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Preliminary communication

Synthesis and structures of two tris(pyrazolyl)boratotin(II) compounds *

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Abstract

The reaction of $SnCl_2$ with 2 or 1 equivalents of $[HB(pz^{\star})_3]K$ in CH_2Cl_2 affords $[HB(pz^{\star})_3]_2Sn$ (I) or $[HB(pz^{\star})_3]SnCl$ (II) ($pz^{\star}$ = 3,5-dimethyl-1-pyrazolyl), respectively. The structures of I and II have been established by X-ray crystallography; I possesses a novel geometry. Compound I crystallizes in the $P\bar{1}$ space group with a 10.975(1), b 11.067(2), c 14.578(3) Å, α 88.64(1), β 85.71(1), and γ 83.74(1)°. Compound II crystallizes in the $P\bar{1}$ space group with a 8.148(1), b 8.827(1), c 13.546(2) Å, α 77.81(1), β 90.02(1), and γ 80.50(1)°.

Following the synthesis [1] and structure prediction [2] of stannocene, $(\eta^5\text{-}C_5H_5)_2Sn$, interest has grown steadily in the chemistry of π-complexes of the group 14 elements [3]. X-ray crystallographic studies have established that the angles of aperture between the two rings of $(\eta^5\text{-}C_5H_5)_2Sn$ [4] and $(\eta^5\text{-}Me_5C_5)_2Sn$ [5] are 55 and 36° respectively. The analogous molecules $[(C_5H_5)Co(\overline{C_2B_2C})]_2Sn$ (C_2B_2C = 4,5-diethyl-1,3-dimethyl-1,3-diborolenyl) [6] and $(\overline{\text{t-BuNBMeCMeCH=CH}})_2Sn$ [7] have been shown to possess similar structures. Increasing the steric demands of the cyclopentadienyl groups, as in e.g. $[(Me_3Si)_3C_5H_2]_2Sn$ [8], diminishes the angle of aperture between the rings and in the interesting case of Ph_5C_5 substitution the rings are parallel [9].

The formal analogy between cyclopentadienyl and tris(pyrazolyl)borato moieties is well established in the realm of transition metal chemistry [10]. Much less attention has been paid, however, to the utility of the latter class of ligand for

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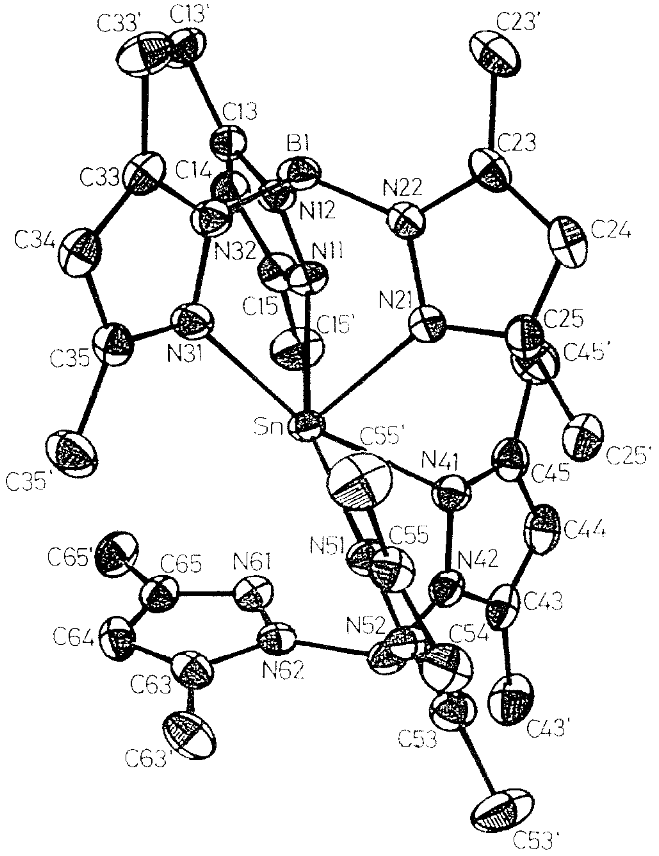

Fig. 1. View (ORTEP) of the structure of $[HB(pz^\star)_3]_2Sn$ (I) showing the atom numbering scheme. Important parameters: Sn–N(11) 2.462(2), Sn–N(21) 2.361(2), Sn–N(31) 2.510(2), Sn–N(41) 2.469(2), Sn–N(51) 2.499(2) Å, N(11)–Sn–N(21) 74.84(8), N(11)–Sn–N(31) 82.22(7), N(11)–Sn–N(41) 95.04(7), N(11)–Sn–N(51) 157.35(8), N(21)–Sn–N(31) 76.50(7), N(21)–Sn–N(41) 83.46(8), N(21)–Sn–N(51) 82.97(8), N(31)–Sn–N(41) 159.80(8), N(31)–Sn–N(51) 97.12(7), N(41)–Sn–N(51) 77.74(7)°.

main-group chemistry [11]. In the present work we describe a new mode of coordination for tin(II) using the hydridotris(3,5-dimethyl-1-pyrazolyl)borato ligand, $[HB(pz^\star)_3]^-$.

