Journal of Organometallic Chemistry, 378 (1989) 139–146
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20272

Organotin(IV) polypyrazolylborates

I. Tris(pyrazolyl)borates

Giancarlo Gioia Lobbia *, **Flavio Bonati, Patrizio Cecchi, Augusto Cingolani, and Adriana Lorenzotti**

Dipartimento di Scienze Chimiche, Università degli Studi, via S. Agostino 1, I-62032 Camerino (Italy)

(Received June 30th, 1989)

Abstract

The compounds $SnCl_3Q$, $RSnX_2Q$ and $XSnR_2Q$ have been prepared ($Q = pz_3BH^-$; X = Cl or Br; R = Me, Et, Bu or Ph). According to the ^1H, ^{13}C and ^{119}Sn NMR spectra in acetone or dichloromethane, the tin is six-coordinate in the trichloro- or dichloro-tin(IV) derivatives, but it may reach a lower coordination number in the monohalogeno compounds. Some of these compounds are fluxional at room temperature.

Introduction

Since the discovery of tris(pyrazol-1-yl)borate ligands, $[pz_3BH]^-$, much work has been carried out on their metal derivatives, but these are mainly of transition elements [1]. Since we are interested in metal derivatives of pyrazoles [2] and we had been investigating [3] tin(IV) and organotin(IV) derivatives of a related family of ligands, the poly(pyrazol-1-yl)alkanes, pz_nCR_{4-n}, we decided to study also the corresponding polypyrazolylborates, and here results for tris(pyrazolyl)borates are presented below.

Results

Interaction of potassium trispyrazolylborate with organotin(IV) halides R_nSnX_{4-n} (X = Cl, $n = 0$, 1 or 2; X = Br, $n = 2$) in acetone gives the compounds **1–10** smoothly as colourless air-stable solids, which are monomeric and non-electrolytes

Table 1

Yields, analyses and physical properties of compounds **1–10**

Compound	Yield (%)	M.p. (°C)	MW (Found. (calcd.))	Elemental analysis (Found (calcd.) (%))			Specific conductivity in acetone	
				C	H	N	(ohm^{-1} cm^2 mol^{-1})	$(CH_3)_2CO$ (c 10^3 M)
$(C_9H_{10}N_6B)CH_3SnCl_2$ (**1**)	82	269–271	419 (417.7)	28.86 (28.76)	3.25 (3.14)	20.04 (20.12)	1.29	1.01
$(C_9H_{10}N_6B)C_4H_9SnCl_2$ (**2**)	88	217–219		33.70 (33.96)	4.19 (4.17)	18.09 (18.28)	2.25	1.00
$(C_9H_{10}N_6B)C_6H_5SnCl_2$ (**3**)	74	244–246	469 (479.7)	37.70 (37.56)	3.32 (3.15)	17.27 (17.52)	1.01	1.01
$(C_9H_{10}N_6B)(CH_3)_2SnCl$ (**4**)	69	173–175	344 (397.2)	33.33 (33.26)	4.26 (4.06)	21.22 (21.16)	1.06	0.99
$(C_9H_{10}N_6B)(CH_3)_2SnBr$ (**5**)	62	176–178	382 (441.7)	29.77 (29.91)	3.52 (3.65)	18.84 (19.03)	2.08	1.14
$(C_9H_{10}N_6B)(C_2H_5)_2SnCl$ (**6**)	80	172–174		36.54 (36.71)	4.36 (4.74)	19.61 (19.76)	2.81	1.00
$(C_9H_{10}N_6B)(C_4H_9)_2SnCl$ (**7**)	84	125–127		42.10 (42.42)	5.81 (5.86)	17.18 (17.46)	4.29	1.00
$(C_9H_{10}N_6B)(C_4H_9)_2SnBr$ (**8**)	76	116–118		38.61 (38.83)	5.22 (5.37)	15.69 (15.98)	4.62	0.98
$(C_9H_{10}N_6B)(C_6H_5)_2SnCl$ (**9**)	69	179–181	472 (521.4)	48.19 (48.38)	3.79 (3.87)	16.02 (16.12)	2.07	1.01
$(C_9H_{10}N_6B)SnCl_3$ (**10**)	88	> 350 [a]		24.36 (24.68)	2.54 (2.30)	18.82 (19.18)	3.79	0.99

[a] It chars without melting

in acetone (Table 1):

$$R_nSnX_{4-n} + K(pz_3BH) \rightarrow KX + \underset{(\mathbf{1-10})}{R_nSn(pz_3BH)X_{4-n-1}} \qquad (1)$$

	R	X	n
1	Me	Cl	1
2	Bu	Cl	1
3	Ph	Cl	1
4	Me	Cl	2
5	Me	Br	2
6	Et	Cl	2
7	Bu	Cl	2
8	Bu	Br	2
9	Ph	Cl	2
10	-	Cl	0

As previously found in the case of bis(pyrazolyl)alkanes [3], no derivative could be isolated under our conditions when trimethyl- or triphenyl-chlorotin(IV) was employed; $Me_3Sn(pz_3BH)$ is, in fact, reported to be unstable in solution [4a]. Analytical data (Table 1) show that only one of the halides is replaced by the $[pz_3BH]^-$ ligand even when the molar ratio is > 1.

