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Trichloro-, mono-, di- and tri-organotin(IV) derivatives of hydridotris-(4-methylpyrazol-1-yl)borates†

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Tin(IV) complexes of general formula $SnR_nCl_{3-n}[HB(mpz)_3]$ (R = Me or Ph; n = 0–2; mpz = 4-methylpyrazolyl) have been synthesised and characterised by IR, far-IR, ^1H, ^{13}C, ^{119}Sn NMR and ^{119}Sn Mössbauer spectroscopy. Their stability towards self-decomposition decreases with increasing number of Sn-bonded aryl or alkyl groups. In addition, triorganotin(IV) complexes of the same ligand as well as of $[HB(pz)_3]^-$ and $[HB(dmpz)_3]$ (pz = pyrazolyl, dmpz = 3,5-dimethylpyrazolyl) have been synthesised and characterised by IR and NMR techniques but, due to their low stability (even in the solid state), could not be characterised by Mössbauer spectroscopy. Both the crystal structures of $SnCl_3[HB(mpz)_3]$ and $SnPhCl_2[HB(mpz)_3]$ show the tin atom in a skewed octahedral environment. The structure of the deboronated adduct $SnMe_2Cl_2(Hmpz)_2$, obtained from attempted recrystallisation of $SnMe_2Cl[HB(mpz)_3]$, in which the Cl, the Me and the *N*-donors are in the all-*trans* configuration, has been determined.

Poly(pyrazolyl)borates[1] have become in recent years the ligands of choice for the synthesis of a huge number of complexes and for investigating a variety of features in co-ordination chemistry. Examples can be found in the study of intramolecular electron-transfer processes,[2] of derivatives which exhibit either photochemical reactivity or alkane activation[3] and in models for bioinorganic systems.[4] We have previously reported organotin(IV) tetrakis(pyrazolyl)borates[5a,b] and tris(pyrazolyl)borates involving unsubstituted,[6] mono-,[7] di-[8] and tri-substituted[9] rings. Since the pyrazole ring-substitution pattern regulates the stereoelectronic environment around the metal centre, it seemed interesting to investigate the interplay of steric and electronic factors arising from interaction of hydrotris(4-methylpyrazolyl)borate, $HB(mpz)_3^-$, with organotin(IV) species.

In related complexes containing the R_nSnCl_{3-n} moiety and differently substituted pyrazolylborate ligands the commonly investigated range of n is 0–2. Some years ago the crystal structure[10] and later the ^{13}C and ^{119}Sn NMR spectra[11] were reported of the somewhat unstable $SnMe_3[HB(pz)_3]$ the only R_3SnN_3 six-co-ordinate tin(IV) derivative known. Nevertheless, its synthesis in dichloromethane seems very difficult, owing to rapid decomposition, and its characterisation lacked IR and far-IR data. In the present work a reliable synthesis of several triorganotin(IV) complexes, not only of $HB(mpz)_3^-$ but also of $HB(pz)_3$ and $HB(dmpz)_3^-$, (dmpz = 3,5-dimethylpyrazolyl), is reported, in order to extend the discussion on the influence of the type and number of R groups linked to tin, on the basis of IR and NMR spectral data.

Experimental

Equipment

Solvent evaporations were always carried out *in vacuo* (water aspirator). The samples were dried till constant weight [20 °C, *ca.* 0.1 Torr (*ca.* 13.3 Pa)]. Carbon, hydrogen and nitrogen analyses together with molecular weight determinations (Knauer membrane osmometer) were performed in the 'Dipartimento di Scienze Chimiche', University of Camerino. Infrared spectra were recorded from 4000 to 250 cm^{-1} on a Perkin-Elmer 2000 System Series FTIR instrument, ^1H, ^{13}C and ^{119}Sn NMR spectra on a Varian VXR-300 spectrometer operating at room temperature (300 MHz for ^1H, 75 MHz for ^{13}C and 111.9 MHz for ^{119}Sn). Some NMR spectra were also recorded on a Varian Gemini-200 spectrometer (200 MHz for ^1H, 50 MHz for ^{13}C). The chemical shifts are reported in ppm from $SiMe_4$ (^1H and ^{13}C, calibration by internal deuterium solvent lock) and $SnMe_4$ (^{119}Sn). The conductivity of acetone solutions was measured with a Crison CDTM 522 conductimeter at room temperature.

Syntheses

All experiments were carried out under a dinitrogen atmosphere Hydrocarbon solvents were dried by distillation from sodium–potassium, dichloromethane from calcium hydride. All solvents were outgassed with dry dinitrogen prior to use.

Potassium hydridotris(4-methylpyrazol-1-yl)borate. Potassium tetrahydroborate (2.7 g, 0.05 mol) and 4-methylpyrazole (16.42 g, 0.20 mol) were gradually heated with stirring in a flask (1 l) at temperatures not exceeding 190 °C. The KBH_4 dissolved slowly with evolution of hydrogen (0.15 mol, *ca.* 3.7 l), and the progress of the reaction was followed on a gas meter. After 60 h the melt was poured dropwise into stirred hot xylene (300 cm^3). Upon cooling a solid precipitated and after repeated washings with heptane–diethyl ether (2:1) the mixture was filtered, yielding *ca.* 12.2 g of a solid (83%), m.p. 258–260 °C (Found: C,

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† Organotin Polypyrazolylborates. Part 11. Part 10 is ref. 5(*c*) and Part 9 is ref. 5(*b*).

48.85; H, 5.50; N, 28.40. Calc. for $C_{12}H_{16}BKN_6$: C, 49.00; H, 5.50; N, 28.55%). NMR ($CDCl_3$): ^{1}H, δ 7.22, 6.82 (s, H^3 or H^5), 2.00 (s, 4-Me); ^{13}C, δ 142.1 (C^3), 134.7 (C^5), 113.6 (C^4) and 9.3 (4-Me). IR: 3115w [ν(C–H)], 2407s [ν(B–H)], 1568s, 1562m cm^{-1} (ring breathing).

Trichloro[hydridotris(4-methylpyrazol-1-yl)borate]tin(IV) 1. An anhydrous solution of $SnCl_4$ in CH_2Cl_2 (1 mol dm^{-3}, 1 cm^3) was added by syringe, under a dinitrogen atmosphere, to a cooled (*ca.* −10 °C) solution/suspension of K[HB(mpz)$_3$] (0.294 g, 1 mmol) in CH_2Cl_2 (35 cm^3), previously dried over CaH_2. The resulting mixture was purged with dry nitrogen and stirred vigorously for 5 min. After filtration the solvent was removed under reduced pressure at room temperature, and the residue (0.36 g, 75%) was recrystallised from dichloromethane. Recrystallisation from dichloromethane–toluene (1:2, v/v) afforded crystals of the toluene solvate suitable for X-ray studies. Yield: 326 mg (68%) (Found: C, 40.25; H, 4.80; N, 12.50. Calc. for $C_{26}H_{32}BCl_3N_6Sn$: C, 40.05; H, 4.85; N, 12.65%). This compound chars without melting (Found: C, 39.55; H, 4.10; N, 14.75. Calc. for $C_{19}H_{24}BCl_3N_6Sn$: C, 39.90; H, 4.25; N, 14.70%). NMR ($CDCl_3$): ^{1}H, δ 7.92, 7.47 (s, H^3 or H^5), 2.08 (s, 4-Me); ^{13}C, δ 140.0 (|^2J(Sn–N–C)| = 24.2 Hz, C^3), 135.2 (C^5), 116.5 (C^4) and 8.5 (4-Me); ^{119}Sn, δ −626. IR: 3116w, 3108w [ν(C–H)], 2510s [ν(B–H)], 1570s, 1560m (ring breathing), 322vs (br) cm^{-1} [ν(Sn–Cl)].

