

Organotin(IV) polypyrazolylborates. XII. Hydridotris(4-bromo-1*H*-pyrazol-1-yl) borates: characterization, Mössbauer study and X-ray crystal structure of $\text{MeCl}_2\text{Sn}(\text{4-BrPz})_3\text{BH}$

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Abstract

A series of tin(IV) and organotin(IV) hydridotris(4-bromo-1*H*-pyrazol-1-yl)borates has been prepared. The compounds of general formula $\text{R}_n\text{SnCl}_{4-n-1}[\text{HB}(4\text{-Br-pz})_3]$ (where R = Me or Ph, $n = 0, 1, 2, \text{ or } 3$) are rigid in solution and contain a six-coordinate tin(IV) site with a tridentate ligand. They were characterised by IR, ¹H, ¹³C, ¹¹⁹Sn NMR, and ¹¹⁹Sn Mössbauer spectroscopy. Their stability towards self-decomposition decreases with increasing number of Sn-bonded aryl or alkyl groups. The compound $\text{MeCl}_2\text{Sn}[\text{HB}(4\text{-Br-pz})_3]$ crystallises in the space group $R\bar{3}$ (no. 148), trigonal, with $a = 35.520(2)$, $b = 35.520(2)$, and $c = 8.688(1)$ Å, $\gamma = 120^\circ$.

Keywords: Boron; Tin; Pyrazolylborates; X-ray; Mössbauer

1. Introduction

Polypyrazolylborates, despite their discovery which dates to about 30 years ago, continue to play an important role in modern coordination chemistry [1].

Since their introduction, extensive investigations on (organo)tin(IV) polypyrazolylborates [2–13] have been performed.

In particular, the use of tris(pyrazolyl)borato ligands has become increasingly popular in synthetic inorganic and bio-inorganic chemistry [14], in that they resemble the imidazole coordination in models for active sites of metallo-enzymes [15]. Examples can be found in the study of intramolecular electron-transfer processes [16], or derivatives which exhibit either photochemical reactivity or alkane activation [17]. Organotin(IV) poly(pyrazolyl)borates have been studied for their potential biological activity [18]. Increasing interest in this field is due to a recent paper on antimutagenic activity of organotin(IV) chelates with (pyrazolyl)borates [19].

Within the various polypyrazolylborato ligands (indicated here as $\text{Tp}^\#$) so far investigated, the one displaying an electron withdrawing substituent in position 4 of the pyrazole ring, namely hydridotris(1*H*-4-Br-pyrazol-1-yl)borate $\text{Tp}^{4\text{Br}}$, has not been examined in connection with (organo)tin(IV) species, nor in general other such ligands with electronegative substituents.

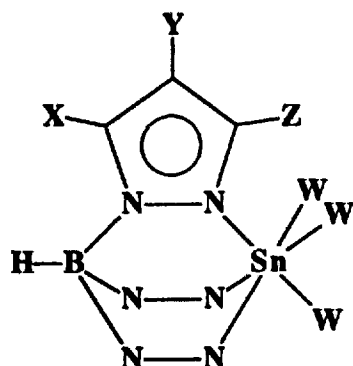
Among the complexes containing the tin moiety $\text{R}_n\text{SnCl}_{4-n-1}$ linked to variously substituted $\text{Tp}^\#$ ligands (Fig. 1), the cases of triorganotin derivatives have rarely been explored [6,20] since the first reports on the crystal structure [20] and ¹³C and ¹¹⁹Sn NMR investigation [21] of the somewhat elusive $\text{Me}_3\text{Sn} \cdot \text{Tp}$.

It is therefore interesting to compare the results with those previously obtained with $\text{Tp}^\#$ ($\text{Tp}^\# = \text{Tp}, \text{Tp}^{\text{Cl}}, \text{Tp}^{4\text{Br}}, \text{Tp}^{4\text{Me}}, \text{Tp}^{4\text{Me}}$) to ascertain the effect of the 4-Br substituent.

2. Results and discussion

The ligand has been obtained through reaction of KBH_4 in molten 4-Br-pyrazole, essentially following the procedures of Trofimenko for other tris(pyra-

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Ligand	X	Y	Z
Tp	H	H	H
Tp ^{3Me}	H	H	Me
Tp ^{4Me}	H	Me	H
Tp [*]	Me	H	Me
Tp ^{*Me}	Me	Me	Me
Tp ^{4Br}	H	Br	H

W = Cl, Me, or Ph

Fig. 1. Identification scheme for the present complexes.

zoly)borates [22], although the reaction is somewhat slower.

The tin complexes ($n = 0-2$) have been prepared according to previously established procedures [6–13]. The triorganotin ones require, as described in the case

of other Tp^{*} ligands [6], special care in order to avoid a premature decomposition (Table 1).

The infrared spectra show all the expected bands. In particular, the complexes show a B–H vibration slightly shifted to higher frequency values (2530–2538 cm⁻¹) than in the corresponding Tp derivatives.

The NMR spectra (Tables 2 and 3) show two sets of signals for the pyrazole protons (ratio 2:1) or carbons (one set greater than the other), except for $n = 0$ or 3. This is expected in the frame of a more or less distorted octahedral geometry around tin, since the pyrazole groups opposed to an organic group and those opposed to a chlorine atom constitute two inequivalent groups. The presence of isomers is ruled out since only one signal ($Sn-Me$) or set of signals ($Sn-Ph$) for tin-bonded organyl groups is observed. Moreover, only one sharp signal is present in the ¹¹⁹Sn NMR spectra, and the values found lie in the appropriate range for octahedral coordinated tin(IV) [3,4,23,24]. As a consequence, fluxionality in solution can be ruled out.

¹³C data show a downfield shift for C-3, C-5, and C-4 atoms of the pyrazole rings, reflecting the flow of charge from the donor ligand to the acceptor metal fragment. As a general trend in poly(pyrazoly)borato ligands [25], the resonance positions for C-4 are very sensitive towards electron density variations. They are shifted to higher fields with increasing n according to the decreasing Lewis acidity of the tin fragment to which the Tp^{*} ligand is bonded.