The infrared spectra show all the expected bands. In particular the pyrazolylborato ligand shows B–H vibration around 2500 cm^{-1}, C–H stretching vibrations

Table 2

IR spectral data

Compound	Pyrazole C–H stretching	B–H	1500–1600	< 500	Others	
$K(HBPz_3)$	3140 w sh	2440 m	1510 s	345 w		
	3120 w	2410 w sh		320 w		
	3080 w sh					
1	3170 w sh	2520 m	1520 s	375 w	540 m	Sn–C
	3140 w			350 w	295 vs	Sn–Cl
	3170 w					
2	3160 vw sh	2520 m	1505 m	380 m	290 s	Sn–Cl
	3140 w			365 w		
	3125 w					
	3120 w					
3	3160 w sh	2520 m	1505 m	455 m	560 vw	Sn–C
	3130 w			370 vw	550 w	
	3120 w			340 w	290 m br	Sn–Cl
4	3145 w	2530 m	1505 m	390 m sh	530 m	Sn–C
	3120 w			380 m	510 m	
	3105 w sh				285 s	Sn–Cl
5	3140 w	2530 m	1510 m	380 m	530 m	Sn–C
	3120 w			370 m sh	510 m	
	3110 w sh					
6	3145 w sh	2515 w	1510 m	380 vw	320 s	Sn–Cl
	3120 w					
7	3150 w	2490 s	1505 m	390 w	280 m	Sn–Cl
	3130 w sh			380 w		
	3100 w			350 w		
				340 w		
8	3140 w	2495 m	1500 m	390 vw		
	3120 vw sh			380 vw		
	3100 w			340 w		
				345 w		
9	3140 w	2530 w	1510 m	360 w	520 m	Sn–C
	3110 w			340 w	500 m	
					280 w	Sn–Cl
10	3160 vw sh	2530 w	1510 s	380 w	320 vs br	Sn–Cl
	3140 w					
	3130 w					

above 3100 cm^{-1}, and ring breathing vibrations at ca. 1510 cm^{-1}, and the bands assignable to Sn–C or Sn–Cl stretching vibrations appear at low frequencies, as shown in Table 2.

The ^{1}H (Table 3), ^{13}C (Table 4) and ^{119}Sn (Table 5) NMR spectra were recorded for all the derivatives; they support the formulae proposed for the compounds. The ^{119}Sn spectra always show a singlet at rather high field, and the chemical shift is roughly additive, as shown in Fig. 1. For certain compounds (**2**, **3**, **4**, **5**, and **9**) in both ^{13}C and ^{1}H spectra there are signals from two types of pyrazole rings, in a 2/1 integration ratio, at least in acetone solution. If it is assumed, as a first hypothesis, that pz_3BH^- is a tridentate ligand, then six-coordinated tin(IV) is likely, especially when, in addition, the Sn–H coupling constant is as high as 120 Hz, as found here for **1** and **4** (acetone solution); in addition, the single crystal X-ray structure of

Table 3

^{1}H NMR data [a]