Treatment of $SnCl_2$ with two equivalents of $[HB(pz^\star)_3]K$ in CH_2Cl_2 at 25 °C afforded, after recrystallization from toluene, a colorless, crystalline material of composition $[HB(pz^\star)_3]_2Sn$ (I) in 80% yield. The electron-impact mass spectrum (70 eV) of I exhibited a parent peak of low intensity at m/z 712. The 100% intensity peak occurred at m/z 416 and is attributable to $\{[HB(pz^\star)_3]Sn\}^+$. The ^1H NMR spectrum of I indicated equivalence of the two tris(pyrazolyl)borate ligands [12*]. However, the ^{119}Sn resonance for I was somewhat broad and suggestive of a fluxional process in solution. The structure of I in the solid state was determined by X-ray crystallography [13*]. The geometry around tin(II) is approximately oc-

* Reference numbers marked with asterisks indicate notes occurring in the list of references.

tahedral (Fig. 1), and the coordination sphere comprises five nitrogen atoms and a lone pair. Thus one tris(pyrazolyl)borato group is tridentate; the other is bidentate hence one of the nitrogen (N(61)) is not coordinated to tin. This unprecedented geometry would correspond to $(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_5R_5)Sn$ (R = H, Me) in terms of cyclopentadienyl ligation. The Sn–N bond lengths fall into three distinct categories, Sn–N(31) and Sn–N(51) (ave. 2.504(2) Å), Sn–N(11) and Sn–N(41) (ave. 2.465(2) Å), and Sn–N(21) 2.361(2) Å. Note that Sn–N(21), the shortest bond, is located *trans* to the Sn lone pair. The stereochemical activity of this lone pair is evident from the pattern of N–Sn–N bond angles (Fig. 1).

The comparable reaction of $[HB(pz^\star)_3]K$ with $SnCl_2$ in 1/1 stoichiometry afforded, after recrystallization from toluene, $[HB(pz^\star)_3]SnCl$ (II) in 90% yield. As in the case of I, the 100% peak in the 70 eV EI-MS of II corresponded to $\{[HB(pz^\star)_3)Sn\}^+$. Other peaks of significant intensity were detected at m/z 451, 357, and 321 and are due to M^+, $[M - pz^\star]^+$, and $[M - pz^\star - Cl]^+$, respectively. The ^{119}Sn NMR signal for II was broad and the ^1H spectrum revealed equivalence of the three pyrazolyl rings. The solid-state structure of II was determined by X-ray diffraction. The Sn geometry can be regarded as approximately trigonal bipyramidal. The two axial positions are occupied by N(11) and Cl, while N(21), N(31),