Dichloro[hydridotris(4-methylpyrazol-1-yl)borato]methyltin(IV) 2. A dichloromethane solution (40 cm^3) of $SnMeCl_3$ (1 mmol, 0.24 g) was added dropwise to a cooled (*ca.* 10 °C) stirred dichloromethane solution/suspension (40 cm^3) of K[HB(mpz)$_3$] (1 mmol, 0.294 g). The resulting cloudy mixture was stirred for 15 min at 10 °C, filtered and the filtrate evaporated under reduced pressure. Further purification of compound **2** was achieved by recrystallisation from chloroform. Yield: 409 mg (89%), *M* 448 (calc. 460), m.p. 218–220 °C (Found: C, 34.15; H, 4.30; N, 18.50. Calc. for $C_{13}H_{19}BCl_2N_6Sn$: C, 33.95; H, 4.15; N, 18.30%). NMR ($CDCl_3$): ^{1}H, δ 7.66, 7.44 [8.01, 7.37] (s, H^3 or H^5), 2.08 [2.02] (s, 4-Me) (signals of lower intensity in square brackets), 1.32 [|^2J(^{119}Sn–H)| = 119.3, |^2J(^{117}Sn–H)| = 113.9, s, SnMe]; ^{13}C, δ 140.5 [140.6] {|^2J(Sn–N–C)| = 12.1 [37.0], C^3}, 134.4 [134.7] (C^5), 116.1 [115.6] (C^4), 8.6 [8.5] (4-Me) and 19.8 (SnMe); ^{119}Sn, δ −486. IR: 3115w, 3110w [ν(C–H)], 2491s [ν(B–H)], 1571s (ring breathing), 528s [ν(Sn–C)], 286vs, 275s cm^{-1} [ν(Sn–Cl)].

Complexes 3, 5 and 6. These were prepared similarly to complex **2**. Recrystallisation of **5** in dichloromethane–toluene gave crystals suitable for X-ray studies. All these compounds, **3**–**6** in particular, are prone to decomposition on standing in solution (as noted earlier[9] and after 1 or 2 weeks decomposition products are visible even in the solid state. Consequently, the attempted recrystallisation of **3** and **6** did not afford the pure compounds in appreciable yields, but decomposition products arising primarily from deboronation resulted.

Chloro[hydridotris(4-methylpyrazol-1-yl)borato]dimethyltin(IV) **3**. Yield: 365 mg (83%), *M* 425 (calc. 439), m.p. 152–154 °C (Found: C, 38.60; H, 5.15; N, 18.90. Calc. for $C_{14}H_{22}BClN_6Sn$: C, 38.30; H, 5.05; N, 19.15%). NMR ($CDCl_3$): ^{1}H, δ 7.71, 7.03 [7.50] (s, H^3 or H^5), 2.06 [2.12] (s, 4-Me) and 0.78 [br, ^2J(Sn–H) = 69.0 Hz, SnMe]; ^{13}C, δ 141.7 [140.9] (C^3), 134.9 [133.5] (C^5); 116.4 [115.8] (C^4), 8.8 [8.7] (4-Me) and 13.5 (SnMe); ^{119}Sn, δ −339. IR: 3096w, 3089w [ν(C–H)], 2470s, 2464s [ν(B–H)], 1570s, 1560m (ring breathing), 522m, 514s [ν(Sn–C)], 277vs, 268s (br) cm^{-1} [ν(Sn–Cl)].

Dichloro[hydridotris(4-methylpyrazol-1-yl)borato]phenyltin(IV) **5**. Yield 459 mg (88%), *M* 513 (calc. 522), m.p. 234–237 °C (Found: C, 41.20; H, 4.15; N, 15.85. Calc. for $C_{18}H_{21}BCl_2N_6Sn$: C, 41.45; H, 4.05; N, 16.1%). NMR ($CDCl_3$): ^{1}H, δ 8.11, 7.42 (s, H^3 or H^5), 2.01 [2.08] (s, 4-Me), 7.35, 7.53 (m, SnPh); ^{13}C, δ 140.2 [140.6] {|^2J(Sn–N–C) = 13.9 [35.5 Hz], (C^3)}, 135.1 [134.9] (C^5), 116.0 [115.7] (C^4), 8.5 [8.6] (4-Me), 133.7, 129.2, 128.1 [|^2J(Sn–C) = 85.7, |^3J(Sn–C)| = 139.3, |^4J(Sn–C)| = 32.1 Hz, SnPh]; ^{119}Sn, δ −532. IR: 3116w, 3110w [ν(C–H)], 2502s (br) [ν(B–H)], 1570s, 1560m (ring breathing), 451vs [ν(Sn–C)] (*y* mode), 265s [ν(Sn–C)] (t mode), 302s, 283vs (br) cm^{-1} [ν(Sn–Cl)].

Chloro[hydridotris(4-methylpyrazol-1-yl)borato]diphenyltin(IV) **6**. Yield 446 mg (79%), *M* 557 (Calc. 564), m.p. 173–175 °C (Found: C, 51.35; H, 4.75; N, 14.65. Calc. for $C_{24}H_{26}BClN_6Sn$: C, 51.15; H, 4.65; N, 14.90%). NMR ($CDCl_3$): ^{1}H, δ 7.40, 7.35 [7.63, 7.12] (s, H^3 or H^5), 1.94 [2.02] (s, 4-Me), 7.28, 7.53 (m, SnPh); ^{13}C, δ 140.3 [|^2J(Sn–N–C)| = 22.0, C^3)], 135.2 (C^5), 114.9 (C^4), 8.6 (4-Me); 140.6, 135.1, 127.7, 128.0 [|^2J(Sn–C)| = 61.8, |^3J(Sn–C)| = 83.7, |^4J(Sn–C)| = 17.6 Hz, SnPh]; ^{119}Sn, δ −459. IR: 3106w [ν(C–H)], 2504s [ν(B–H)], 1568s (ring breathing), 460s, 447s (br) [ν(Sn–C)] (*y* mode), 247s [ν(Sn–C)] (t mode), 290s, 278s (br) cm^{-1} [ν(Sn–Cl)].

[Hydridotris(4-methylpyrazol-1-yl)borato]trimethyltin(IV) 4. A solution of $SnMe_3Cl$ (0.20 g, 1 mmol) in outgassed (dry N_2), anhydrous (molecular sieves) toluene (25 cm^3) at 0 °C was added to a flask (100 cm^3) containing a solution/suspension of K[HB(mpz)$_3$] (0.294 g, 1 mmol) in toluene (25 cm^3) (as above) with stirring and purging with dry N_2. After 5 min the solution was filtered (KCl) in an atmosphere of dry N_2 and the filtrate evaporated at *ca.* 0 °C under reduced pressure. The resulting oily liquid was purified in light petroleum diethyl–ether (10:1, v/v) at 0 °C. Yield 247 mg (59%), m.p. 115–117 °C (Found: C, 42.85; H, 6.15; N, 19.90. Calc. for $C_{15}H_{25}BN_6Sn$: C, 43.00; H, 6.00; N, 20.05%). NMR ($CDCl_3$): ^{1}H, δ 7.39, 7.30 (s, H^3 or H^5), 2.02 (s, 4-Me) and 0.42 [|^2J(Sn–H)| = 63.2 Hz, SnMe]; ^{13}C, δ 138.7 (br, C^3), 133.6 (br, C^5), 115.1 (br, C^4), 8.7 (4-Me), and −11.4 (SnMe); ^{119}Sn δ −198. IR: 3090w [ν(C–H)], 2454s [ν(B–H)], 1570s (ring breathing), 546m, 505vs cm^{-1} [ν(Sn–C)].

Compounds 7–11. These were prepared similarly to compound **4**. As previously observed for **8**,[9] they are rather unstable in chlorinated solutions ($CHCl_3$, CH_2Cl_2) although slightly less so in aromatic solvents. Even in the solid state they are prone to slow decomposition.[1e,f]

[Hydridotris(4-methylpyrazol-1-yl)borato]triphenyltin(IV) **7**. Yield 369 mg (61%), m.p. 134–136 °C (Found: C, 59.25; H, 4.95; N, 13.55. Calc. for $C_{30}H_{31}BN_6Sn$: C, 59.55; H, 5.15; N, 13.90%). NMR ($CDCl_3$): ^{1}H, δ 7.71, 7.05 (s, H^3 or H^5), 1.98 (s, 4-Me), 7.40, 7.22 (m, SnPh); ^{13}C, δ 141.1 [|^2J(Sn–N–C)| = 10.5, C^3], 134.1 (C^5), 114.6 (C^4), 9.1 (4-Me), 137.8, 136.6, 130.9, 129.6 [|^2J(Sn–C)| = 51.1, |^3J(Sn–C)| = 62.7, |^4J(Sn–C)| = 13.5 Hz, SnPh]; ^{119}Sn, δ −381. IR: 3102w [ν(C–H)], 2493m (br) [ν(B–H)], 1576m, 1560m (ring breathing), 459s, 446s [ν(Sn–C)] (*y* mode), 255s, 245s cm^{-1} [ν(Sn–C)] (t mode).