Compound	Solvent	4-CH	3- or 5-CH	R	
$K(HBPz_3)$	$(CD_3)_2CO$	6.00 t (2.2)	7.37 d (1.6)		
			7.58 d (2.0)		
	CD_2Cl_2	6.22 t (2.8)	7.52 d (1.8)		
			7.48 d (1.6)		
$Zn(HBPz_3)_2$	$(CD_3)_2CO$	6.17 t (2.4)	7.86 d (1.5)		
			7.09 d (1.8)		
	CD_2Cl_2	6.16 t (2.6)	7.80 d (1.8)		
			7.14 d (1.9)		
1	$(CD_3)_2CO$	6.36 t (2.8)	7.87 d (1.6)	Me 0.80 s (118)*	
			7.98 d (2.0)		
	CD_2Cl_2 (r.t.)	6.38 t (2.8)	8.20 d (1.2)	Me 0.78 s (99)*	
			7.90 d (1.3)		
		6.32 t (2.6)	7.79 d (1.5)		
			7.70 d (1.4)		
	CD_2Cl_2 (−30 °C)	6.35 t (2.6)	8.18 d (2.0)	Me 1.31 s (120*)	
			7.90 d (1.3)		
		6.32 t (2.4)	7.79 d (1.8)		
			7.70 d (1.8)		
2	$(CD_3)_2CO$	6.48 t (3.0)	8.08 d (1.6)	Bu 0.92 t (3.6)	1.40–1.55 m
			8.04 d (1.2)		1.80–1.93 m
		6.41 t (2.2)	8.22 d (1.4)		
			7.96 d (2.1)		
	CD_2Cl_2	6.37 t (3.2)	7.90 d (2.6)	Bu 0.95 t (3.8)	1.38–1.50 m
			7.79 d (2.8)		1.70–1.92 m
		6.31 t (2.7)	8.20 d (2.0)		
			7.69 d (2.1)		
3	$(CD_3)_2CO$	6.48 t (2.6)	8.30 d (1.8)	Ph 7.34 m	7.50 m
			8.12 d (2.1)		
		6.43 t (3.0)	8.02 d (2.4)		
			7.62 d (2.5)		
	CD_2Cl_2	6.37 t (2.8)	8.30 d (2.0)	Ph 7.39 m	7.49 m
			7.88 d (2.2)		
		6.31 t (3.0)	7.77 d (1.8)		
			7.58 d (2.0)		
4	$(CD_3)_2CO$	6.46 t (3.0)	8.10 d (2.0)	Me 1.31 s (120)*	
			8.04 d (2.2)		
		6.42 t (2.4)	8.18 d (1.7)		
			7.98 d (1.8)		
	CD_2Cl_2 (r.t.)	6.29 br	7.89 br	Me 0.80 s (66)*	
			7.65 br		
	CD_2Cl_2 (−30 °C)	6.18 t (1.6)	7.88 d (1.8)	Me 0.75 s (72)*	
			7.74 d (1.6)		
		6.37 t (2.2)	7.63 d (2.0)		
			7.58 d (2.4)		
5	$(CD_3)_2CO$	6.52 t (3.2)	8.02 d (2.0)	Me 0.92 s (62)*	
			7.90 d (1.8)		
		6.36 br			
6	$(CD_3)_2CO$	6.35 t (3.0)	7.96 d (1.8)	Et 1.27 t	1.42 m
			7.84 d (2.4)		
7	$(CD_3)_2CO$	6.31 t (3.2)	7.95 d (1.6)	Bu 0.90 t	1.30–1.50 m
			7.85 d (2.0)		

Table 3 (continued)

Compound	Solvent	4-CH	3- or 5-CH	R	
8	$(CD_3)_2CO$	6.32 t (2.8)	7.98 d (1.4)	Bu 0.90 t	1.35–1.55 m
			7.84 d (2.0)		
9	$(CD_3)_2CO$	6.44 t (3.6)	8.19 d (1.8)	Ph 7.28 m	7.52 m
			7.95 d (2.2)		
		6.28 t (2.4)	7.90 d (1.4)		
			7.64 d (1.8)		
10	$(CD_3)_2CO$	6.58 t (2.2)	8.18 d (1.4)		
			8.13 d (1.8)		

[a] Chemical shifts in ppm from internal TMS; *J* in parentheses in Hz; when starred it is $^2J(^{119}Sn\text{–}H)$.

$Me_3Sn(pz_3BH)$ revealed six-coordinated tin(IV) [4a]. Inspection of Fig. 2 shows that for the $R_nSnCl_{3-n}(pz_3BH)$ compounds with $n = 1$ or 2, octahedral coordination requires one type of alkyl and two types of pyrazole rings in a 1/2 integration ratio,

Table 4

^{13}C NMR data [a]

