some suspended solid. Extraction with diethyl ether followed by filtration and evaporation of the filtrate yielded a yellow oil which crystallised on standing. This was recrystallised from hexane to give **13** as colourless crystals (1.15 g, 63%), m.p. 58°C. *Anal.* Found: C, 56.6; H, 9.03; N, 17.6. Calc. for $C_{15}H_{28}N_4Si_2$: C, 56.3; H, 8.80; N, 17.5%. ^1H NMR (δ ppm): 0.01 (s, 18H, SiCH$_3$); 2.10 (s, 6H, C(CH$_3$)$_2$); 6.54 (d, 2H, [$J = 1.8$ Hz], 4,4'-C$_3$H$_2$N$_2$); 7.48 (d, 2H, [$J = 1.7$ Hz], 3,3'-C$_3$H$_2$N$_2$). ^{13}C NMR (δ ppm): 0.08 (SiCH$_3$); 32.0 (C(*C*H$_3$)$_2$); 81.1 (*C*(CH$_3$)); 119.8 (4,4'-C$_3$H$_2$N$_2$); 137.0 (3,3'-C$_3$H$_2$N$_2$); 143.3 (5,5'-C$_3$H$_2$N$_2$). ^{29}Si NMR (δ ppm): -9.9. IR (KBr, cm^{-1}): 2953, 2901, 1307, 1296, 1263, 1182, 1103, 1014, 924, 843, 788, 765, 636, 526.

2.14. Crystallography

Suitable crystals of **10** for X-ray study were obtained by recrystallisation from a chloroform/ether solution. Crystal data and experimental details are summarised in Table 1. Phenyl rings were refined as rigid hexagons and hydrogens included at calculated positions throughout. Refinement was based on F_o. Software used: SHELXS-86 [16], SHELXL-97 [17], ORTEX [18]. The asymmetric unit is displayed in Fig. 1 along with the atomic numbering scheme; selected bond lengths and bond angles are given in Table 2.

3. Results and discussion

3.1. Synthesis

2-(Thien-2-ylmethyl)thiophene (**1**) was synthesised via the condensation of thiophene and 1,3,5-trioxane employing 37% hydrochloric acid as catalyst [19,20]
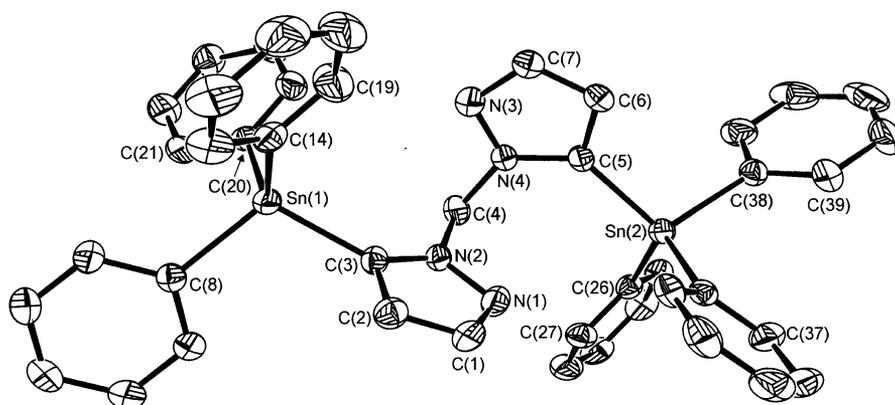

Fig. 1. The asymmetric unit of **10** showing the labelling scheme used in the text. Thermal ellipsoids are at the 30% probability level.

Table 2
Selected bond lengths (Å) and bond angles (°) for **10**

Bond lengths

Sn(1)–C(3)	2.135(3)	Sn(1)–C(14)	2.147(2)
Sn(1)–C(20)	2.156(2)	Sn(1)–C(8)	2.157(2)
Sn(2)–C(5)	2.142(3)	Sn(2)–C(32)	2.141(2)
Sn(2)–C(38)	2.158(2)	Sn(2)–C(26)	2.160(2)
N(1)–C(1)	1.315(5)	N(1)–N(2)	1.357(4)
N(2)–C(3)	1.362(4)	N(2)–C(4)	1.449(4)
N(3)–C(7)	1.321(5)	N(3)–N(4)	1.352(4)
N(4)–C(5)	1.363(4)	N(4)–C(4)	1.452(4)