[Hydridotris(1-pyrazol-1-yl)borato]trimethyltin(IV) **8**. Yield 238 mg (63%), m.p. 111–113 °C (Found: C, 37.95; H, 5.20; N, 22.05. Calc. for $C_{12}H_{19}BN_6Sn$: C, 38.25; H, 5.10; N, 22.30%). NMR ($CDCl_3$): ^{1}H, δ 7.61, 7.55 (d, H^3 or H^5), 6.18 (pseudo t, H^4) and 0.44 [|^2J(Sn–H)| = 52.0 Hz, SnMe]; ^{13}C, δ 138.0 (br, C^3), 133.6 (br, C^5), 104.0 (br, C^4) and −11.3 (SnMe); ^{119}Sn, δ −184. IR: 3116w, 3110w [ν(C–H)], 2515m [ν(B–H)], 1508m, 1499m (ring breathing), 520m, 504vs cm^{-1} [ν(Sn–C)].

[Hydridotris(pyrazol-1-yl)borato]triphenyltin(IV) **9**. Yield 405 mg (72%) m.p. 143–145 °C (Found: C, 57.35; H, 4.65; N, 14.60. Calc. for $C_{27}H_{25}BN_6Sn$: C, 57.60; H, 4.50; N, 14.95%. NMR ($CDCl_3$): ^{1}H δ 7.70, 7.38 (d, H^3 or H^5), 6.08 (pseudo t, H^4), 7.22, 7.41 (m, SnPh); ^{13}C, δ 141.5 [|^2J(Sn–N′–C)| = 12.5; C^3], 134.9 (C^5), 104.5 (C^4), 136.4, 134.3, 128.0, 129.1 [|^2J(Sn–C)| = 55.5, |^3J(Sn–C)| = 66.6, |^4J(Sn–C)| = 11.1 Hz, SnPh]; ^{119}Sn, δ −373. IR: 3100w [ν(C–H)], 2476m [ν(B–H)], 1503s (ring breathing), 459vs, 448s [ν(Sn–C)] (*y* mode), 247s (br) cm^{-1} [ν(Sn–C)] (t mode).

[*Tris*(3,5-*dimethylpyrazol*-1-*yl*)*hydridoborato*]*trimethyltin*(IV) **10**. Yield 286 mg (62%), m.p. 165–167 °C (Found: C, 47.15; H, 6.85; N, 17.90. Calc. for $C_{18}H_{31}BN_6Sn$: C, 46.90; H, 6.80; N, 18.25%). NMR ($CDCl_3$): ^{1}H, δ 2.38, 2.32 (d, 3- or 5-Me), 5.70 (s, H^4) and 0.32 (SnMe); ^{13}C, δ 145.4 (C^3), 142.8 (C^5), 105.6 (C^4), 12.9, 12.2 (3- or 5-Me), −11.6 (SnMe); ^{119}Sn, δ −212. IR: 3125w [ν(C–H)], 2540m, 2523m [ν(B–H)], 1540m (ring breathing), 544m, 511s cm^{-1} [ν(Sn–C)].

[*Tris*(3,5-*dimethylpyrazol*-1-*yl*)*hydridoborato*]*triphenyltin*(IV) **11**. Yield 408 mg (63%), m.p. 185–187 °C (Found: C, 61.05; H, 5.85; N, 12.75. Calc. for $C_{33}H_{37}BN_6Sn$: C, 61.25; H, 5.75; N, 13.00%). NMR ($CDCl_3$): ^{1}H δ 2.50, 1.10 (s, 3- or 5-Me), 5.62 (s, H^4), 7.15, 7.50 (m, SnPh); ^{13}C, δ 150.1 (C^3), 143.0 (C^5), 106.0 (C^4), 13.2, 13.0 (3- or 5-Me), 135.7, 128.3, 127.5, 126.7 [$|^{2}J(\mathrm{Sn–C})| = 53.6$, $|^{3}J(\mathrm{Sn–C})| = 63.1$, $|^{4}J(\mathrm{Sn–C})| = 13.9$ Hz, SnPh]; ^{119}Sn, δ −424. IR: 3120w [ν(C–H)], 2558m, 2527w [ν(B–H)], 1537m, 1523w (ring breathing), 472vs, 449m [ν(Sn–C)] (*y* mode), 248s, 240 (sh) cm^{-1} [ν(Sn–C)] (t mode).

Dichlorodimethylbis(4-methylpyrazole)tin(IV) 12. This compound resulted as the main product from the attempted recrystallisation of **3** in dichloromethane–acetonitrile. The sample was dried *in vacuo* till constant weight (20 °C, 0.1 Torr) (Found: C, 31.40; H, 4.80; N, 14.45. Calc. for $C_{10}H_{18}Cl_2N_4Sn$: C, 31.30; H, 4.75; N, 14.60%). $M = 383.9$. NMR ($CDCl_3$): ^{1}H, δ 7.56 (s, H^3 or H^5), 2.16 (s, 4-Me) and 1.24 [$|^{2}J(^{119}\mathrm{Sn–H})| = 80.5$, $|^{2}J(^{117}\mathrm{Sn–H})| = 77.1$ Hz, s, SnMe]; ^{13}C, δ 133.5 (C^3 or C^5), 117.2 (C^4), 18.9 (4-Me) and 9.2 (SnMe). IR: 1580w (ring breathing), 340s, 290s cm^{-1} [ν(Sn–Cl)].

Crystallography

Intensity data for compounds **1**, **5** and **12** were collected at room temperature with a Philips PW 1100 diffractometer by using Mo-Kα radiation (λ = 0.710 69 Å). The intensities were corrected for Lorentz-polarisation effects and for absorption. Crystal data, data collection, and refinement parameters are listed in Table 1. The structures were solved by direct methods using the SHELXS 86 program.[12] Blocked full-matrix least-squares refinement on *F* minimised the function $\Sigma w[|F_o| - |F_c|]^2$. The non-hydrogen atoms were refined anisotropically, except for the C atoms of the toluene molecules in **1** (attempted refinement of using partial occupancy was unsuccessful). The positions of the hydrogen atoms were calculated but not refined.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Cambridge Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/43.

Mössbauer spectroscopy

The Ca^{119m}SnO$_3$ Mössbauer source and the absorbers were kept at 4.2 K. A sinusoidal velocity waveform and a proportional detector were used. The spectra have been least-squares fitted with sets of equal Lorentzian lines by the program MOS 90. The hyperfine parameters such as isomer shift (i.s.) (relative to SnO_2), average linewidth, and experimental quadrupole splitting q.s. are in mm s^{-1}, the relative resonance area in %.

Results and Discussion

The complexes were prepared by a metathetic reaction of the potassium salt of the pyrazolylborate with the appropriate chloroorganotin(IV) derivative SnR_nCl_{4-n} which proceeds smoothly in dichloromethane (**1**–**3** and **5**, **6**, n = 0–2) or toluene (**4** and **7**–**11**, n = 3) solution/suspension. The derivatives **1**, **2** and **5** are reasonably stable in chlorinated solvents as well as in the solid state. Recent studies[1e,f] have suggested that alkali-metal poly(pyrazol-1-yl)borates are hygroscopic. Thus, the traces of moisture which can be introduced into a system with the reagents may not necessarily interfere with the initial formation of the complexes, but then cause complications on storage. The diorganotin derivatives **3** and **6**, and mainly the triorganotin derivatives **4** and **7**–**11**, are unstable not only in chlorinated solvents, but also in the solid state, even under nitrogen. Decomposition of these compounds proceeds through hydrolytic B–N cleavage, with formation of pyrazole–metal adducts, such as compound **12**.

Conductivity and molecular weight determinations

Conductivity measurements made in acetone and the values (where determined) of the molecular weights, determined osmometrically in chloroform, which fall near the calculated ones, concur to indicate the non-electrolyte nature and formulation of the complexes in solution.