Compound	Solvent	C(3)	C(4)	C(5)	Others				
$K(HBPz_3)$	$(CD_3)_2CO$	139.6	103.3	134.7					
	CD_2Cl_2	140.6	104.7	135.6					
$Zn(HBPz_3)_2$	$(CD_3)_2CO$	139.7	104.5	135.2					
	CD_2Cl_2	139.5	104.0	134.7					
1	$(CD_3)_2CO$	140.1	105.7	135.8	Me	15.1			
	CD_2Cl_2 (r.t.)	141.1	105.9	136.0	Me	19.8			
		139.7	105.3	135.8					
	CD_2Cl_2 (−30 °C)	140.5	105.6	135.8	Me	19.3			
		139.2	105.1	135.6					
2	$(CD_3)_2CO$	141.0	106.5	137.0	Bu	13.8	26.1	28.6	38.8
		141.9	105.9	136.7					
	CD_2Cl_2	140.1	105.8	136.0	Bu	13.6	25.9	28.1	38.9
		141.2	105.2	135.8					
3	$(CD_3)_2CO$	141.9	106.7	137.7	Ph	128.9	130.1	134.4	
		141.7	106.3	137.1					
	CD_2Cl_2	140.9	105.8	136.5	Ph	128.4	129.3	133.8	
		141.2	105.5	136.0					
4	$(CD_3)_2CO$	140.9	106.8	137.2	Me	19.8			
		141.8	106.1	136.9					
	CD_2Cl_2 (r.t.)	139.5	104.8	134.6	Me	14.9			
	CD_2Cl_2 (−30 °C)	138.1	104.5	134.3	Me	14.5			
		139.1	105.2	135.4					
5	$(CD_3)_2CO$	141.7	106.5	137.5	Me	17.1			
		140.8	105.9	135.6					
6	$(CD_3)_2CO$	140.5	105.5	135.7	Et	11.1	24.8		
7	$(CD_3)_2CO$	140.3	105.4	135.4	Bu	13.9	27.4	29.4	32.8
8	$(CD_3)_2CO$	140.5	105.3	135.5	Bu	13.9	29.5	29.7	30.1
9	$(CD_3)_2CO$	141.5	105.5	136.1	Ph	128.6	129.1	135.7	
		142.3	106.3	137.7					
10	$(CD_3)_2CO$	141.6	107.2	138.2					

[a] Chemical shifts in ppm from internal TMS.

Table 5
^{119}Sn NMR data

Compound	δ(ppm) from $(CH_3)_4Sn$
1	−478.4
2	−483.0
3	−526.0
4	−328.8
5	−367.9
6	−327.4
7	−332.3
8	−352.4
9	−450.3
10	−620.5

as found for the compounds. The presence of only one set of pz signals for compound **10** ($n = 0$) is expected, and the single set for each of the species **1**, **6**, **7** or **8** in acetone solution may be due to fluxionality: indeed in dichloromethane there are two sets of pz signals at room (compound **1**) or lower temperature (compound **4**). Fluxionality requires that at least one of the Sn–N bonds becomes weaker and longer than in the rigid molecules, so that if the Sn–N distance is sufficiently long a tin coordination number of < 6 is reached, a not improbable situation, especially for the cases in which ^2J(Sn–H) is as low as in **4** (66 Hz in dichloromethane) or **5** (62 Hz in acetone) [5]. In such cases the tris(pyrazolyl)borate ligand cannot be tridentate, as it usually is.

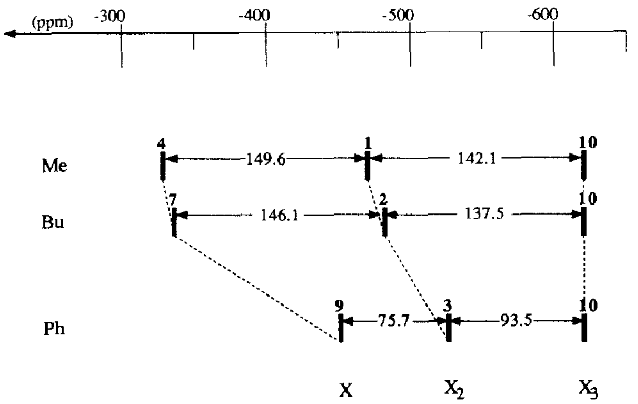

Fig. 1. Effect of substitution on the ^{119}Sn chemical shift of the $HB(pz)_3SnR_nX_{4-n}$ complexes.

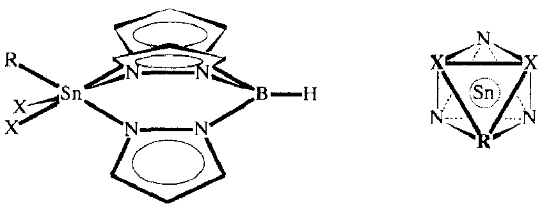

Fig. 2. Octahedral coordination around tin(IV); left: side view; right: view along H–B–Sn axis, here the pyrazole rings are not drawn.

In both ^1H and ^{13}C spectra (acetone solution) the chemical shifts for the pz groups always have lower values than those for the starting K[pz$_3$BH] compound. The symbol $d(i)$ (or $d'(i)$) indicates the difference between the chemical shift of the H (or of carbon) at the position i of the ring of a compound taken as reference, in this case the potassium salt, and that of the tin derivative. In the case of the ^1H spectra the biggest values are for $d(3)$, i.e. those for the pyrazole proton nearest to the tin coordination center: $d(3)$ is in the range 0.31–0.90 ppm, while $d(4)$ or $d(5)$ fall within smaller ranges, 0.22–0.52 ppm or 0.04–0.54 ppm, respectively.