Bond angles

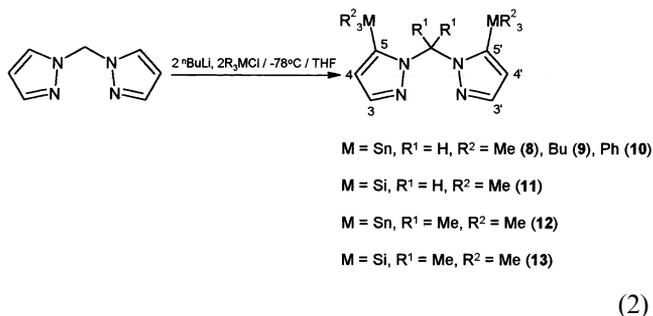|			
C(3)–Sn(1)–C(14)	103.31(12)	C(3)–Sn(1)–C(20)	120.74(12)
C(14)–Sn(1)–C(20)	109.03(10)	C(3)–Sn(1)–C(8)	104.48(11)
C(14)–Sn(1)–C(8)	112.36(10)	C(20)–Sn(1)–C(8)	106.96(9)
C(5)–Sn(2)–C(32)	111.78(11)	C(5)–Sn(2)–C(38)	101.46(11)
C(32)–Sn(2)–C(38)	107.78(9)	C(5)–Sn(2)–C(26)	115.87(11)
C(32)–Sn(2)–C(26)	111.69(9)	C(38)–Sn(2)–C(26)	107.36(9)

and was isolated from the higher condensation products also produced by vacuum distillation; the colourless oil crystallised on standing. The bis-pyrazolyl-substituted methane (**2**) was synthesised by the reaction of potassium pyrazolide and di-iodomethane in THF solution while bis-pyrazole-substituted propane (**3**) was synthesised by the acid-catalysed reaction of pyrazole and 2,2-dimethoxypropane and purified by recrystallisation from heptane [21].

Using standard dry, anaerobic conditions, **1** was lithiated at room temperature with 1.6 M BuLi in diethyl ether. Under these conditions lithiation occurred at the 2,5′-positions, anion formation being apparent from the formation of a dark brown solution. The appropriate triorganotin or triorganosilicon chloride was then added dropwise to quench the di-lithiobis-thiophene, with a resulting precipitate of lithium chloride (Eq. (1)). After filtration, the crude products were purified either by vacuum distillation (**4**, **6**) to produce yellow, moderately air-stable oils, or by column chromatography (**5**, **7**) to afford amorphous, pale yellow solids, both in modest yield (30–40%). It was found that the analogous lithiation reactions performed in THF solution produced excessive charring and non-specific ring substitution, as evidenced by ^{119}Sn and ^{29}Si NMR spectra of the quenched products.

$M = Sn, R = Bu$ (**4**), Ph (**5**)

$M = Si, R = Me$ (**6**), Ph (**7**)
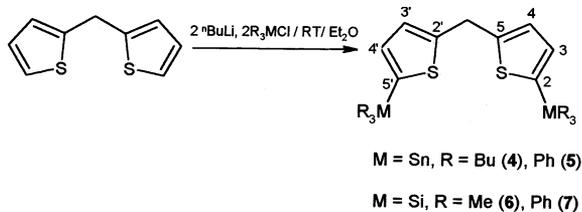
(1)

The bis-pyrazole compounds (**2**, **3**) were lithiated with 2 equiv. of 1.6 M *n*-butyl lithium in THF solution at −78°C, the appearance of a yellow solution and a yellow suspension, respectively, indicating that anion formation had occurred. Quenching with a variety of triorganotin and triorganosilicon chlorides at 0°C gave in each case the 5,5′ ring-substituted products (**8–13**) (as deduced from NMR data and the crystal structure of **10**) (Eq. (2)). Compounds **9** and **12** were isolated by column chromatograpy on silica gel as moisture-sensitive, colourless oils while **8**, **10**, **11** and **13** were recrystallised in air to yield colourless, moderately air-stable crystalline materials in poor to fair yield (12–60%).