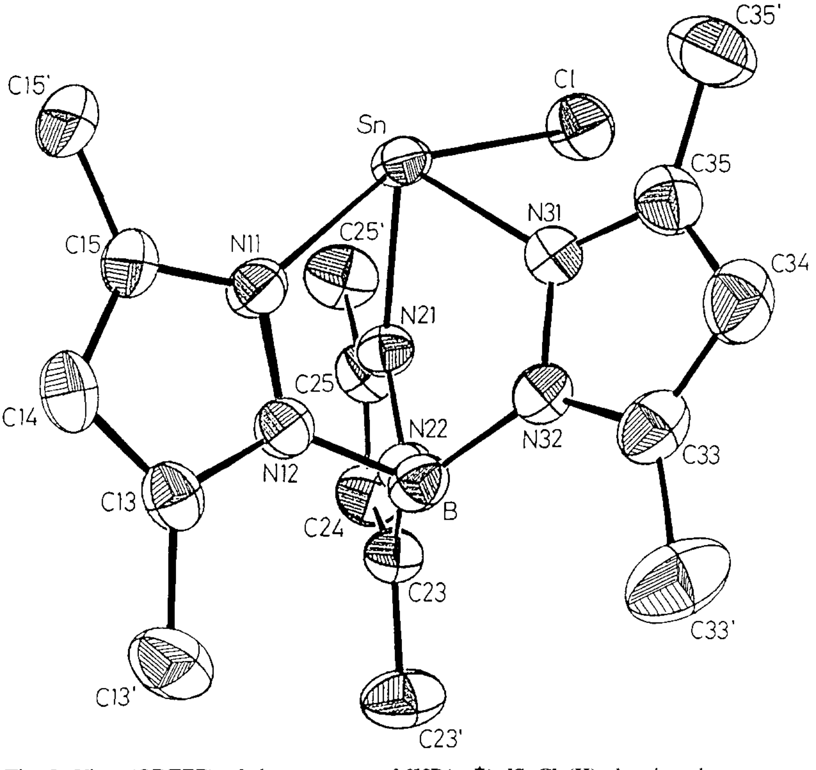

Fig. 2. View (ORTEP) of the structure of $[HB(pz^\star)_3]SnCl$ (II) showing the atom numbering scheme. Important parameters: Sn–Cl 2.629(1), Sn–N(11) 2.491(2), Sn–N(21) 2.214(3), Sn–N(31) 2.215(3) Å, Cl–Sn–N(11) 156.91(7), Cl–Sn–N(21) 85.94(7), Cl–Sn–N(31) 86.48(7), N(11)–Sn–N(21) 76.99(9), N(11)–Sn–N(31) 76.56(9), N(21)–Sn–N(31) 84.3(1)°.

and the tin lone pair are located in the equatorial positions. As expected, the Sn–N(21) and Sn–N(31) bond lengths are shorter than the Sn–N(11) bond length. The pattern of N–Sn–N and N–Sn–Cl bond angles (Fig. 2) is indicative of a stereochemically active tin lone pair.

Finally we note that, viewed from the N(11)–N(21)–N(31) face, the structure of II resembles that of $(C_5H_5)SnCl$ [14]. In both compounds the SnCl moiety is displaced from the center of the N_3 or C_5 face and the longest bonds to Sn occur opposite to the Cl ligand.

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12 I: ^1H NMR (300.15 MHz, $CDCl_3$, 25 °C); δ (ppm) 1.85 (s, 18H, pz*–Me), 2.33 (s, 18H, pz*–Me), 4.75 (broad s, 2H, B–H), 5.79 (s, 6H, pz*–H). ^{119}Sn NMR (111.8 MHz, CH_2Cl_2, 25 °C), δ (ppm) −935 (s, $w_{1/2}$ 300 Hz).
II: ^1H NMR (300.15 MHz, C_6D_6, 25 °C); δ (ppm) 1.96 (s, 9H, pz*–Me), 2.36 (s, 9H, pz*–Me), 5.40 (s, 3H, pz*–H). ^{119}Sn NMR (111.8 MHz, CH_2Cl_2, 25 °C); δ (ppm) −1460 (s, $w_{1/2}$ > 300 Hz).
13 Crystal data for I: $C_{30}H_{44}B_2N_{12}Sn$, M = 713.08, triclinic, space group $P\bar{1}$ (No. 2), a 10.975(1), b 11.067(2), c 14.578(3) Å, α 88.64(1), β 85.71(1), γ 83.74(1)°, U 1754.9 Å^3, D_c 1.349 g cm^{-3}, Z = 2, λ(Mo-K_α) 0.71073 Å, μ(Mo-K_α) 7.7 cm^{-1}.
Crystal data for II: $C_{15}H_{22}BClN_6Sn$, M = 451.34, triclinic, space group $P\bar{1}$ (No. 2), a 8.148(1), b 8.827(1), c 13.546(2) Å, α 77.81(1), β 90.02(1), γ 80.50(1)°, U 938.6 Å^3, D_c 1.597 g cm^{-3}, λ(Mo-K_α) 0.71073 Å, μ(Mo-K_α) 15.2 cm^{-1}. Totals of 6156 and 3303 unique reflections were measured on an Enraf–Nonius CAD-4 diffractometer at 25 °C for I and II, respectively in the range $3 \leqslant 2\theta \leqslant 50$°. The data were corrected for Lorentz, polarization and absorption. In the case of I a decay correction was also made. The structures of I and II were solved by Patterson and Fourier methods and refined by full-matrix least-squares using 5245 and 2787 reflections respectively with $I > 3.0\sigma(I)$. The final residuals were R = 0.0234 and R_w = 0.0255 for I, and R = 0.0232 and R_w = 0.0255 for II.
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