Infrared and NMR data

All the expected bands for the ligands and the tin moieties can be detected in the IR spectra of compounds **1**–**11** in the solid state (Nujol mull). There are weak absorptions around 3100 cm^{-1} due to the pz ring C–H stretching; typical medium or strong bands, related to ring 'breathing' vibrations, have been found at 1560–1580 cm^{-1} in the mpz derivatives **1**–**7**, and at 1500–1520 cm^{-1} for the pz and dmpz derivatives **8**–**11**. The ν(B–H) vibrations fall between 2450 and 2510 cm^{-1}, at higher values with respect to the potassium salts, in accordance with a strengthening of the covalent character of the B–H bond due to an overall increase of electronic flow towards the tin(IV) centre in the complexes. Moreover, this is consistent with the effect of changing the number of Me groups on the tin centre. It has been noted that the ν(B–H) frequency decreases with increasing number of Me groups bonded to tin.[5-9] The effect of substitution of Cl with Me is regular (about 20 cm^{-1}, for each group), while this trend is less pronounced for the phenyl derivatives **5**–**7**, because of the lower electron-releasing power of Ph in comparison with Me.

Strong ν(Sn–C) and ν(Sn–Cl) vibrations appear in the far-infrared region: ν(Sn–Me) at 500–550[13] and ν(Sn–Ph) at 440–460 (*y* mode) and at 240–270 (t mode),[14] whereas ν(Sn–Cl) is at 270–330 cm^{-1}[15] as very strong and broad absorptions increasing in wavenumber with the number of tin-bonded Cl atoms. The ν(Sn–N) stretching bands cannot be assigned with certainty, because they are probably hidden under ligand vibrations.

The integrated ^{1}H NMR spectra of the derivatives **1**–**11** are consistent with their empirical formulae. The ^{1}H chemical shifts for the pz hydrogens always have lower values than those for the starting potassium salts.[5-9] The same trend is observed for the 3-Me and 5-Me groups in derivatives **10** and **11**,[8] while in **1**–**7** the position of the 4-Me absorption remains essentially unchanged. In the spectra of **2**–**4** the expected upfield shift of the SnMe resonances,[14] on going from the mono- (δ 1.32) to the di- (δ 0.78) and then to the tri-methyltin(IV) derivative (δ 0.42) is observed. In the ^{13}C NMR spectra the pz carbon shifts are generally very similar to those for the potassium salts, whereas the 4-Me (in **1**–**7**) or 3- and 5-Me resonances (in **10**, **11**) are shifted slightly upfield.[8]

In the context of octahedral co-ordination the derivatives not containing three equal groups (besides pyrazolylborate) on tin (**2**, **3** and **5**, **6**) show the presence of two types of pyrazole rings in the ^{1}H and ^{13}C NMR spectra, the ratio of two sets of pyrazole signals being 2 : 1 in the proton spectra. This excludes fluxionality around tin for these compounds in chloroform solution, and the sharp singlet seen in their ^{119}Sn NMR spectra is thus due to a single species.

In the ^{1}H, ^{13}C and ^{119}Sn NMR spectra of trichloro- or triorgano-tin(IV) derivatives **1**, **4** and **8**–**11** only one set of signals is present as expected for a C_{3v} local symmetry. The signals of decomposition products, due to the high instability of triorganotin pyrazolylborate compounds, have been often detected, and for **4**, **8** and **10** the ^{13}C Me$_3$Sn resonances have been observed at *ca.* δ −11 *vs.* SiMe$_4$.[11]

The ^2J-, ^3J- and ^4J-(Sn–C) values for Ph groups bonded to tin (derivatives **5**–**7**, **9** and **11**) fall in the range expected for mono-, di- and tri-phenyltin(IV) compounds.[16] Moreover, also ^2J[Sn–(N)–C(3)] has been observed in some cases.[5–9] The tin–proton ^2J coupling constants of **3**, **4** and **8**, according to Lockhart's equation,[17] provide values of the C–Sn–C angle of 119, 114 and 108°, respectively. For comparison, it may be noted that the value found by Nicholson[10] from the crystal structure of **8** is 105°. These values should be taken only as hints owing to the lack of tridentate ligands in the data the cited equation is based on. However, some distortion from an octahedral structure in solution parallels the deviations found in the solid state (see below) which cannot be accounted for only by packing effects. The values for all the ^{119}Sn chemical shifts (which span an interval of more than 400 ppm) lie in the appropriate range for octahedral tin(IV) species.[6–9,18]

It was previously observed[6–9] that the ^{119}Sn chemical shift values for the SnR$_n$Cl$_{3-n}$ complexes of pyrazolylborates plotted against *n* (0, 1 or 2), showed linear correlations within each ligand series, with very similar slopes. Now we are able to extend the trends also to $n = 3$: these points are spaced from those for $n = 2$ with gaps similar to those found between the points for $n = 0$, 1 or 2 (*ca.* 140 ppm for each Me and *ca.* 80 ppm for each Ph). The present case is illustrated in Fig. 1 for R = Me (*a*) or Ph (*b*). The distance between each pair of lines has been empirically interpreted as roughly proportional to the difference in the donating power of each pair of ligands. It may be noted that the ^{119}Sn resonances of the dmpz derivatives are shifted upfield (*ca.* 20–30 ppm) with respect to those of the mpz derivatives, which are essentially similar to those of the pz derivatives. So that we can hypothesise that, at least in solution, the 3,5-dimethyl-substituted ligand seems to be a better donor than the other two.

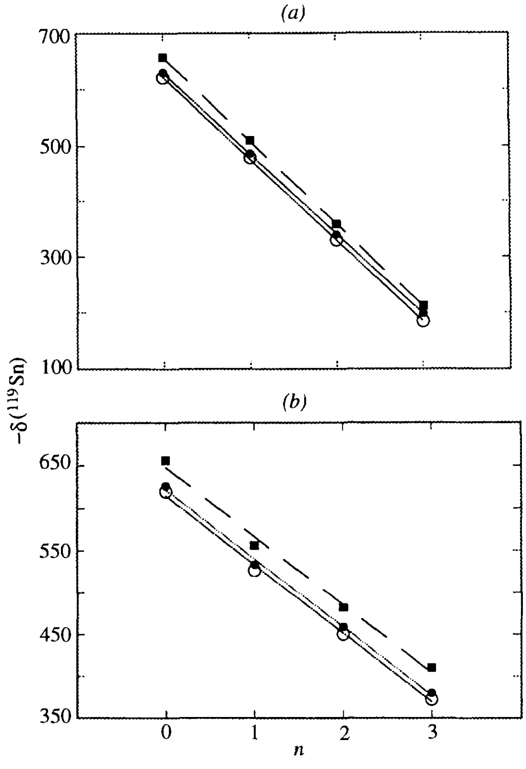

Fig. 1 Plots of the ^{119}Sn chemical shift of SnMe$_n$Cl$_{3-n}$ (*a*) and SnPh$_n$Cl$_{3-n}$ (*b*) pyrazolylborate complexes *vs.* *n* ○, pyrazolylborate; ■, 3,5-dimethylpyrazolylborate; ●, 4-methylpyrazolylborate

Crystal structures

SnCl$_3$[HB(mpz)$_3$] 1. The asymmetric unit of this compound contains two independent molecules of SnCl$_3$[HB(mpz)$_3$] and two molecules of toluene [Fig. 2(*a*)]. Since the two tin sites have very similar bond lengths and angles (see Table 2), for clarity only one molecule has been drawn in the ORTEP[19] plot. The geometry around the two tin sites is that of a distorted octahedron with N–Sn–N bond angles of about 82° and Cl–Sn–Cl angles ranging from 94.2(3) to 97.0(2)°.