$M = Sn, R^1 = H, R^2 = Me$ (**8**), Bu (**9**), Ph (**10**)

$M = Si, R^1 = H, R^2 = Me$ (**11**)

$M = Sn, R^1 = Me, R^2 = Me$ (**12**)

$M = Si, R^1 = Me, R^2 = Me$ (**13**)

(2)

Of the ten *C*-triorganometallated bis-heterocycles synthesised, it was noted that in general those compounds isolated as oils at ambient temperatures (**4**, **6**, **9** and **12**) exhibited a lower degree of air/moisture stability than the remaining crystalline or amorphous solids. In common with other *C*-organometallated heterocyles [22] however, all the compounds are ultimately attacked by atmospheric moisture and do not exhibit indefinite stability if exposed to the open atmosphere. This degradation eventually leads to the free bis-heterocyle and the corresponding organotin- or organosilicon oxide.

3.2. Spectroscopy

The ^{1}H and ^{13}C NMR data of all the compounds (**1–13**) are consistent with the proposed structures. The disappearance of the C^2, $C^{5'}$ proton resonance of the metallated bis-thiophenes (**4–7**) indicates substitution at the 2- and 5′-sites which is consistent with previous work, which has shown that mono-thienyl compounds are known to undergo lithiation exclusively at the 2(5)-position of the ring. In common with other stannylated thiophene compounds, attachment of the triorganotin moiety in the cases of **4** and **5** is accompanied by a pronounced downfield shift of approximately 10 ppm of the ^{13}C signals of the $C^{2,5'}$ and $C^{3,4'}$ while the methine $C^{4,3'}$ and quaternary $C^{5,2'}$ signals are left largely unaffected [23,24]. Similar trends are noted for the silicon-substituted **6** and **7**.

The $^1J(^{13}C-^{119}Sn)$ value obtained for the tributyltin-substituted bis-thiophene (**4**) of 356.9 Hz is typical of

tetrahedral geometry of tin. The semi-empirical equation of Holecek and Lycka [25] for the estimation of C–Sn–C bond angles in *n*-tributyltin compounds gives a calculated value of 108.3° consistent with this structural assignment. The $^2J(o\text{-}^{13}C_6H_5\text{-}^{119}Sn)$ and $^3J(m\text{-}^{13}C_6H_5\text{-}^{119}Sn)$ values of 36.3 and 56.2 Hz are also consistent with other four-coordinate tetraaryltin compounds [24] confirming the four-coordinated nature of all these compounds. Similarly, the ^{119}Sn chemical shifts in $CDCl_3$ solution are consistent with a four-coordinate, near tetrahedral geometry at the metal. The resonances at −39.4 ppm for the tributyltin derivative **4** and −137.4 ppm for the triphenyltin derivative **5** compared with the values reported for the similar tin environments in $(2\text{-}C_4H_3S)SnMe_3$ $[\delta(^{119}Sn) = -27.5$ ppm] [24] and $(2\text{-}C_4H_3S)SnPh_3$ $[\delta(^{119}Sn) = -135.5$ ppm] [7] and are both to considerably lower field than tetraorganotins which show enhanced coordination at tin, e.g. the pseudo-octahedral bis-[3-(2-pyridyl)-2-thienyl-*C*–*N*]diphenyltin $[\delta(^{119}Sn) = -245.5$ ppm] [26].

The ^1H and ^{13}C NMR spectra of the bis-pyrazolyl alkanes (**2** and **3**) have been assigned following the work of Julia et al. [27]. Lithiation and subsequent organometallation in the cases of **8**–**13** is observed to occur at the 5,5′ positions as would be expected from the work of Katritzky [28]. This is confirmed by the disappearance of the signals at 7.61 and 7.37 ppm in the proton spectra of **2** and **3**, respectively, and the collapse of the doublet of doublets splitting pattern attributed to the 4,4′ protons at approximately 6.2 ppm to a simple doublet. Further confirmation comes from the crystallographic analysis of **10** reported below. The C^5 and C^4 signals are deshielded by approximately 10 ppm compared to the parent bis-pyrazole, while the signal due to the C^3 is affected much less, experiencing only a minor shielding of approximately 1.0 ppm. The ^1H chemical shifts of the H^4 and H^3 protons are left largely unaffected.

