SHORT PAPER

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Synthesis and crystal structure of diorganotin(IV) derivatives containing the bis(3,5-dimethylpyrazol-1-yl) acetate ligand[†]

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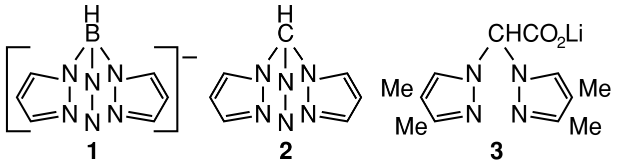
Two new diorganotin(IV) derivatives containing the heteroscorpionate ligand have been synthesised by reaction of diphenyltin halides with bis(3,5-dimethylpyrazol-1-yl)acetate lithium and have been characterised by X-ray analysis.

Keywords: diorganotin (IV) derivatives, bis (3,5-dimethylpyrazol-1-yl)acetate ligand

The coordination behaviour of organotin(IV) toward poly(pyrazol-1-yl)borate ligands (*e.g.* **1**) has been extensively investigated in recent years. A number of tin complexes containing poly(pyrazol-1-yl)borate ligands have been synthesised and characterised[1-4] in which the coordinate geometry around the central tin atom depends very much on the steric and electronic properties of the poly(pyrazol-1-yl)borate ligands, which can be easily controlled by changing the substituents on the pyrazole ring. Some organotin(IV) complexes containing poly(pyrazol-1-yl)borate ligands have also shown interesting structural characteristics and reactivities.[5-7] As the isoelectronic and isosteric ligands of poly(pyrazol-1-yl)borates, poly(pyrazol-1-yl)alkanes (*e.g.* **2**) have also been found to act as good donors to organotin(IV) acceptors. The interactions between poly(pyrazol-1-yl)alkanes and organotin(IV) acceptors have also been extensively studied.[8-12] Studies on the heteroscorpionate ligands are very attractive owing to their advantages, compared to scorpionate ligands, such as the presence of polyfunctional donor spheres, water-solubility and stability towards hydrolysis *etc*.[13-16] These novel heteroscorpionate ligands are good precursors of transition metal complexes. However, few main group metal complexes have reported.[15] We herein report the synthesis and crystal structure of diorganotin(IV) derivatives containing the bis(3,5-dimethylpyrazol-1-yl)acetate ligand.

The reaction of bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza) lithium (**3**) and Ph_2SnX_2 in a 1 : 1 ratio involved the elimination of LiCl to produce $Ph_2SnX(bdmpaza)$ (X = Cl, **4**; Br, **5**) in reasonable yield. However, the reaction of bis(3,5-dimethylpyrazol-1-yl)acetate lithium with Ph_3SnCl did not take place under the same conditions, possibly owing to the increased electron density around the tin atom and steric hindrance. The IR spectra of the two compounds (**4** and **5**) are similar. The $\nu_{asym}(CO_2^-)$ signal appears at 1692.5 cm^{-1} for compound **4** and 1677.3 cm^{-1} for compound **5**, which are higher frequencies than that for the free ligand,[15] and the $\nu_{sym}(CO_2^-)$ bands in the two compounds are similar, 1460.3 cm^{-1} for compound **4** and 1460.9 cm^{-1} for compound **5**. These IR data suggest that the carboxylate may act as a monodentate ligand. The band at *ca* 1558 cm^{-1} observed in compounds **4** and **5** is assigned to a pyrazole ring vibration. The ^{119}Sn NMR chemical shift for compound **4** occurred at –410.5 ppm in CD_3COCD_3 which is comparable to the shifts reported for six-coordinate organotin derivatives containing poly(pyrazol-1-yl)borates,[2-4] indicating that this compound should be six-coordinate in solution.



Scheme 1

In order to confirm the coordination mode of bis(3,5-dimethylpyrazol-1-yl)acetate in the two compounds, X-ray diffraction analysis of compound 4 was undertaken. As shown in Fig.1, bis(3,5-dimethylpyrazol-1-yl)acetate anion is a tridentate ligand, which coordinates to the tin atom by the two nitrogen atoms of the pyrazole ring and an oxygen atom from a carboxylate anion, and the latter is a monodentate ligand which is consistent with the result from the IR spectra. The coordination geometry around the tin atom is a six-coordinate distorted octahedron. The Sn–O bond distance is 2.137(3) Å. The average Sn–N bond distance of 2.357 Å is shorter than that in organotin derivatives containing neutral poly(pyrazol-1-yl)methane ligands, such as $CH_2(4\text{-}MePz)_2SnMe_2Cl_2$ (2.436 Å)[10] and $CH_2(3\text{-}iPrPz)_2SnPh_2Br_2$ (2.435 Å),[12] but longer than the reported data for organotin derivatives containing poly(pyrazol-1-yl)borate ligands,[2] indicating that the bis(3,5-dimethylpyrazol-1-yl)acetate anion is a better donor than the