As previously reported [6,9–13], the ¹¹⁹Sn chemical shift values for the complexes R_nSnCl_{4-n-1} · Tp^{*} follow an almost straight line within each ligand series,

Table 1
Yields, analyses, and physical properties of the compounds

No.	Compound	Yield (%)	Anal. Found/Calc. (%)			MW	M.p.	Λ ^b
			C	H	N			
	K · Tp ^{4Br}	77	22.24	1.49	16.94	^a	287–289	
1	SnCl ₃ · Tp ^{4Br}	59	22.11	1.44	17.19	488	c	8.9
			15.94	1.10	12.40	665		
2	MeSnCl ₂ · Tp ^{4Br}	85	16.04	1.05	12.47	674	234–236	10.4
			18.45	1.60	12.68	642		
3	Me ₂ SnCl · Tp ^{4Br}	68	18.37	1.54	12.86	653	160–162	12.5
			20.90	2.10	13.26	^a		
4	Me ₃ Sn · Tp ^{4Br}	60	20.86	2.07	13.27	633	98–100	15.9
			23.49	2.68	13.54	^a		
5	PhSnCl ₂ · Tp ^{4Br}	91	23.52	2.63	13.71	612	c	7.6
			25.19	1.73	11.69	698		
6	Ph ₂ SnCl · Tp ^{4Br}	83	25.17	1.69	11.74	715	(247–249)	(0.9)
			33.35	2.27	11.07	748		
7	Ph ₃ Sn · Tp ^{4Br}	55	33.30	2.26	11.10	757	(193–200)	(1.0)
			40.50	2.81	10.60	^a		
			40.58	2.77	10.52	799	114–116	10.9
								(1.0)

^a Not performed.

^b Specific conductivity (Ω⁻¹ cm² mol⁻¹) in acetone solution at room temperature; molar concentration (× 10⁻³) indicated in parentheses.

^c Melted with decomposition.

Table 2
¹H NMR data ^a

No.	Compound	Solvent	δ		R–Sn, $ ^nJ(^{119}\text{Sn–H})$ (Hz)
			5-H	3-H	
1	KTP ^{Br}	CD ₃ OH	7.30	7.59	
			7.32	7.64	
2	SnCl ₃ · Tp ^{4Br}	D ₂ O	8.29	8.36	
			(CD ₃) ₂ CO	8.29	
3	MeSnCl ₂ · Tp ^{4Br}	CDCl ₃	7.73	7.88	Me: 1.36; 117.3
			7.62	8.20	
4	Me ₂ SnCl · Tp ^{4Br}	CDCl ₃	7.58	7.80 br	Me: 0.90; 69.0
			7.62 br		
5	Me ₃ Sn · Tp ^{4Br}	CDCl ₃	7.54	7.60	Me: 0.48; ^b
			7.59	7.80	
6	PhSnCl ₂ · Tp ^{4Br}	CDCl ₃	7.68	8.30	Ph: 7.30–7.45
			7.53	7.70	
7	Ph ₂ SnCl · Tp ^{4Br}	CDCl ₃	7.44	7.90	Ph: 7.25–7.40
			7.40	7.60	
7	Ph ₃ Sn · Tp ^{4Br}	CDCl ₃	7.40	7.60	Ph: 7.27–7.46

^a The upper line signal has twice the intensity of that in the lower line.

^b Not observed.

and the lines corresponding to the various ligands are nearly parallel. Their distance is roughly proportional to the difference in donating power of the ligand. The complexes of the present ligand are compared in Fig. 2 with the corresponding ones containing Tp^{4Me}, for R = Me (a) and R = Ph (b). The calculated line belonging to Tp, not drawn for simplicity, is intermediate between these. This is in agreement with the expected donating power of the ligands Tp^{4M} > Tp > Tp^{4Br}.

2.1. Molecular structure of MeCl₂Sn(4-BrPz)₃BH

Crystal data. Space group $R\bar{3}$ (no. 148), trigonal, $a = 35.520(2)$, $b = 35.520(2)$, $c = 8.688(1)$ Å, $\gamma =$

120.00°, $V = 9493$ Å³, formula C₁₀H₁₀BBr₃Cl₂N₆Sn, formula weight $M = 654$, $Z = 18$, $D_{\text{calc}} = 2.06$ g cm⁻³, $F(000) = 5508$.

The crystal structure of the title compound, displayed in Fig. 3, consists of discrete MeCl₂Sn(4-BrPz)₃BH units. The tin atom displays an octahedral coordination geometry with two Cl, one Me, and three N from the pyrazole rings. While the Sn–Cl bond lengths are sufficiently similar, the three Sn–N bond distances are different. In particular, the Sn–N(3) (opposite to the methyl group) bond is the shorter one. The average Sn–N distance is 2.23 Å, which is slightly shorter than the corresponding one (2.24 Å) in MeSnCl₂ · Tp^{4Me} [12], where the presence of the Me groups in position 3 of

Table 3
¹³C and ¹¹⁹Sn NMR data

No.	Compound	Solvent	δ ^{a,b}		C-4 δ ^b	R–Sn δ ^a	¹¹⁹ Sn δ
			C-3	C-5			
1	KTP · Tp ^{4Br}	CD ₃ OH	142.8	136.6	93.9		
			144.7	138.2	95.6		
2	SnCl ₃ · Tp ^{4Br}	D ₂ O	141.5	136.7	95.2		–613.1
			(CD ₃) ₂ CO	142.4	136.6		
3	MeSnCl ₂ · Tp ^{4Br}	CDCl ₃	141.0	136.4	94.4	20.6	–470.6
			140.0	135.1	93.7		
4	Me ₂ SnCl · Tp ^{4Br}	CDCl ₃	139.8	134.5	93.2	15.4	–307.9
			139.1	134.5	93.7		
5	Me ₃ Sn · Tp ^{4Br}	CDCl ₃	139.1	134.5	93.7	–11.5	–171.8
			141.5 ^c	136.6	94.6		
6	PhSnCl ₂ · Tp ^{4Br}	CDCl ₃	142.1 ^d	136.0 ^e	94.4	133.4 ^f , 130.0 ^g	–520.4
			141.5	135.3	93.9		
7	Ph ₂ SnCl · Tp ^{4Br}	CDCl ₃	141.7	136.9	93.6	128.7 ^h , 149.5 ⁱ	–436.4
			141.6	137.3	93.9		
7	Ph ₃ Sn · Tp ^{4Br}	CDCl ₃	141.6	137.3	93.9	134.7 ^j , 128.9 ^k	–436.4
						128.3 ^l , 150.5 ^m	
						136.1, 130.5 ⁿ	–368.1
						129.1, 150.5 ^o	

^a When coupling constants are detected they are reported in a footnote.