Four-coordinate tetrahedral trimethyltin compounds generally have $^2J(^1H\text{-}^{119}Sn)$ values of less than 59 Hz. Accordingly the $^2J(^1H\text{-}^{119}Sn)$ values recorded for the trimethyltin-substituted bis-pyrazolyl derivatives **8** and **12** are 55.7 and 57.3 Hz, yielding calculated bond angles of 109.8 and 110.6°, respectively [29]. The $^1J(^{13}C\text{-}^{119}Sn)$ values for **8** and **12** of 382.3 and 366.8 Hz, respectively, are also typical of four-coordinate *C*-trimethyltin-substituted heterocyclic compounds, as is the corresponding ^1J constant for the triphenyltin derivative **10** of 587.6 Hz [30].

The ^{119}Sn NMR data of **8**–**10** and **12** are similar to those of the corresponding substituted bis-thiophenes. The tributyltin and triphenyltin-substituted bis-pyrazoles **9** and **10** are observed to have slightly higher field shifts than the analogous bis-thiophene compounds **4** and **5** (−162.5 vs −137.4 ppm and −47.1 vs −39.4 ppm, respectively).

The ^{119}Sn Mössbauer data for the tetraorganotin compounds show partially resolved spectra with quadrupole splitting values ranging from 0.62 to 1.00 mm s^{-1}, except for **5**. Such splittings are unusual for R_4Sn compounds for which differences in Sn–C bond polarities are often too small to generate an electric field gradient at the tin nucleus. That no resolvable splitting was apparent for the triphenyltin-substituted **5** however, is to be expected given that similar singlet spectra have previously been noted in numerous comparable cases such as $(2\text{-}C_4H_3S)SnPh_3$ and $(3\text{-}C_4H_3S)_2Sn(p\text{-tolyl})_2$ [31]. Small differences in bond polarities have been proposed to account for the similarly small splittings (Q.S. = 0.80–1.20 mm s^{-1}) observed for Ph$_3$SnBox, Ph$_3$SnBtz and Bu$_3$SnBtz (Box = 2-benzoxazole; Btz = 2-benzothiazole); the tetrahedral geometry at tin in these latter cases has been confirmed by an X-ray crystallographic study of Ph$_3$SnBtz [22]. Following our previous work [22], the magnitudes of the observed quadrupole splittings can be taken to reflect the polarity imbalance in the Sn–C bonds. This allows the relative polarities of the Sn–R bonds to be estimated as: R = Me, Bu < Ph, thiophene < pyrazole < Box, Btz.

3.3. The structure of 5-triphenylstannyl-1-[(5-triphenylstannyl-1H-pyrazol-1-yl)methyl]-1H-pyrazole (10)

The structure of **10** is shown in Fig. 1 and confirms the C^5 and $C^{5'}$ positions as the points of ring lithiation and subsequent substitution. The tin-substituted C(3) and C(5) atoms of the pyrazole rings are positioned in an essentially *anti*-conformation with respect to the bridging methylene carbon C(4) so as to minimise steric interactions between the bulky triphenyltin groups. The two unique tin sites show the expected tetrahedral geometry, although in both cases the bond angle ranges are somewhat distorted from a perfectly regular 109° [103.4(2)–120.6(2)° for Sn(1); 101.5(2)–115.9(2)° for Sn(2)]. Similar distortions in the structure of triphenyltin benzothiazole have been employed to rationalise the observed reactivity and Mössbauer quadrupole splittings based upon the observation that the angles involving the heterocycle carbon were in each case smaller (approximately 104–108°) than those involving only the phenyl groups [22]. This, however, is not the case for **10** and no consistent trend is discernible. This suggests that the electronegativity of the pyrazole and phenyl rings are much closer and as such compete more evenly for the s, p-electron density on tin. Rather, it appears that the angular distortions are induced by the presence of the non-bonded pyrazole ring adjacent to each tin site and its steric interaction with the tin-bonded phenyl groups. Although it is also apparent from Fig. 1 that the free pyrazole ring atoms

N(3) and N(1) are oriented towards the Sn(1) and Sn(2) sites, respectively, the Sn(1)–N(3) and Sn(2)–N(1) distances of 4.13 and 3.46 Å are rather long to be anything other than non-bonding and make it unlikely that any residual N: → Sn interaction affects the overall structure of the molecule. In contrast to the bond angle data, the eight Sn–C bond lengths are identical within experimental error and closely compared to the bond lengths determined for the similar tin environments presented by Ph_3SnBtz (2.16 Å) [22], and tetrakis-(2-thienyl)tin (2.15 Å) [32].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 156253. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-336033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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