There is no significant interaction among these molecules, the crystal packing being determined by normal van der Waals contacts: the closest contact is between atoms C(4) and C(15) ($x - 1, y, z - 1$) at 3.46 Å. The six pyrazolato rings belonging to the asymmetric unit, except for the 4-Me groups which deviate somewhat, are nearly planar. The atoms of the following least-squares planes do not deviate significantly from planarity: Ia N(11), N(12), C(21)–C(24); IIa N(9), N(10), C(17)–C(20): IIIa

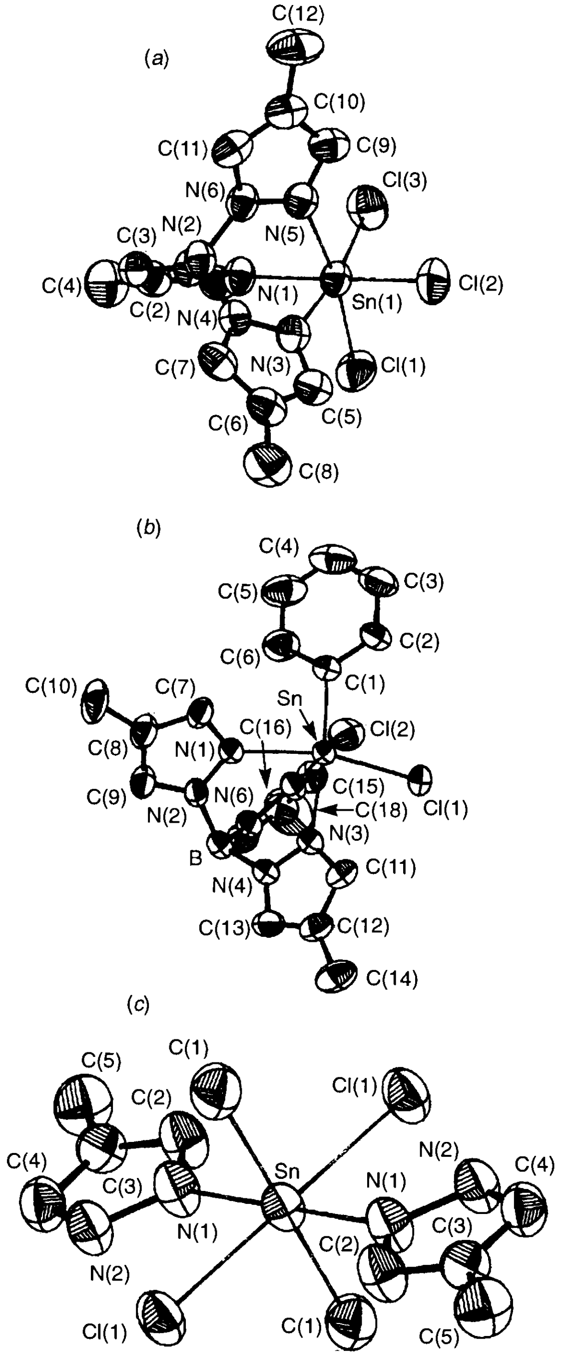

Fig. 2 ORTEP plots for (*a*) SnCl$_3$[HB(mpz)$_3$], (*b*) SnPhCl$_2$[HB(mpz)$_3$] and (*c*) SnMe$_2$Cl$_2$(Hmpz)

Table 1 Crystal data, data collection and refinement parameters of the structures

	$SnCl_3[HB(mpz)_3]\cdot C_6H_5Me$	$SnPhCl_2[HB(mpz)_3]$	$SnMe_2Cl_2(Hmpz)_2$
Formula	$C_{12}H_{16}BCl_3N_6Sn\cdot C_7H_8$	$C_{18}H_{21}BCl_2N_6Sn$	$C_{10}H_{18}Cl_2N_4Sn$
M	572.3	521.81	383.9
Space group	Triclinic, $P\bar{1}$ (no. 2)	Monoclinic, $P2_1/c$ (no. 14)	Triclinic, $P\bar{1}$ (no. 2)
Crystal size/mm	0.34 × 0.30 × 0.24	0.40 × 0.34 × 0.28	0.20 × 0.25 × 0.32
a/Å	12.138(2)	11.645(1)	7.986(1)
b/Å	24.182(2)	10.145(1)	7.267(1)
c/Å	8.814(1)	19.666(2)	7.325(1)
α/°	91.9(1)		83.8(1)
β/°	102.0(1)	97.2(1)	109.0(1)
γ/°	87.1(1)		107.1(1)
U/Å^3	2526(1)	2304.9(6)	384.1(3)
Z	2	4	1
D_c/g cm^{-3}	1.50	1.50	1.66
μ(Mo-Kα)/cm^{-1}	12.36	12.43	18.44
Data collection range/°	$4.7 < 2\theta < 50$	$4.2 < 2\theta < 56$	$5.6 < 2\theta < 56$
No. unique reflections	8904	4632	1859
No. data with $F < 3\sigma(F)$	5643	3351	1748
No. parameters	447	241	153
F(000)	1144	1040	190
R	0.045	0.036	0.045
R'	0.047	0.037	0.047

Table 2 Selected bond distances (Å) and angle (°) for $SnCl_3\cdot[HB(mpz)_3]\cdot C_6H_5Me$ **1**

Sn(1)–Cl(1)	2.380(3)	Sn(1)–Cl(2)	2.368(2)	Sn(2)–Cl(5)	2.374(3)	Sn(2)–Cl(4)	2.370(3)
Sn(1)–Cl(3)	2.370(3)	Sn(1)–N(1)	2.185(5)	Sn(2)–N(7)	2.180(6)	Sn(2)–Cl(16)	2.373(3)
Sn(1)–N(3)	2.180(6)	Sn(1)–N(5)	2.186(6)	Sn(2)–N(11)	2.166(5)	Sn(2)–N(9)	2.193(6)
B(1)–N(2)	1.560(8)	B(1)–N(4)	1.52(1)	B(2)–N(10)	1.544(9)	B(2)–N(8)	1.535(9)
B(1)–N(6)	1.54(1)	N(1)–N(2)	1.350(8)	N(7)–N(8)	1.352(8)	B(2)–N(12)	1.544(9)
N(1)–C(1)	1.335(8)	N(2)–C(3)	1.357(8)	N(8)–N(9)	1.327(8)	N(9)–N(10)	1.364(8)
N(3)–N(4)	1.365(8)	N(3)–C(5)	1.341(8)	N(11)–N(12)	1.369(8)	N(10)–C(19)	1.353(9)
N(4)–C(7)	1.339(9)	N(5)–N(6)	1.354(8)	N(12)–C(23)	1.346(7)	N(11)–C(21)	1.361(8)
N(5)–C(9)	1.351(9)	N(6)–C(11)	1.350(9)				
N(3)–Sn(1)–N(5)	82.1(2)	N(1)–Sn(1)–N(5)	82.3(3)	N(7)–Sn(2)–N(11)	83.1(2)	N(7)–Sn(2)–N(9)	82.5(3)
N(1)–Sn(1)–N(3)	82.6(3)	Cl(3)–Sn(1)–N(5)	90.5(2)	Cl(6)–Sn(2)–N(11)	169.3(3)	Cl(6)–Sn(2)–N(9)	89.9(2)
Cl(3)–Sn(1)–N(3)	170.3(3)	Cl(3)–Sn(1)–N(1)	90.2(3)	Cl(6)–Sn(2)–N(7)	88.8(2)	Cl(5)–Sn(2)–N(11)	90.4(3)
Cl(2)–Sn(1)–N(5)	91.8(3)	Cl(2)–Sn(1)–N(3)	89.7(3)	Cl(5)–Sn(2)–N(9)	171.2(2)	Cl(5)–Sn(2)–N(7)	92.2(3)
Cl(2)–Sn(1)–N(1)	170.9(2)	Cl(2)–Sn(1)–Cl(3)	96.8(3)	Cl(5)–Sn(2)–Cl(6)	97.0(2)	Cl(4)–Sn(2)–N(11)	91.7(2)
Cl(1)–Sn(1)–N(5)	169.9(3)	Cl(1)–Sn(1)–N(3)	90.8(2)	Cl(4)–Sn(2)–N(9)	90.5(3)	Cl(4)–Sn(2)–N(7)	171.8(2)
Cl(1)–Sn(1)–N(1)	89.7(3)	Cl(1)–Sn(1)–Cl(3)	95.7(1)	Cl(4)–Sn(2)–Cl(6)	95.5(1)	Cl(4)–Sn(2)–Cl(5)	94.2(3)
Cl(1)–Sn(1)–Cl(2)	95.3(2)	N(4)–B(1)–N(6)	109.0(8)	N(10)–B(2)–N(12)	107.2(7)	N(8)–B(2)–N(12)	107.5(7)
N(2)–B(1)–N(6)	106.4(6)	N(2)–B(1)–N(4)	107.5(6)	N(8)–B(2)–N(10)	108.3(6)	Sn(2)–N(7)–C(13)	131.1(5)
Sn(1)–N(1)–C(1)	130.4(5)	Sn(1)–N(1)–N(2)	121.6(5)	Sn(2)–N(7)–N(8)	121.2(6)	N(8)–N(7)–C(13)	107.6(6)
N(2)–N(1)–C(1)	108.0(7)	B(1)–N(2)–N(1)	120.0(7)	B(2)–N(8)–N(7)	120.7(7)	N(7)–N(8)–C(15)	108.0(6)
N(1)–N(2)–C(3)	108.4(6)	B(1)–N(2)–C(3)	131.6(6)	B(2)–N(8)–C(15)	131.3(6)	Sn(2)–N(9)–C(17)	132.4(5)
Sn(1)–N(3)–C(5)	130.8(5)	Sn(1)–N(3)–N(4)	121.0(5)	Sn(2)–N(9)–N(10)	120.4(5)	N(10)–N(9)–C(17)	107.1(6)
N(4)–N(3)–C(5)	108.1(6)	B(1)–N(4)–N(3)	120.8(6)	B(2)–N(10)–N(9)	120.8(7)	N(9)–N(10)–C(19)	108.7(6)
N(3)–N(4)–C(7)	108.0(7)	B(1)–N(4)–C(7)	131.3(7)	B(2)–N(10)–C(19)	130.5(6)	Sn(2)–N(11)–C(21)	132.6(5)
Sn(1)–N(5)–C(9)	131.5(5)	Sn(1)–N(5)–N(6)	120.3(5)	Sn(2)–N(11)–N(12)	121.1(5)	N(12)–N(11)–C(21)	106.3(5)
N(6)–N(5)–C(9)	108.1(6)	B(1)–N(6)–N(5)	121.6(6)	B(2)–N(12)–N(11)	120.5(5)	N(11)–N(12)–C(23)	108.8(7)
N(5)–N(6)–C(11)	108.3(7)	B(1)–N(6)–C(11)	130.1(7)	B(2)–N(12)–C(23)	130.7(7)	N(7)–C(13)–C(14)	110.6(7)