^b The signals in the upper line are more intense than those in the lower line.

^c $|^2J(^{119}\text{Sn–}^{13}\text{C})| = 34.0$ Hz. ^d $|^2J(^{119}\text{Sn–}^{13}\text{C})| = 13.4$ Hz. ^e $|^4J(^{119}\text{Sn–}^{13}\text{C})| = 12.1$ Hz. ^f $|^2J(^{119}\text{Sn–}^{13}\text{C})| = 84.3$ Hz. ^g $|^4J(^{119}\text{Sn–}^{13}\text{C})| = 28.5$ Hz. ^h $|^3J(^{119}\text{Sn–}^{13}\text{C})| = 140.7$ Hz. ⁱ $|^2J(^{119}\text{Sn–}^{13}\text{C})| = 61.9$ Hz. ^j $|^4J(^{119}\text{Sn–}^{13}\text{C})| = 18.2$ Hz. ^k $|^3J(^{119}\text{Sn–}^{13}\text{C})| = 89.8$ Hz. ^l $|^4J(^{119}\text{Sn–}^{13}\text{C})| = 13.4$ Hz.

ⁿ C-*ipso* for compounds 5, 6 and 7 is observed around 150 ppm, coupling satellites could not be seen due to the low intensity of the main signal.

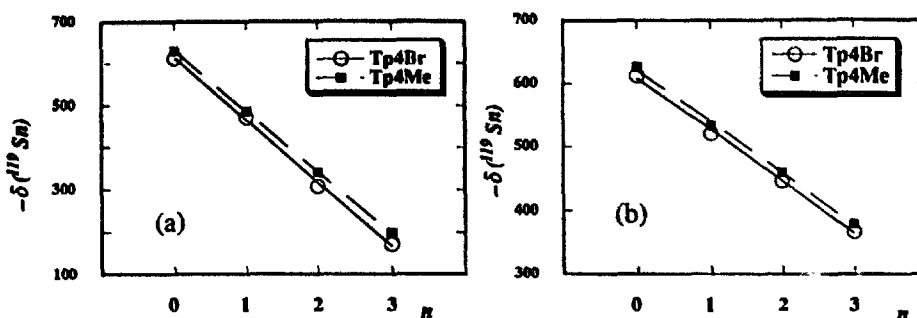


Fig. 2. ^{119}Sn chemical shift of (a) $\text{Cl}_{4-n-1}\text{Me}_n\text{Sn} \cdot \text{Tp}^\#$ and (b) $\text{Cl}_{4-n-1}\text{Ph}_n\text{Sn} \cdot \text{Tp}^\#$ versus n , where $\text{Tp}^\#$ represents $\text{Tp}^{4\text{Me}}$ and $\text{Tp}^{4\text{Br}}$.

the pyrazole rings is likely to crowd somewhat the tin environment. Furthermore, in the couple of analogue complexes $\text{RSnCl}_2 \cdot \text{Tp}$ and $\text{RSn}(\text{NCS})_2 \cdot \text{Tp}$ ($\text{R} = -\text{CH}_2\text{CH}_2\text{COOMe}$) [26], such distances amounts to 2.22 Å for each. Although the R group is certainly greater than the Me one, the lack of any substituent in position 3 of the pyrazole rings in the ligand Tp is reflected, as in $\text{Tp}^{4\text{Br}}$, by the lesser steric requirement of the ligand itself. Consequently, the average Sn–N bond distance is lower. The bond angles in the coordination site show large deviations from the ideal values, since they vary from 77.8 to 100.90°. Selected bond distances and angles together with their standard deviations are reported in Tables 4 and 5. The fractional coordinates together with the equivalent isotropic thermal parameters are listed in Table 6.

Least-squares analysis of the coordination planes shows that the planes of the pyrazolate rings A (N1, N2, C2, C3, C4); B (N3, N4, C5, C6, C7) and C (N5, N6, C8, C9, C10) are planar. The dihedral angles between the planes A/B, A/C, and B/C are 120.7(7)°, 64.4(7)°, and 56.4(6)° respectively. No significant intermolecular contacts are present among the 18 molecules of the cell.

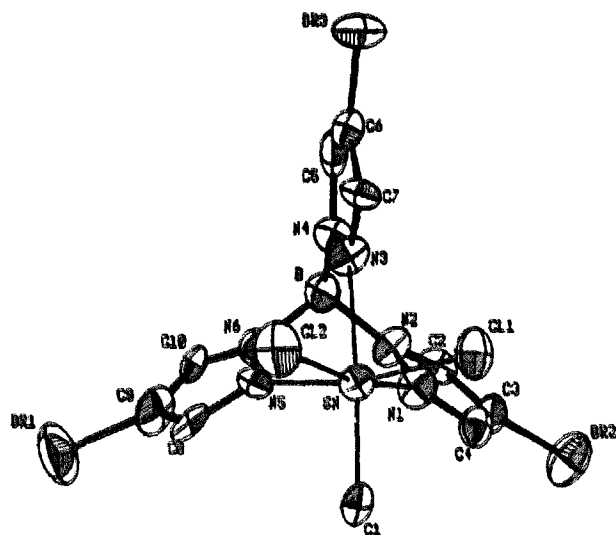


Fig. 3. Crystal structure of $\text{MeCl}_2\text{Sn}(4\text{-BrPz})_2\text{BH}$.

