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Organotin(IV) polypyrazolylborates

III. Tris(3,5-dimethylpyrazolyl)borates

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Abstract

The compounds $R_nSnX_{3-n}Q$ where R = Me, Et, Bu or Ph; X = Cl or Br: $n = 0, 1$, or 2 and Q is the sterically demanding title ligand have been shown to be stable and non-fluxional and to contain six-coordinate tin(IV) and the tridentate ligand Q.

Introduction

In earlier papers [1,2] several complexes $R_{3-n}X_nSn(\mu\text{-Pz-}N,N')_3BR'$ were described where PzH is pyrazole, $n = 3, 2$, or 1, R = alkyl or phenyl, X = Cl or Br and R′ = H [1] or R′ = 1-pyrazolyl [2]. It was concluded that these monomeric, not-ionic Sn^{IV} derivatives of the tripodal ligand $(Pz)_3BH$ or $(Pz)_3B(Pz\text{-}N)$ (Q′ or Q″ respectively) are non-fluxional, and that the tin atom is surrounded by six atoms in some sort of skewed trapezoidal bipyramid, as discussed by Das [3] for another organotin(IV) derivative, *cis*-(*p*-chlorophenyl)(*p*-tolyl)bis(8-quinolato)tin(IV).

In view of the ability of several organotin(IV) derivatives to undergo distortion from an octahedral geometry while remaining six-coordinate, we decided to try to prepare their derivatives with another tripodal ligand, $(Pz'\text{-}N)_3BH^-$ (Q) where Pz′H is 3,5-dimethylyrazole. This ligand is considered to be sterically demanding [4–6] and the X-ray structure reported for the vanadium derivative formulated as QV(=O) [7] shows that the metal atom is only five-coordinate and the Q ligand is only bidentate, instead of tridentate as expected. Our purpose was to see whether $R_{3-n}X_nSnQ$ complexes are stable in spite of the bulk of the ligand Q and if so, whether tin is six-coordinate and Q tridentate. We were also interested in whether these sterically crowded molecules are still non-fluxional, and if so why.

Results and discussion

Interaction of potassium hydrotris(3,5-dimethylpyrazol-1-yl)borate with organotin(IV) halides R_nSnX_{4-n} (R = Me, Et, Bu or Ph; X = Cl, Br; $n = 0, 1, 2$) in

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Table 1

Yields, analyses, and physical properties of compounds **1–11**

Compound [a]	Yield (%)	Elemental analysis (Found (calcd.)) (%)			Low frequency bands (cm^{-1})		
		C	H	N			
CH_3SnCl_2Q [b]	87	38.04	4.96	16.48	540 m	480 w	380 vw
(**1**)		(38.30)	(5.02)	(16.75)	290 s		
$C_4H_9SnCl_2Q$	89	36.37	4.07	21.08	470 m	380 w, sh	370 w
(**2**)		(36.55)	(4.03)	(21.31)	290 s		
$C_6H_5SnCl_2Q$	82	44.66	5.02	14.58	475 m	460 w	370 w
(**3**)		(44.73)	(4.83)	(14.90)	290 s		
$(CH_3)_2SnClQ$ [b]	76	41.98	5.75	17.12	520 w	470 w	370 vw
(**4**)		(42.42)	(5.86)	(17.46)	280 m		
$(CH_3)_2SnBrQ$	68	39.0	5.28	15.66	470 w		
(**5**)		(38.83)	(5.37)	(15.98)			
$(C_2H_5)_2SnClQ$	70	44.69	6.32	16.62	540 w	470 w	365 vw
(**6**)		(44.79)	(6.33)	(16.50)	320 w		
$(C_2H_5)_2SnBrQ$	68	40.93	5.83	14.88	520 w	480 w	
(**7**)		(41.20)	(5.82)	(15.17)			
$(C_4H_9)_2SnClQ$ [b]	78	48.58	7.38	14.62	575 w	470 w	390 w
(**8**)		(48.85)	(7.13)	(14.86)	290 w		
$(C_6H_5)_2SnClQ$	74	52.98	5.22	13.47	555 w	475 m	370 w
(**9**)		(53.55)	(5.33)	(13.88)	290 m		
$SnCl_3Q$ [b]	84	34.08	4.38	15.77	480 m	380 w	330 vs
(**10**)		(34.50)	(4.25)	(16.09)	310 s		
$SnBr_3Q$	81	27.16	3.38	12.56	480 m	380 w	
(**11**)		(27.48)	(3.38)	(12.82)			