Table 3 Comparison of structural data for trichlorotin pyrazolylborate complexes

L*	Sn–N/Å	Sn–Cl/Å	N–Sn–N/°	Cl–Sn–Cl/°	Ref.
$HB(mpz)_3$	2.184(3)	2.373(2)	82.3(2)	95.9(1)	This work
$HB(dmcpz)_3$	2.213(1)	2.345(4)	81.8(3)	96.9(2)	9(*b*)
$HB(dmpz)_3$	2.198(1)	2.382(1)	84.1(1)	93.9(1)	21
$HB(pz)_3$	2.234(7)	2.376(3)	81.6(2)	98.5(2)	20
$B(mpz)_4$	2.191(2)	2.372(1)	81.9(6)	96.2(1)	5(*b*)

* dmcpz = 3,5-Dimethyl-4-chloropyrazolyl.

N(7), N(8), C(13)–C(16); IVa N(1), N(2), C(1)–C(4); Va N(3), N(4), C(5)–C(8); VIa N(5), N(6), C(9)–C(12). Analogously, the atoms of the Sn(1) co-ordination plane [VIIa Sn(1), Cl(1), Cl(3), N(3), N(5)] are planar while those of Sn(2) [VIIIa Sn(2), Cl(4), Cl(5), N(7), N(9)] deviate significantly. The dihedral angles between least-squares planes associated with the Sn(1) and Sn(2) sites are very similar: Ia/IIa, 121.9(3); IVa/Va, 117.4(3); Ia/IIIa, 112.8(3); IVa/VIa, 120.4(3); IIa/IIIa, 59.3(3); Va/VIa, 57.6(3)°. The dihedral angles between analogous pyrazolato rings are small: Ia/IVa, 2.6(3); IIa/VIa, 5.6(3); IIIa/Va, 6.1(3)°. The dihedral angle VIIa/VIIIa between the Sn(1) and Sn(2) co-ordination planes is 65.5(2)°.

A notable feature is the shortening of the average Sn–N bond distance in comparison with similar structures containing different pyrazolylborate ligands, as in Table 3, while the average Sn–Cl length is essentially the same.

$SnPhCl_2[HB(mpz)_3]$ 5. The molecular structure is shown in the ORTEP plot of Fig. 1(*b*). Selected bond distances and angles are reported in Table 4. The tin atom displays a distorted-octahedral co-ordination geometry with the bond angles ranging from 80.7(1) to 98.6(1)°, where the two Cl–Sn–C angles are 98.6(1) and 97.9(1)°, and Sn–Cl 2.430 and 2.417, Sn–C 2.137 Å and Sn–N 2.206, 2.221, and 2.240 Å. There are no significant intermolecular contacts less than 3.50 Å.

The atoms of the weighted least-squares plane Ib [C(1)–C(6)] do not deviate significantly from planarity. On the contrary, those of the pyrazolato rings IIb [N(1), N(2), C(7)–C(10)], IIIb [N(3), N(4), C(11)–C(14) and IVb [N(5), N(6), C(15)–C(18)] deviate significantly from planarity. The steric arrangement of the planes can be inferred from their dihedral angles: Ib/IIb, 61.1(1); Ib/IIIb, 9.5(1); Ib/IVb, 114.2(1); IIb/IIIb, 113.2(1); IIb/IVb, 53.6(1); IIIb/IVb, 59.6(1)°.

Table 4 Selected bond distances (Å) and angles (°) for $SnPhCl_2[HB(mpz)_3]$ 5

Sn–Cl(1)	2.430(1)	Sn–Cl(2)	2.417(2)
Sn–N(1)	2.221(3)	Sn–N(3)	2.206(3)
Sn–N(5)	2.240(4)	Sn–C(1)	2.137(3)
B–N(2)	1.545(6)	B–N(4)	1.543(6)
B–N(6)	1.547(6)	N(1)–N(2)	1.369(4)
N(1)–C(7)	1.339(5)	N(2)–C(9)	1.337(5)
N(3)–N(4)	1.366(5)	N(3)–C(11)	1.341(6)
N(4)–C(13)	1.348(6)	N(5)–N(6)	1.361(5)
N(5)–C(15)	1.331(6)	N(6)–C(13)	1.342(5)
N(3)–Sn–N(5)	80.7(1)	N(1)–Sn–C(1)	94.9(1)
N(1)–Sn–N(5)	81.2(1)	N(1)–Sn–N(3)	79.9(1)
Cl(2)–Sn–C(1)	98.6(1)	Cl(2)–Sn–N(5)	167.2(1)
Cl(2)–Sn–N(3)	87.5(1)	Cl(2)–Sn–N(1)	92.0(1)
Cl(1)–Sn–C(1)	97.9(1)	Cl(1)–Sn–N(5)	89.3(1)
Cl(1)–Sn–N(3)	86.4(1)	Cl(1)–Sn–N(1)	164.4(1)
Cl(1)–Sn–Cl(2)	94.9(5)	N(4)–B–N(6)	107.4(3)
N(2)–B–N(6)	108.6(4)	N(2)–B–N(4)	107.2(4)
Sn–N(1)–C(7)	130.3(3)	Sn–N(1)–N(2)	122.3(3)
N(2)–N(1)–C(7)	107.4(3)	B–N(2)–N(1)	120.5(3)
N(1)–N(2)–C(9)	109.0(4)	B–N(2)–C(9)	130.5(4)
Sn–N(3)–C(11)	130.0(3)	Sn–N(3)–N(4)	122.9(3)
N(5)–Sn–C(1)	92.8(1)	N(3)–Sn–C(1)	172.2(1)
N(4)–N(3)–C(11)	107.1(4)	B–N(4)–N(3)	120.3(4)
N(3)–N(4)–C(13)	108.2(3)	B–N(4)–C(13)	131.4(4)
Sn–N(5)–C(15)	130.8(3)	Sn–N(5)–N(6)	122.2(2)
N(6)–N(5)–C(15)	106.9(4)	B–N(6)–N(5)	120.3(3)
N(5)–N(6)–C(17)	108.2(3)	B–N(6)–C(17)	131.4(4)
Sn–C(1)–C(6)	120.6(2)	Sn–C(1)–C(2)	119.4(2)

A comparison of the bond distances and angles in this compound and in related complexes is given in Table 5, in which a common numbering scheme is used. The values, though generally falling into acceptable ranges, show significant differences, especially when mpz derivatives are compared with 3-methylpyrazolylborate (3-mpz) or dmcpz ones containing the same tin moiety. In particular, the average Sn–N distances in $[SnPhCl_2(3\text{-mpz})]$ or in $[SnPhCl_2[HB(dmcpz)_3]$ [2.249(3) or 2.249(2) Å, respectively] are longer (*ca.* 0.03 Å) than in the present crystal structure [2.222(2) Å]. This underscores once again that the present ligand is a better donor than 3-mpz or dmcpz.