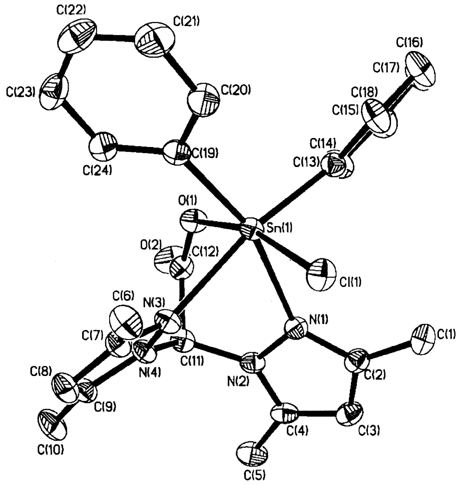


Fig. 1 The molecular structure of **4**. Selected bond distance [Å] and angles [°]: Sn(1)–O(1) 2.137(3), Sn(1)–N(3) 2.314(4), Sn(1)–N(1) 2.399(3), Sn(1)–Cl(1) 2.419(3), O(2)–C(12) 1.197(4) and O(1)–C(12) 1.287(4); N(3)–Sn(1)–N(1) 73.9(1), O(1)–Sn(1)–Cl(1) 165.33(7), C(13)–Sn(1)–C(19) 107.6(1), O(1)–Sn(1)–C(19) 92.11(14), C(19)–Sn(1)–N(1) 162.13(11), N(3)–Sn(1)–Cl(1) 89.40(7) and O(1)–Sn(1)–N(1) 80.9(1).

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

neutral poly(pyrazol-1-yl)alkane, but its electron-donating ability is weaker than that of poly(pyrazol-1-yl)borate ligands.

Experimental

Preparation of **4**: A solution of Ph_2SnCl_2 (0.172 g, 0.5 mmol) and bis(3,5-dimethylpyrazol-1-yl)acetate lithium[15] (0.127 g, 0.5 mmol) in 20 ml of CH_2Cl_2 was stirred for 5 h at room temperature, and then filtered. The filtrate was concentrated under a reduced pressure to *ca* 5 ml, and the same volume of hexane was slowly added. The solution was left at room temperature to yield colourless crystals **4**. Yield: 78%. ^1H NMR ($CDCl_3$): δ 2,22 (s, 12H, CH_3), 5.88 (s, 2H, H^4 of pyrazole ring), 6.72 (s, 1H, CH), 7.23–7.68 (m, 10H, C_6H_5). ^{119}Sn NMR (CD_3COCD_3): δ -410.5. IR (KBr): ν_{CO} 1692.5 (s), 1460.3 (m) cm-1; $\nu_{\text{pyrazole ring}}$ 1557.6 (m) cm^{-1}. Found: C, 52.21; H, 4.36; N, 10.37%. $C_{24}H_{25}ClN_4O_2Sn$ requires C, 51.85; H, 4.50; N, 10.08%.

Preparation of **5**: This compound was obtained using Ph_2SnBr_2 instead of Ph_2SnCl_2 as described above for **4**. Yield: 70%. ^1H NMR ($CDCl_3$): δ 2.22 (s, 12H, CH_3), 5.89 (s, 2H, H^4 of pyrazole ring), 6.92 (s, 1H, CH), 7.24–7.67 (m, 10H, C_6H_5). IR (KBr): ν_{CO} 1677.3 (s), 1460.9 (m) cm^{-1}; $\nu_{\text{pyrazole ring}}$ 1558.9 (m) cm^{-1}. Found: C, 48.32; H, 4.38; N, 9.48%. $C_{24}H_{25}BrN_4O_2Sn$ requires C, 48.00; H, 4.17; N, 9.33%.

Crystal data of **4**: $C_{24}H_{25}ClN_4O_2Sn$, M = 555.62, monoclinic space group P2(1)/n, a = 8.598(12), b = 15.90(2), c = 17.95(2) Å, β = 103.856(14)°, V = 2383(6) $Å^3$, Z = 4, ρ_{calc} = 1.548 Mg/m^3, $\mu(MoK\alpha)$ = 1.212 mm^{-1}, T = 293(2) K. 9618 Reflections of which 4195 with $I > 2\sigma(I)$ were measured ($1.73 < \theta < 25.03°$) on a Siemens SMART/CCD area detector equipped with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was resolved by the direct method and refined by full-matrix least-squares on F^2 using the SHELXL-97 program, R_1 = 0.029 and R_w = 0.0749 with GOF =1.069. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located on the calculated position. Full crystallographic details have been deposited at the Cambridge Crystallographic Data Centre (CCDC 172980).

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