The trends observed in the displacement of chemical shifts in acetone can be expressed as follows: $d(3) > d(4)$, $d(3) > d(5)$, $d'(3) < d'(4)$, $d'(4) > d'(5)$; they are valid even if K(pz$_3$BH) is replaced as reference by covalent $Zn(pz_3BH)_2$ [6], the only difference being that $d(5)$ may be slightly negative (up to -0.24 ppm).

Experimental

Concentration was always carried out in vacuo (water aspirator). The samples were dried in vacuo to constant weight (20 ° C, ca. 0.1 torr). Carbon, hydrogen, and nitrogen analyses were carried out in our Department; molecular weight determinations were performed at Pascher's Mikroanalytisches Laboratorium, Remagen, F.R.G.. Infrared spectra were recorded from 4000 to 250 on a Perkin–Elmer 457 instrument and from 4000 to 600 cm^{-1} as a 1600 Series FTIR instrument. ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Varian EM-390 or VX-300 spectrometers at room temperature (90 and 300 MHz for ^1H, 75 MHz for ^{13}C and 111.9 MHz for ^{119}Sn). The electrical resistances of solutions were measured with a Philips GM-4249 bridge at room temperature, and melting points were determined with a IA 8100 Electrothermal Instrument.

[Tris(1-pyrazolyl)borato]methyldichlorotin(IV) (1)

An acetone solution (25 ml) of potassium tris(1-pyrazolyl)borate (1009 mg, 4 mmol) was added to a stirred acetone solution (30 ml) of CH_3SnCl_3 (480 mg, 2 mmol). The filtered solution was evaporated to dryness, and the residue was washed with water (30 ml) and dried at 100 ° C to give compound **1**. Compounds **3**, **4** and **5** were obtained similarly. Compounds **1** and **4** have been described before [4b] but the reported analytical data agreed with incorrectly calculated values; furthermore the melting points given [4b] were not be confirmed in the present work.

[Tris(1-pyrazolyl)borato]butyldichlorotin(IV) (2)

Butyltrichlorotin(IV) (2 mmol) was added to a solution of potassium tris(1-pyrazolyl)borate (4 mmol in 50 ml dichloromethane) at room temperature. The filtrate was concentrated to give **2**.

[Tris(1-pyrazolyl)borato]dibutylchlorotin(IV) (7)

Dibutyldichlorotin(IV) (1.2 g, 4 mmol) and potassium tris(1-pyrazolyl)borate (1.01 g, 4 mmol) were refluxed in acetone (60 ml) under stirring. After 12–18 h the hot filtrate was evaporated to dryness and the residue was extracted with dichloromethane. Evaporation of the extract gave compound **7**. Compounds **6**, **8**, **9** and **10** (from anhydrous tin(IV) chloride) were obtained similarly; in the first two cases the residue was initially an oil but solidified when stirred with diethyl ether.

Acknowledgments

We thank Dr. Gianni Rafaiani for recording the ^{119}Sn NMR spectra and F. Lupidi for technical assistance. Financial support was provided by "Ministero della Pubblica Istruzione" and the "Consiglio Nazionale delle Ricerche".

Literature

1 A.H. Cowley, R.L. Geerts, C.M. Nunn, S. Trofimenko, J. Organomet. Chem., 365 (1989) 19, and ref. therein.
2 F. Bonati, Gazz. Chim. Ital., 119 (1989) 291; F. Bonati, Chim. Ind. (Milan), 62 (1980) 323.
3 G. Gioia Lobbia, A. Cingolani, D. Leonesi, A. Lorenzotti and F. Bonati, Inorg. Chim. Acta, 130 (1987) 203; G. Gioia Lobbia, F. Bonati, A. Cingolani, D. Leonesi and A. Lorenzotti, Synth. React. Inorg. Metal-Org. Chem., 18 (1988) 535; G. Gioia Lobbia, F. Bonati, A. Cingolani, D. Leonesi and A. Lorenzotti, J. Organomet. Chem., 359 (1989) 21.
4 (a) B.K. Nicholson, J. Organomet. Chem., 265 (1984) 153; (b) S.K. Lee and B.K. Nicholson, J. Organomet. Chem., 309 (1986) 257.
5 T.P. Lockhart, W.F. Manders, Inorg. Chem., 25 (1986) 892 and ref. therein.
6 S. Trofimenko, J. Am. Chem. Soc., 89 (1967) 3170.