2.2. Mössbauer spectroscopy

The fit of the Mössbauer spectra of the compounds 2, 3 and 5, 6 of Table 7 (Fig. 4) is consistent with the presence of two electric quadrupole interactions attributable to two different tin sites. The more intense doublet can be attributed to the octahedral tin(IV) site found in the present X-ray crystal structure of 2. The less intense doublet, owing to its large splitting, is related to the presence of decomposition products containing probably an all-*trans* octahedral tin(IV) site. This site is similar to that previously reported for deboronated compounds such as *trans*- $\text{ClMe}_2\text{SnTp}^*$ [29] and *trans*- $\text{Cl}_2\text{Me}_2\text{Sn}(4\text{-Me-pz})_2$ [6]. This attribution is in substantial agreement with the *QS* values calculated by point-charge approximation [27,28].

The Mössbauer spectra of the compounds 4 (displayed in Fig. 4) and 7 are similar to those reported for $\text{Me}_3\text{SnTp}^{4\text{Me}}$ and $\text{Ph}_3\text{SnTp}^{4\text{Me}}$ [6]. Instead of the single spectral line expected for the species $\text{R}_3\text{Sn}(\text{N-N})_3$ ($\text{R} = \text{Me}$ or Ph), the fit indicates two main components, in an approximate ratio of 1:2, together with a minor component. Their presence is related to the well-known instability on standing of triorganotin(IV) specimens. The nature of the decomposition products is questionable. Following the point-charge method a trigonal-bipyramidal Sn(IV) site with one axial and one equatorial

Table 4
Selected bond distances (Å)

Sn–Cl(1)	2.395(4)	Sn–Cl(2)	2.401(5)
Sn–N(1)	2.23(1)	Sn–N(3)	2.20(2)
Sn–N(5)	2.27(1)	Sn–Cl(1)	2.21(2)
Br(1)–C(3)	1.87(2)	Br(2)–C(6)	1.88(2)
Br(3)–C(9)	1.89(2)	N(1)–N(2)	1.39(2)
N(1)–C(4)	1.33(2)	N(2)–C(2)	1.35(2)
N(2)–B	1.53(3)	N(3)–N(4)	1.37(2)
N(3)–C(7)	1.33(2)	N(4)–C(5)	1.39(3)
N(4)–B	1.51(3)	N(5)–N(6)	1.39(2)
N(5)–C(8)	1.37(2)	N(6)–C(10)	1.31(2)
N(6)–B	1.51(2)	C(2)–C(3)	1.39(3)
C(3)–C(4)	1.43(2)	C(5)–C(6)	1.40(2)
C(6)–C(7)	1.38(3)	C(8)–C(9)	1.40(2)
C(9)–C(10)	1.35(3)		

Table 5
Selected bond angles (°)

N(5)–Sn–C(1)	91.9(6)	N(3)–Sn–C(1)	167.5(5)
N(3)–Sn–N(5)	77.8(5)	N(1)–Sn–C(1)	92.1(6)
N(1)–Sn–N(5)	80.5(5)	N(1)–Sn–N(3)	79.2(5)
Cl(2)–Sn–C(1)	100.9(5)	Cl(2)–Sn–N(5)	90.8(3)
Cl(2)–Sn–N(3)	86.6(4)	Cl(2)–Sn–N(1)	164.6(4)
Cl(1)–Sn–C(1)	101.1(4)	Cl(1)–Sn–N(5)	163.3(4)
Cl(1)–Sn–N(3)	87.9(4)	Cl(1)–Sn–N(1)	88.5(3)
Cl(1)–Sn–Cl(2)	97.0(2)	Sn–N(1)–C(4)	128(1)
Sn–N(1)–N(2)	125.0(9)	N(2)–N(1)–C(4)	106(1)
N(1)–N(2)–B	118(1)	N(1)–N(2)–C(2)	112(1)
C(2)–N(2)–B	130(1)	Sn–N(3)–C(7)	130(1)
Sn–N(3)–N(4)	123(1)	N(4)–N(3)–C(7)	107(1)
N(3)–N(4)–B	122(1)	N(3)–N(4)–C(5)	110(1)
C(5)–N(4)–B	128(1)	Sn–N(5)–C(8)	130(1)
Sn–N(5)–N(6)	122.0(9)	N(6)–N(5)–C(8)	107(1)
N(5)–N(6)–B	120(1)	N(5)–N(6)–C(10)	109(1)
C(10)–N(6)–B	132(1)	N(2)–C(2)–C(3)	106(1)
Br(1)–C(3)–C(2)	127(1)	C(2)–C(3)–C(4)	107(1)
Br(1)–C(3)–C(4)	126(1)	N(1)–C(4)–C(3)	109(1)
N(4)–C(5)–C(6)	105(1)	Br(2)–C(6)–C(5)	126(1)
C(5)–C(6)–C(7)	108(1)	Br(2)–C(6)–C(7)	126(1)
N(3)–C(7)–C(6)	110(1)	N(5)–C(8)–C(9)	107(1)
Br(3)–C(9)–C(8)	123(1)	C(8)–C(9)–C(10)	107(1)
Br(3)–C(9)–C(10)	130(1)	N(6)–C(10)–C(9)	111(1)
N(4)–B–N(6)	108(1)	N(2)–B–N(6)	107(1)
N(2)–B–N(4)	110(1)		

Table 6
Fractional coordinates with equivalent isotropic thermal parameters (\AA^2)