$SnMe_2Cl_2(Hmpz)_2$ 12. This compound was obtained from attempted recrystallisation of compound **3**. Its molecular structure is displayed in the ORTEP plot of Fig. 2(*c*). Selected bond distances and angles are in Table 6. The tin atom displays an octahedral co-ordination geometry with the Cl, Me, and the pyrazole ligands in the all-*trans* configuration. The tin co-ordination site is distorted with bond angles ranging from 89.6(2) to 93.0(1)° and the bond lengths Sn–Cl 2.572 Å, Sn–C 2.128 Å and Sn–N 2.351 Å. The pyrazole atoms N(1), N(2), C(2)–C(4) do not deviate significantly from planarity and the weighted least-squares plane forms a dihedral angle of 88.7(2)° with the co-ordination plane Sn, C(1) and Cl(1). For comparison, structural data for some corresponding *trans*-$[SnR_2Cl_2L_2]$ complexes with *N*-donor heterocycles[23–28] are reported in Table 7: it should be noted that in related derivatives the ligand 4-methylpyrazole (Hmpz) forms Sn–N bonds shorter than those with the hindered (Hdmpz) and 3,4,5-trimethyl-

Table 6 Selected bond distances (Å) and angles (°) for $SnMe_2Cl_2(Hmpz)_2$ **12**

Sn–Cl(1)	2.572(2)	N(1)–C(2)	1.336(7)
Sn–C(1)	2.128(6)	N(1)–N(2)	1.330(7)
Sn–N(1)	2.351(5)	N(2)–C(4)	1.351(6)
N(1)–Sn–C(1)	89.6(2)	N(2)–N(1)–C(2)	105.5(5)
Cl(1)–Sn–C(1)	90.7(2)	N(1)–N(2)–C(4)	110.8(5)
Cl(1)–Sn–N(1)	93.0(1)	N(1)–C(2)–C(3)	111.6(5)
Sn–N(1)–C(2)	131.0(5)	N(2)–C(4)–C(3)	108.6(5)
Sn–N(1)–N(2)	123.5(3)		

Table 5 Comparison of structural data (distances in Å, angles in °) for Cl_2RSn pyrazolylborate complexes

	$HB(mpz)_3$[a] R = Ph	HB(3-mpz)[7] Ph	$HB(pz)_3$[23] *b*	$HB(dmpz)_3$[9a] Me	$HB(dmcpz)_3$[9b] Ph
Sn–N(1)	2.221(3)	2.289(5)	2.191(7)	2.239(6)	2.257(4)
Sn–N(3)	2.206(3)	2.241(6)	2.237(6)	2.240(6)	2.237(3)
Sn–N(5)	2.240(4)	2.218(6)	2.225(7)	2.247(6)	2.254(4)
Sn–C(1)	2.137(3)	2.228(1)	2.140(7)	2.244(7)	2.140(5)
Sn–Cl(1)	2.430(1)	2.420(2)	2.413(2)	2.425(3)	2.426(2)
Sn–Cl(2)	2.417(2)	2.438(2)	2.442(2)	2.451(3)	2.416(2)
N(1)–Sn–N(3)	79.9(1)	81.4(2)	79.0(2)	82.2(2)	82.3(1)
N(1)–Sn–N(5)	81.2(1)	81.8(2)	81.5(2)	83.1(2)	81.7(2)
N(3)–Sn–N(5)	80.7(1)	81.6(2)	80.4(3)	81.0(2)	81.0(2)
N(1)–Sn–C(1)	94.9(1)	94.6(4)	95.0(3)	93.3(3)	92.3(2)
N(3)–Sn–C(1)	172.2(1)	174.0(3)	171.4(3)	172.6(2)	172.2(2)
N(5)–Sn–C(1)	92.8(1)	93.4(4)	93.2(3)	92.6(2)	92.0(2)
Cl(1)–Sn–N(1)	164.4(1)	167.8(1)	166.4(2)	169.9(2)	168.9(1)
Cl(1)–Sn–N(3)	86.4(1)	87.7(1)	88.1(2)	89.0(2)	89.0(3)
Cl(1)–Sn–N(5)	89.3(1)	91.5(2)	92.3(2)	90.6(2)	91.8(2)
Cl(1)–Sn–C(1)	97.9(1)	97.2(4)	99.4(2)	94.8(2)	96.8(2)
Cl(1)–Sn–Cl(2)	94.91(5)	93.81(8)	94.3(1)	94.45(9)	94.2(2)
Cl(2)–Sn–N(1)	92.0(1)	91.1(2)	89.3(2)	90.2(2)	91.5(2)
Cl(2)–Sn–N(3)	87.5(1)	87.3(2)	87.4(2)	87.8(2)	87.9(1)
Cl(2)–Sn–N(5)	167.2(1)	167.7(2)	165.9(2)	167.6(2)	168.5(1)
Cl(2)–Sn–C(1)	98.6(1)	95.8(4)	96.2(2)	98.1(2)	96.8(1)

[a] This work. [b] R = $CH_2CH_2CO_2Me$.

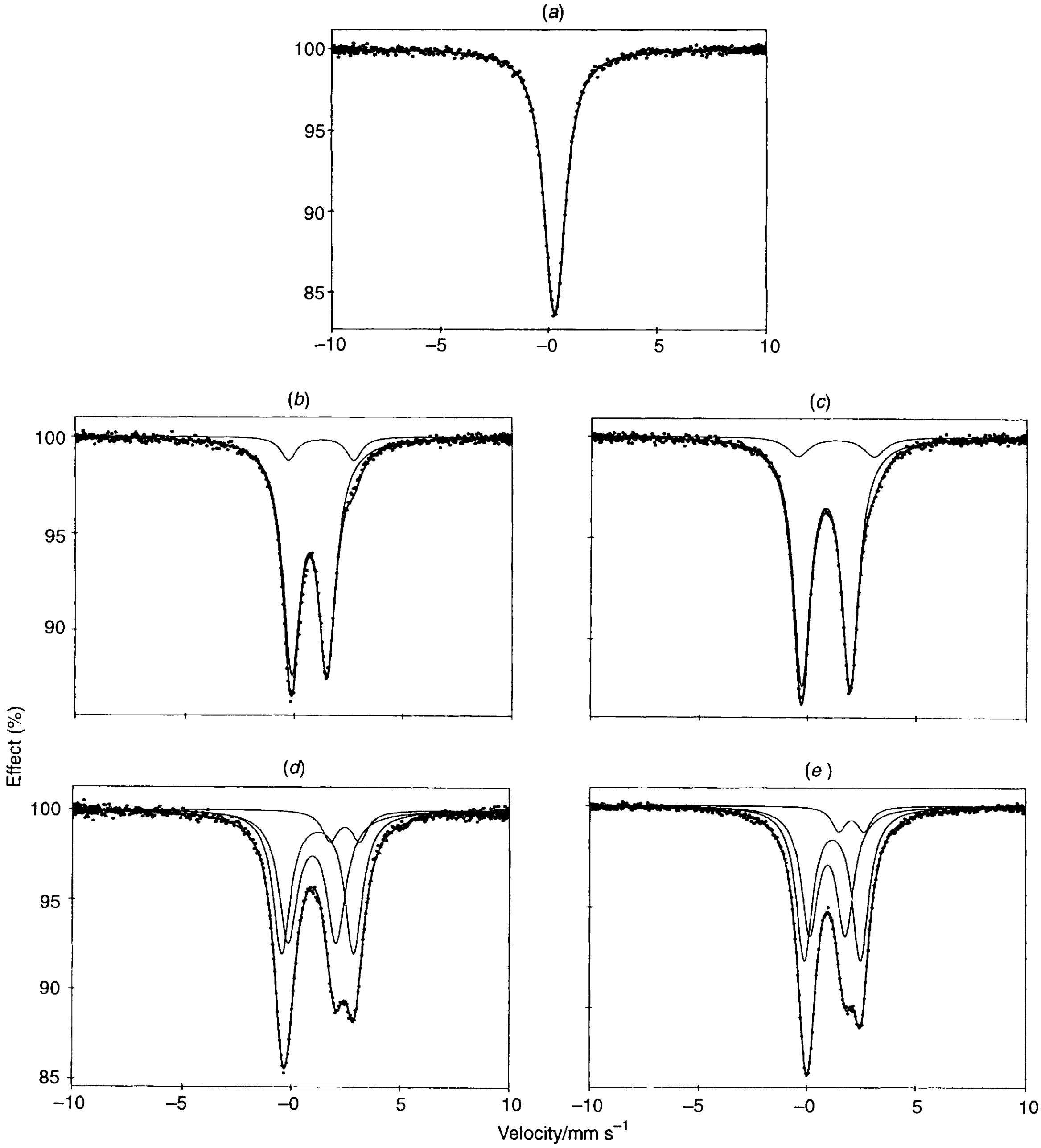

Fig. 3 Tin-119 Mössbauer spectra at 4.2 K of (*a*) $SnCl_3[HB(mpz)_3]$ **1**, (*b*) $SnMe_2Cl[HB(mpz)_3]$ **3**, $SnMe_3[HB(mpz)_3]$ **4**, (*d*) $SnPhCl_2[HB(mpz)_3]$ **5** and (*e*) $SnPh_3[HB(mpz)_3]$ **7**