[a] Q is hydrotris(3,5-dimethylpyrazol-1-yl)borato $C_{15}H_{22}N_6B$. [b] Monomer according to molecular weight determination by osmometry in dichloromethane.

dichloromethane gives the compounds **1–11** smoothly as depicted below:

$$R_nSnX_{4-n} + KQ \rightarrow KX + R_nSnQX_{4-n-1}$$

(1–11)

Comp.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
R	Me	Bu	Ph	Me	Me	Et	Et	Bu	Ph	–	–
X	Cl	Cl	Cl	Cl	Br	Cl	Br	Cl	Cl	Cl	Br
n	1	1	1	2	2	2	2	2	2	0	0

The compounds are air-stable solids, which usually decompose gradually when heated above ca. 300 ° C; only the trichloro and the dibromo derivative melt sharply, at 330–332° C and 324–326 ° C, respectively. The compounds were identified from their analytical data (which appear in Table 1 together with yields). Their specific conductivities show that they are non-electrolytes in acetone, Λ being 4–11 ohm^{-1} cm^2 $mole^{-1}$ for a millimolar acetone solution. Furthermore, molecular weight determinations by osmometry show them to be monomer (Table 1).

The most significant absorptions in the IR spectra (Table 1) are as follows: a weak bond at ca. 3120 cm^{-1} (C–H stretching vibration(s) characteristic of the pyrazole ring), a strong or very strong band at ca. 1540 cm^{-1} (ring "breathing"),

Table 2

^{1}H NMR data

Compound	Solvent	4-H (singlets) δ ^{a,b,c}		3- or 5-Me δ ^{a}		R–Sn and ^2J(Sn–H)	
KQ	$(CD_3)_2CO$	5.55		2.20	2.02		
ZnQ_2	$CDCl_3$	5.59		2.42	1.39		
$MeSnCl_2Q$	CD_2Cl_2	5.90	(17)	2.55	2.41	Me: 1.48	J = 122; 113
(**1**)				2.78	2.39		
	$CDCl_3$	5.86	(18)	2.82	2.38	Me: 1.50	J = 120; 112
				2.56	2.35		
	$(CD_3)_2CO$	6.06		2.55	2.47	Me: 1.42	J = 119;111
		5.88		2.78	2.44		
$BuSnCl_2Q$	$CDCl_3$	5.88		2.58	2.33	Bu: 1.98–1.90m,	
(**2**)		5.85	(17)	2.82	2.40	1.72–1.60m	
						1.40 sextet	J = 105; 98
						0.91 t	
$PhSnCl_2Q$	$CDCl_3$	6.80		2.45	1.86	Ph: 7.26–7.30m,	
(**3**)		6.90	(18)	2.90	2.38	7.40–7.48m,	
						7.52–7.61m	
Me_2SnClQ	$(CD_3)_2CO$	5.85		2.58	2.40	Me: 0.86	J = 72; 67
(**4**)				2.45	2.18		
	$CDCl_3$	5.76		2.60	2.34	Me: 0.92	J = 72; 67
		5.82		2.40	2.32		
Me_2SnBrQ	$CDCl_3$	5.75		2.30	2.21	Me: 1.06	J = 85; 79
(**5**)		5.82		2.65	2.28		
Et_2SnClQ	CD_2Cl_2	5.80		2.33	2.23	Et: 1.02t(2.8)	
(**6**)		5.82		2.56	2.41	1.60q(2.8)	
Et_2SnBrQ	CD_2Cl_2	5.90		2.35	2.20	Et: 1.04t(3.0)	
(**7**)		5.82		2.55	2.12	1.60q(3.0)	
Bu_2SnClQ	$CDCl_3$	5.82		2.62	2.26	Bu: 1.84–1.80m,	
(**8**)		5.70		2.60	2.30	1.54–1.26m,	
						0.89t	
Ph_2SnClQ	$CDCl_3$	5.70		2.42	1.84	Ph: 7.70m	
(**9**)		5.78		2.53	1.25	7.52m,	
						7.22m	
$SnCl_3Q$	CD_2Cl_2	5.94	(16)	2.70	2.38		
(**10**)							
$SnBr_3Q$	$CDCl_3$	5.88	(15)	2.87	2.39		
(**11**)							

[a] In ppm from internal TMS. [b] Upper line: more intense signal. [c] The value in brackets is ^4J[Sn–H(4)].

and a weak or medium intensity band between 2540 and 2565 cm^{-1} due to the B–H stretching; this last band is less intense and lies at significantly higher frequences these for the potassium or zinc derivative, 2435 or 2505 cm^{-1} respectively. Other strong bands due to ring out of plane vibrations appear at ca. 810 cm^{-1}; in addition, some of the low frequency absorptions are due to Sn–C or Sn–Cl stretching. Comparison of these values with the corresponding ones for Q′ or Q″ compounds [1,2], reveals that there is a general agreement except for a displacement of the mean of B–H values, which is slightly raised.