Atom	x	y	z	U_{eq}
Sn	0.23269(4)	0.09681(3)	0.1052(1)	0.0378(5)
Br(1)	0.28809(7)	0.22611(6)	0.6449(2)	0.073(1)
Br(2)	0.37650(6)	0.04973(7)	0.1199(2)	0.068(1)
Br(3)	0.08122(8)	–0.06068(8)	0.4374(3)	0.102(1)
Cl(1)	0.2927(2)	0.1586(1)	–0.0126(5)	0.061(2)
Cl(2)	0.2146(2)	0.0483(2)	–0.1100(5)	0.069(3)
N(1)	0.2552(4)	0.1300(4)	0.332(1)	0.043(6)
N(2)	0.2601(4)	0.1110(4)	0.464(1)	0.042(7)
N(3)	0.2784(4)	0.0751(4)	0.174(1)	0.038(6)
N(4)	0.2815(4)	0.0636(4)	0.322(1)	0.037(6)
N(5)	0.1913(4)	0.0402(4)	0.264(2)	0.047(7)
N(6)	0.2064(4)	0.0353(4)	0.406(1)	0.040(6)
C(1)	0.1814(5)	0.1146(5)	0.088(2)	0.043(7)
C(2)	0.2732(5)	0.1386(5)	0.585(2)	0.039(8)
C(3)	0.2739(5)	0.1758(5)	0.532(2)	0.044(8)
C(4)	0.2620(5)	0.1690(5)	0.373(2)	0.048(8)
C(5)	0.3142(5)	0.0531(5)	0.332(2)	0.047(9)
C(6)	0.3301(5)	0.0576(5)	0.182(2)	0.045(8)
C(7)	0.3085(5)	0.0727(5)	0.091(2)	0.040(8)
C(8)	0.1482(6)	0.0090(6)	0.255(2)	0.06(1)
C(9)	0.1375(6)	–0.0137(5)	0.395(2)	0.06(1)
C(10)	0.1741(6)	0.0036(5)	0.480(2)	0.046(9)
B	0.2534(6)	0.0650(6)	0.450(2)	0.05(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

organic group is present, together with a tetrahedral Sn(IV) site containing one organic group in its coordination sphere. The third component with spectral intensity of less than 5% is not attributed.

The Mössbauer parameters of these compounds are compared in Table 8 and Fig. 5 with those reported for analogous systems containing poly(pyrazolyl)borato ligands in the octahedral tin(IV) geometry. In particular, the variations on the Mössbauer parameters related to the substitutions on the pyrazolyl groups for poly(pyrazolyl)borates of type $\text{Me}_2\text{SnCl}_2 \cdot \text{Tp}^\#$ and

$\text{Me}_2\text{SnCl} \cdot \text{Tp}^\#$ (with $\text{Tp}^\# = \text{Tp}$, $\text{Tp}^{4\text{Me}}$, $\text{pZTp}^{4\text{Me}}$, and $\text{Tp}^{4\text{Br}}$) have been evidenced.

The trend of the QS values for the compounds 2, 2', 2'', and 3, 3', 3'' in Table 8 shows that, on going from Me- to H-, and Br-substituent in position 4, *p*-electron asymmetry around the tin site increases. The substitution of a σ -donor (such as Me) with a withdrawing σ -acceptor (such as Br) in position 4 varies substantially the *p*-electronic asymmetry at the tin site, and an increase in splitting is observed. The substitution in position 4 on the pyrazolyl groups also affects the IS

Table 7

Compound	IS (mm s^{-1})	QS (mm s^{-1})	QS ^a (mm s^{-1})	LW (mm s^{-1})	Λ (%)	Site
2 $\text{Me}_2\text{SnCl}_2 \cdot \text{Tp}^{4\text{Br}}$	0.79(1)	1.86(1)	(+)2.06	1.11(1)	94	O_h
	1.61(3)	3.72(5)	(+)3.93	0.77(5)	6	all- <i>trans</i> O_h
3 $\text{Me}_2\text{SnCl} \cdot \text{Tp}^{4\text{Br}}$	0.93(1)	2.44(3)	(–)2.06	0.93(1)	93	O_h
	1.37(2)	3.98(5)	(+)3.93	1.10(9)	7	all- <i>trans</i> O_h
4 $\text{Me}_3\text{Sn} \cdot \text{Tp}^{4\text{Br}}$	1.05(1)	2.69(4)	(–)2.02	0.90(5)	31	tbp Sn(IV)
	1.32(1)	3.66(1)	(+)2.44	0.84(1)	65	Td Sn(IV)
	2.12(6)	0.27(15)		0.63(20)	4	
5 $\text{PhSnCl}_2 \cdot \text{Tp}^{4\text{Br}}$	0.72(1)	1.58(1)	(+)1.90	0.95(1)	96	O_h
	1.28(2)	3.08(4)	(+)3.62	0.65(6)	4	all- <i>trans</i> O_h
6 $\text{Ph}_2\text{SnCl} \cdot \text{Tp}^{4\text{Br}}$	0.88(1)	2.08(1)	(–)1.90	0.92(1)	81	O_h
	1.14(1)	3.04(2)	(+)3.60	0.82(4)	19	all- <i>trans</i> O_h
7 $\text{Ph}_3\text{Sn} \cdot \text{Tp}^{4\text{Br}}$	1.10(1)	1.98(3)	(–)1.75	0.84(5)	34	tbp Sn(IV)
	1.23(1)	2.75(1)	(+)2.22	0.89(2)	61	TdSn(IV)
	1.43(4)	0.56(6)		0.79(20)	5	

^a Calculated by the point-charge method assuming a regular geometry and using literature values [27,28].

values (Table 8), i.e. the *s*-electron density at the tin nucleus. Within the trispyrazolylborates, the donor power of the ligands decreases in the following order: $\text{Tp}^{4\text{Me}} > \text{Tp} > \text{Tp}^{4\text{Br}}$, paralleling the *QS* and *IS* parameters in homologous series of compounds as well as the ^{119}Sn NMR chemical shift.