Table 7 Structural data for dihalogenodialkyltin(IV) pyrazole complexes

		N–H ··· X/Å		
Complex	Sn–N/Å	Intra-	Inter-molecular	Ref.
$SnMe_2Cl_2(Hmpz)_2$	2.351(5)	3.332	3.292	This work
$SnMe_2Cl_2(Htmpz)_2$	2.38(2)	3.32	3.45	23
	2.37(2)	3.37	3.38	
$SnMe_2Cl_2(Hbpz)_2$	2.359(4)	3.297	3.327	24
$Sn(C_6H_{11})_2Br_2(Hpz)_2$ A	2.375(9)	3.41	3.40	25
B	2.368(8)	3.53	3.59	
	2.359(9)	3.50		
$Sn(CH_2CHPh)_2Cl_2(Hpz)_2$	2.322(5)	3.410(7)	3.320(8)	26
$SnMe_2Cl_2(Hpz)_2$	2.338(6)	3.480	3.297	27
$SnMe_2Cl_2(Hdmpz)_2$	2.379(6)	3.264	3.452	27, 28

pyrazole (Htmpz) donors, similar to those of 4-bromopyrazole (Hbpz) and longer than those of unsubstituted pyrazole (Hpz), as one would expect.

The H atoms on N(2) are involved in intramolecular, N(2) ··· Cl(1) 3.332 Å ($x - 1, y, z$), and intermolecular bonding N(2) ··· Cl(1) 3.292 Å ($x, -y, -z + 2$). The distance N–H ··· Cl of about 2.5 Å and the angles N–H ··· Cl, from 122 to 130°, show the hydrogen bondings are strong.

Table 8 Tin-119 Mössbauer parameters measured at 4.2 K; L = $HB(mpz)_3$

Compound	i.s./mm s^{-1}	q.s./mm s^{-1} obs.	Calc.[a]	Γ/mm s^{-1}	Relative resonance area (%)	Tin site
1 $SnCl_3L$	0.28(1)	0.28(2)	0.00	1.09(1)	100	O_h
2 $SnMe_2ClL$	0.72(1)	1.72(1)	2.06	1.01(1)	92	O_h
	1.42(2)	3.77(4)	3.93	0.85(6)	8	all-*trans* O_h
3 $SnMe_2Cl(L)$	0.84(1)	2.25(1)	−2.06	0.93(1)	89	O_h
	1.43(2)	3.19(2)	3.93	1.34(3)	11	all-*trans* O_h
4 $SnMe_3L$	0.95(1)	2.22(1)	−2.02	1.05(2)	45	*TBPY* Sn^{IV}[b]
	1.21(1)	3.32(1)	2.44	0.97(2)	46	T_d Sn^{IV}
	2.45(2)	1.37(4)		0.87(2)	9	*c*
5 $SnPhCl_2(L)$	0.70(1)	1.63(1)	1.90	0.97(1)	92	O_h
	1.24(3)	3.03(5)	3.62	0.86(1)	8	all-*trans* O_h
6 $SnPh_2Cl(L)$	0.80(1)	2.04(1)	−1.90	0.93(1)	94	O_h
	1.2(1)	3.1(2)	3.62	1.4(2)	6	all-*trans* O_h
7$SnPh_3(L)$	0.97(1)	1.65(1)	−1.75	0.93(2)	42	*TBPY* Sn^{IV}
	1.20(1)	2.59(1)	2.22	0.92(1)	51	T_d Sn^{IV}
	2.07(2)	1.17(4)		0.78(4)	7	*b*

[a] By point-charge model assuming a regular geometry and using literature values.[28,29] [b] *TBPY* = Trigonal bipyramidal. [c] Unidentified products.

In the pyrazole rings the bond angles are in accord with the empirical rules of Bonati.[29] The angle Sn–N(1)–C(2) 131.0(5)° is larger than Sn–N(1)–N(2) 123.5(3)° and C(2)–C(3)–C(4) is the smallest [103.5(5)°] internal angle, in accordance with rules 1 and 3 respectively. Moreover, also rule 5, valid for pyrazoles in adducts with metal centres, is followed: the internal angle C(2)–N(1)–N(2) 105.5(5)° is smaller than N(1)–N(2)–C(4) 110.8(5)° and N(2)–C(4)–C(5) is smaller than N(1)–C(2)–C(3) 111.6(5)°.

Mössbauer data

The Mössbauer spectrum of the $SnCl_3[HB(mpz)_3]$ **1** displays the single line expected for C_{3v} local symmetry, as shown in Fig. 3(*a*). The broad linewidth, the largest in Table 8, can be related to the small differences in bonds and angles between the two tin co-ordination sites present in its elementary cell.

The fit of the spectra of mono- and di-organotin compounds (**2**, **5**, and **3**, **6** respectively) is consistent with the presence of two quadrupole-split doublets with relative resonance areas in a ratio of about 9:1. Fig. 3(*b*) and (*c*) show, for **5** and **3**, respectively, the contribution of the second tin site to the total resonance. The doublet with larger intensity, in the spectra of **2**, **3**, **5** and **6**, can be related to the expected octahedral tin(IV) site, similar to that found in the present crystal structure of **5**. As in Table 8, this attribution is consistent with the splitting calculated by the point-charge model.[30,31] The less-intense doublet, in the spectra of **2**, **3**, **5** and **6**, is instead attributable, owing to its very large splitting, to all-*trans* octahedral tin(IV) geometries produced upon decomposition. A site of this type has been found in the present crystal structure of **12**. It is interesting that deboronated products, exhibiting Mössbauer doublets with splittings of comparable size, have been previously detected, as minor components.[9b,20,23]

The unsplit line expected for the triorganotin(IV) compounds of C_{3v} symmetry, $SnMe_3[HB(mpz)_3]$, **4** and $SnPh_3[HB(mpz)_3]$ **7** is not present in their Mössbauer spectra [Fig. 3(*d*) and (*e*) respectively]. On the contrary, there are three quadrupole-split doublets, two of which have similar intensity and the third is a minor component. Among the various decomposition processes possible on standing, such as progressive elimination of the organic groups, deboronation seems also in these cases in better agreement with the parameters in Table 8. The quadrupole splitting of the first doublet of **4** and **7** is consistent with that calculated for a trigonal-bipyramidal tin(IV) geometry with one axial and two equatorial organic groups.[32] The quadrupole splitting of the second doublet is consistent (more for **7** than for **4**) with that calculated for a tetrahedral tin(IV) geometry with three organic groups.[32] Lastly there is a less-intense doublet for **4** and **7**, with a very positive isomeric shift, but still falling in the range generally accepted[32] for tin(IV) species, the nature of which is difficult to hypothesise. Even in absence of Mössbauer measurements, a decomposition trend similar to that reported for **4** and **7** is expected for the triorganotin(IV) compounds **8**–**11**, owing to their instability on standing.[11]

In conclusion, the Mössbauer parameters of Table 8 evidence the main decomposition process: deboronation in mono- and di-organotin compounds with formation of stable all-*trans* tin(IV)-containing products; progressive elimination of the pz rings in triorganotin compounds with formation of various decomposition materials.

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