These Mössbauer results cannot be related to possible distortions in compounds containing $\text{Tp}^{4\text{Br}}$ ligands, since bond lengths and angles for the present X-ray crystal structure of $\text{MeSnCl}_2 \cdot \text{Tp}^{4\text{Br}}$ are comparable with those reported for $\text{Cl}_2\text{MeSn} \cdot \text{Tp}^{4\text{Me}}$ [6]. The scarce effect of distortion on the Mössbauer parameters is also

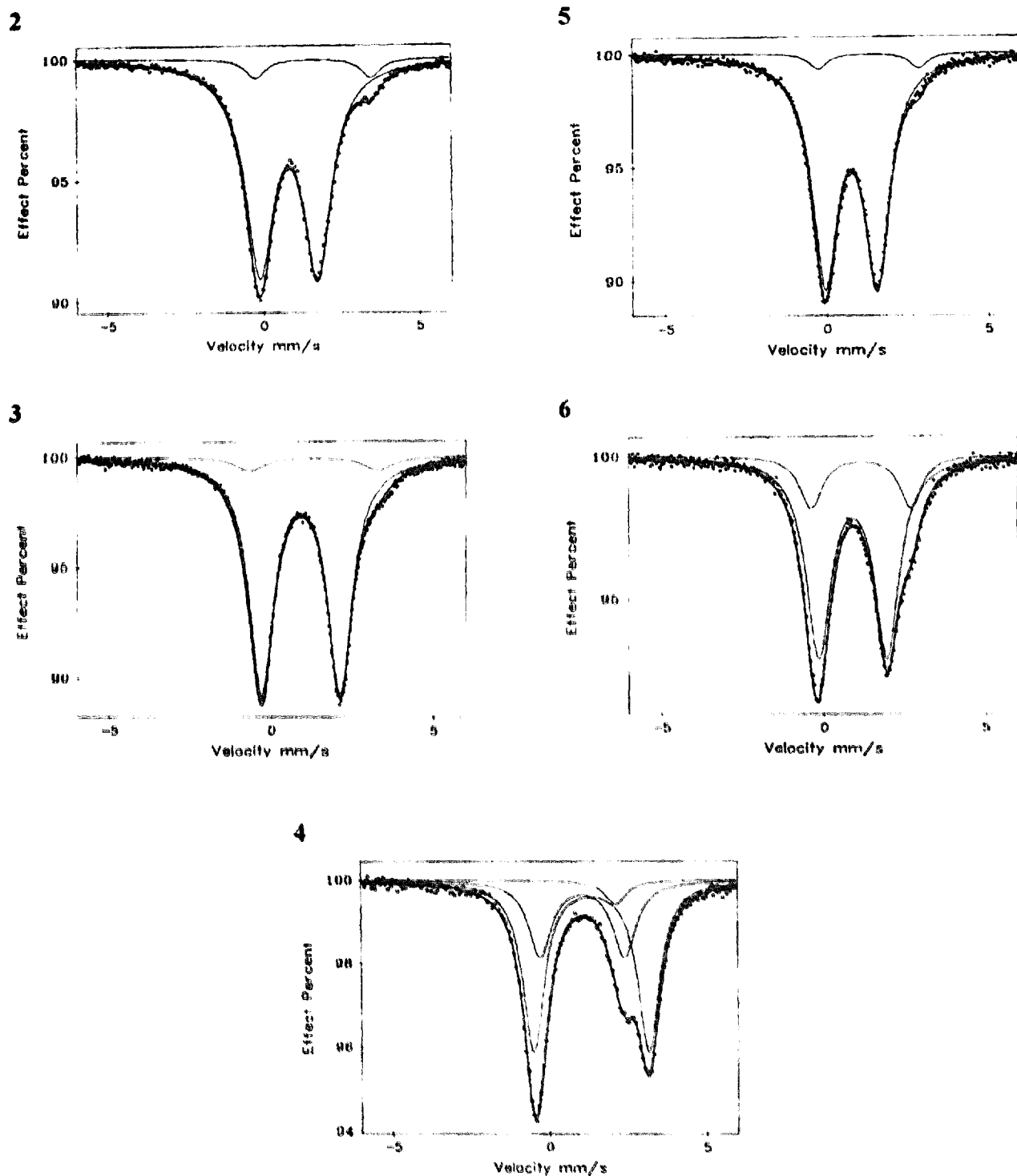


Fig. 4. Mössbauer spectra of complexes 2–6.

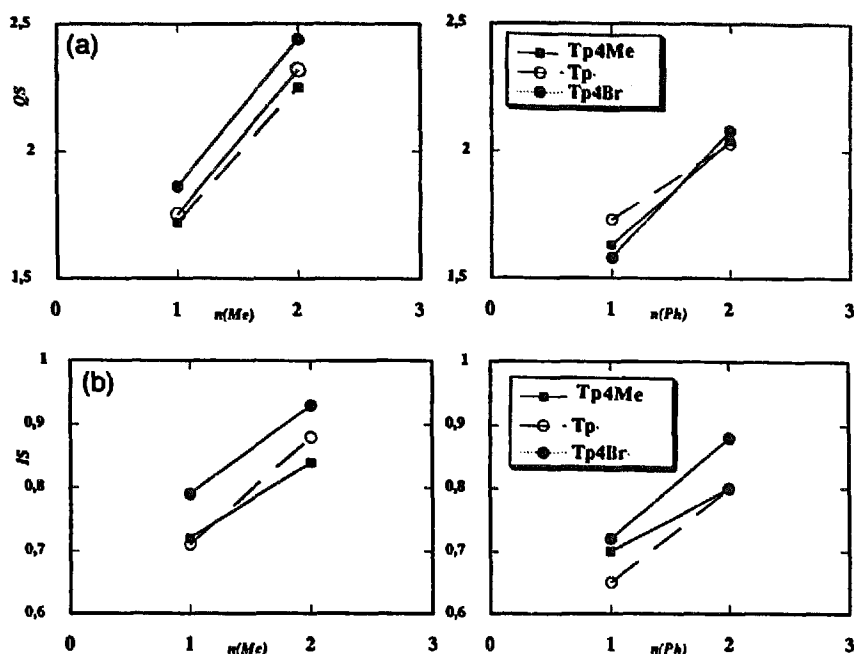


Fig. 5. Trends of (a) quadrupole splitting and (b) isomer shift values (mm s^{-1}) as a function of n in the complexes $\text{Cl}_{4-n-1}\text{R}_n\text{Sn} \cdot \text{Tp}^\#$, with $\text{R} = \text{Me}$ or Ph . ●, $\text{Tp}^{4\text{Br}}$; ○, Tp ; ■, $\text{Tp}^{4\text{Me}}$.

evidenced by comparing the couples of compounds $2'$, $2''$ (and $3'$, $3''$) containing the ligands $\text{Tp}^{4\text{Me}}$ and $\text{pzTp}^{4\text{Me}}$, i.e. tetrakis(1*H*-pyrazol-1-yl)borate. In spite of the greater steric requirements of $\text{pzTp}^{4\text{Me}}$, the Mössbauer parameters are practically unchanged.

For complexes containing Ph groups in place of Me ones (5 , $5'$, $5''$ and 6 , $6'$, $6''$ in Table 8), similar trends are observed. In any case the Mössbauer parameters for the $\text{Tp}^{4\text{Br}}$ compounds are always different from those previously reported for complexes containing the ligands $\text{Tp}^{4\text{Me}}$ or Tp .

Table 8
 ^{119}Sn Mössbauer parameters at 4.2 K

Compound	QS	IS	Ref.
2 $\text{MeSnCl}_2 \cdot \text{Tp}^{4\text{Br}}$	1.86	0.79	this work
$2'$ $\text{MeSnCl}_2 \cdot \text{Tp}^{4\text{Me}}$	1.72	0.72	[6]
$2''$ $\text{MeSnCl}_2 \cdot \text{Tp}$	1.75	0.71	[17]
$2'''$ $\text{MeSnCl}_2 \cdot \text{pzTp}^{4\text{Me}}$ ^a	1.74	0.71	[8]
3 $\text{Me}_2\text{SnCl} \cdot \text{Tp}^{4\text{Br}}$	2.44	0.93	this work
$3'$ $\text{Me}_2\text{SnCl} \cdot \text{Tp}^{4\text{Me}}$	2.25	0.84	[6]
$3''$ $\text{Me}_2\text{SnCl} \cdot \text{Tp}$	2.32	0.88	[17]
$3'''$ $\text{Me}_2\text{SnCl} \cdot \text{pzTp}^{4\text{Me}}$ ^a	2.23	0.89	[8]
5 $\text{PhSnCl}_2 \cdot \text{Tp}^{4\text{Br}}$	1.58	0.72	this work
$5'$ $\text{PhSnCl}_2 \cdot \text{Tp}^{4\text{Me}}$	1.63	0.70	[6]
$5''$ $\text{PhSnCl}_2 \cdot \text{Tp}$	1.73	0.65	[17]
6 $\text{Ph}_2\text{SnCl} \cdot \text{Tp}^{4\text{Br}}$	2.08	0.88	this work
$6'$ $\text{Ph}_2\text{SnCl} \cdot \text{Tp}^{4\text{Me}}$	2.04	0.80	[6]
$6''$ $\text{Ph}_2\text{SnCl} \cdot \text{Tp}$	2.03	0.80	[17]

^a $\text{pzTp}^{4\text{Me}} = \text{tetrakis}(4\text{-Me-pyrazol-1-yl})\text{borate}$.

3. Experimental

3.1. General comments

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 on a Fisons Instruments EA 1108 CHNS-O, while molecular weight determinations were performed by a Knauer vapour pressure osmometer. Infrared spectra were recorded from 4000 to 250cm^{-1} on a Perkin-Elmer 2000 System Series FTIR instrument. ^1H , ^{13}C and ^{119}Sn NMR spectra were recorded on a Varian VXR-300 spectrometer operating at room temperature (299.95 MHz for ^1H , 75.43 MHz for ^{13}C and 111.9 MHz for ^{119}Sn). Some spectra were also recorded on a Varian Gemini-200 (199.98 MHz for ^1H , 50.29 MHz for ^{13}C). The chemical shift is reported in ppm from Me_4Si (^1H and ^{13}C , calibration from internal deuterium solvent lock) and Me_4Sn (^{119}Sn) values. The conductivity of the acetone solutions was measured with a Crison CDTM 522 conductimeter at room temperature.

3.2. Syntheses

3.2.1. Potassium[hydridotris(4-bromo-1*H*-pyrazol-1-yl)borato] ($\text{KTP}^{4\text{Br}}$)

A mixture of 4-Br-pyrazole (20 g, 0.136 mol) and KBH_4 (1.83 g, 0.034 mol) was heated gradually. Melting with a slight evolution of hydrogen occurred at ca.

90°C. The mixture was finally heated at 170°C until 3 equivalents of hydrogen per KBH_4 had evolved. The mixture was allowed to cool to room temperature and xylene was added with vigorous stirring. The xylene solution was separated by filtration. This treatment was repeated several times to remove unreacted 4-Br-pyrazole. The remaining solid was eventually washed with hexane-petroleum ether (1:1, v/v) to give a white crystalline solid, that was identified as $\text{Tp}^{4\text{Br}}$.

3.2.2. [Hydridotris(4-bromo-1H-pyrazol-1-yl)borato]trichlorotin(IV) (1)

SnCl_4 (1 ml, 1 M solution in CH_2Cl_2) and $\text{KTp}^{4\text{Br}}$ (0.489 g, 1 mmol) were introduced into a round-bottomed flask. The solution was cooled (ca. -10°C) and THF (30 ml) was added. The mixture was stirred for 5 min, filtered and the filtrate evaporated under reduced pressure. The residue was recrystallised from CH_2Cl_2 to yield a white solid, that was identified as compound 1.

3.2.3. [Hydridotris(4-bromo-1H-pyrazol-1-yl)borato]dichloromethyltin(IV) (2)

A CH_2Cl_2 solution (30 ml) of MeSnCl_3 (0.24 g, 1 mmol) was mixed with a CH_2Cl_2 solution (30 ml) of $\text{Tp}^{4\text{Br}}$ (0.489 g, 1 mmol) at room temperature. The mixture was stirred for 30 min, filtered and the filtrate was evaporated under reduced pressure. The residue was recrystallised from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:1, v/v) and dried under reduced pressure to yield a white solid, that was identified as compound 2.

3.2.4. [Hydridotris(4-bromo-1H-pyrazol-1-yl)borato]chlorodimethyltin(IV) (3)

A CH_2Cl_2 solution (30 ml) of Me_2SnCl_2 (0.22 g, 1 mmol) was added to a cooled (ca. 0°C) CH_2Cl_2 solution (30 ml) of $\text{Tp}^{4\text{Br}}$ (0.489 g, 1 mmol). The mixture was stirred for 30 min, filtered and the filtrate was evaporated under reduced pressure. The residue was recrystallised from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:1, v/v) and dried under reduced pressure to yield a white solid, that was identified as compound 3.

3.2.5. [Hydridotris(4-bromo-1H-pyrazol-1-yl)borato]trimethyltin(IV) (4)

A solution of Me_3SnCl (0.199 g, 1 mmol) in 25 ml of outgassed (dry N_2) anhydrous benzene at ca. 8°C was added to a flask (100 ml) containing a solution/suspension of 0.489 g (1 mmol) of $\text{KTp}^{4\text{Br}}$ in 25 ml of benzene. After 1 h the solution was filtered (KCl) in an atmosphere of dry N_2 and the filtrate was evaporated at ca. 8°C under reduced pressure. The resulting oily liquid was purified by repeated washing with *n*-pentane upon which a white solid was obtained and identified as 4.

3.2.6. [Hydridotris(4-bromo-1H-pyrazol-1-yl)borato]dichlorophenyltin(IV) (5)

A CH_2Cl_2 solution (30 ml) of PhSnCl_3 (0.302 g, 1 mmol) was added to a cooled (ca. 0°C) CH_2Cl_2 solution (30 ml) of $\text{Tp}^{4\text{Br}}$ (0.489 g, 1 mmol). The mixture was stirred for 30 min, filtered and the filtrate was evaporated under reduced pressure. The oily residue was crystallised by addition of petroleum ether to yield a white solid, identified as compound 5.

3.2.7. [Hydridotris(4-bromo-1H-pyrazol-1-yl)borato]chlorodiphenyltin(IV) (6)

This complex was prepared as described in Section 3.2.6 using Ph_2SnCl_2 (0.343 g, 1 mmol) and $\text{Tp}^{4\text{Br}}$ (0.489 g, 1 mmol) to yield a white solid, that was identified as compound 6.

3.2.8. [Hydridotris(4-bromo-1H-pyrazol-1-yl)borato]triphenyltin(IV) (7)

A CH_2Cl_2 solution (30 ml) of Ph_3SnCl (1 mmol, 0.385 g) was added to a cooled (ca. -20°C) CH_2Cl_2 solution (30 ml) of $\text{Tp}^{4\text{Br}}$ (0.489 g, 1 mmol). The mixture was stirred for 15 min, filtered and the filtrate was evaporated under reduced pressure. The oily residue was recrystallised from *n*-heptane to yield a white solid, that was identified as compound 7.

3.3. Mössbauer spectroscopy

A source of $^{119\text{m}}\text{Sn}$ in a matrix of CaSnO_3 was used for tin measurements. Both source and absorber were kept at the liquid helium temperature, a sinusoidal velocity waveform and a proportional counter were used. Owing to the large non-resonant scattering of the heavy Br atoms in the specimens, about a week was necessary to collect a spectrum with good statistics. This means that the measurements were performed on samples after a standing of months. The fit was performed with the program MOS 90 by appropriate superpositions of Lorentzian lines. The hyperfine parameters, such as *IS* isomer shift (relative to SnO_2), *QS* quadrupole splitting, *LW* average line width (mm s^{-1}), and *A* relative resonance area in per cent are listed in Table 7.

3.4. X-ray crystal procedure

A crystal with approximate dimensions $0.3 \times 0.4 \times 0.3 \text{ mm}^3$ was used. Intensity data for the compound 2 were collected at room temperature with a Philips PW 1100 diffractometer using $\text{Mo K}\alpha$ radiation in the range $4.6^\circ < 2\theta < 44.0^\circ$; 4288 reflections were read. Of these 1685, with $F > 3\sigma(F)$, were used in the structure analysis. Data were corrected for Lorentz and polarization effects. The structure was solved by SHELXS-86

direct methods [30]. Full-matrix least-squares refinement on F was computed, and the function $\sum_w [|F_o| - |F_c|]^2$ minimised. The non-hydrogen atoms were refined anisotropically. The position of the hydrogen atoms was calculated but not refined. The final R values were 0.058 ($R_w = 0.059$). (Supplementary material including anisotropic thermal parameters, hydrogen coordinates and structural factors are available from the Editor).

4. Concluding remarks

The $\text{Tp}^{4\text{Br}}$ complexes investigated in this paper contain hexa-coordinate tin atoms and are not fluxional in solution. The values for all the ^{119}Sn NMR chemical shifts lie in the appropriate range for octahedral tin(IV) species. It may be noted the ^{119}Sn resonances of the $\text{Tp}^{4\text{Br}}$ derivatives are shifted upfield with respect to other tris(pyrazolyl)borates. In particular, the values are different by ca. 5–13, 13–25, 30–40, and 40–55 ppm in comparison with tin(IV) complexes with Tp , $\text{Tp}^{4\text{Me}}$, $\text{Tp}^{3\text{Me}}$, and Tp^* respectively. In addition, the variations of the Mössbauer parameters for these compounds, related to the substitutions on the pyrazolyl groups, confirm that the ligand $\text{Tp}^{4\text{Br}}$ is a less donating one. Accordingly, the scale for the series is: $\text{Tp}^{4\text{Br}} < \text{Tp} < \text{Tp}^{4\text{Me}} < \text{Tp}^{3\text{Me}} < \text{Tp}^*$.

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