The NMR data for our compounds are shown in Tables 2 (^{1}H) and 3 (^{13}C and ^{119}Sn); in each case data for the parent potassium salt KQ and the zinc derivative ZnQ_2 are included for comparison. As required for six-coordination around tin(IV)

Table 3

^{13}C and ^{119}Sn NMR data

Compound	Solvent	C-3 or C-5		C-4	Pz–CH_3		R–Sn[a] and	^{119}Sn
		δ[a,b,c]		δ[d]	δ[a,b]		J(Sn–C)	$-\delta$[g]
KQ	$(CD_3)_2CO$	146.2	143.4	103.9	13.9	13.1		
ZnQ_2	CD_2Cl_2	148.5	142.6	104.3	12.8	11.6		
$MeSnCl_2Q$	CD_2Cl_2	150.5	145.6	107.7	13.9	12.6	Me: 26.3	509.3
(**1**)		152.1#	145.3#	108.4*	15.5	13.0	^1J = 1136,	
							1088	
	$(CD_3)_2CO$	150.8	146.2	108.2	13.9	12.4	Me: 26.3	
		152.2	145.8	108.8*	15.5	12.8		
	$CDCl_3$	150.2	144.6	107.5	13.8	12.5	Me: 26.1	
		152.0#	144.3#	108.4*	15.4	12.9	^1J = 1136,	
							1079	
$BuSnCl_2Q$	$CDCl_3$	150.3	144.8	107.4	14.0	12.6	Bu: 41.8, 27.1[e],	506.6
(**2**)		152.0#	144.3#	108.3*	13.7	13.0	25.8[f], 15.4	
							^1J = 1153,	
							1090	
$PhSnCl_2Q$	$CDCl_3$	151.7	144.8	107.4	15.3	13.5	Ph: 134.8, 131.7	554.6
(**3**)		152.0#	144.5#	108.3*	13.0	12.6	128.7, 127.0	
Me_2SnClQ	$CDCl_3$	149.4	143.3	107.1	14.5	12.8	Me: 19.2	357.6
(**4**)		148.0	144.4	106.7	13.4	12.6		
Me_2SnBrQ	$CDCl_3$	147.1	144.4	104.2	13.4	12.2	Me: 21.3	
(**5**)		146.8	143.3	107.1	14.5	12.7		
Et_2SnClQ	CD_2Cl_2	151.0	144.6	104.3	12.4	12.3	Et: 9.65; 26.5	339.8
(**6**)		149.8	147.2	107.0	11.2	12.9	^1J = 643, 598	
Et_2SnBrQ	CD_2Cl_2	149.7	144.8	107.2	12.9	12.4	Et: 9.9; 28.3	
(**7**)		151.7	147.0	107.8	14.6	10.7	^1J = 620, 576	
Bu_2SnClQ	CD_2Cl_2	149.6	143.3	106.9	13.8	13.0	Bu: 34.5, 28.0,	348.8
(**8**)		148.0	144.1	104.4	13.3	12.4	27.3, 14.6	
							^1J = 623, 580	
Ph_2SnClQ	$CDCl_3$	156.9	143.4	107.0	13.7	12.8	Ph: 134.9, 128.5	482.1
(**9**)		151.0	144.7	106.7	13.5	12.6	127.7	
$SnCl_3Q$	CD_2Cl_2	152.2#	146.1#	108.4*	14.5	12.7		656.2
(**10**)								
$SnBr_3Q$	CD_2Cl_2	151.7#	144.5#	108.6*	15.1	12.6		
(**11**)								

[a] In ppm from internal TMS; J in Hz. [b] The signals on the upper line are more intense than those on the lower line. [c] ^2J (Sn–C) are detected for the compounds **1**, **2**, **3**, **10** and **11** (27–32 Hz), the signals affected being marked with the symbol #. [d] ^3J(Sn–C) are detected for the compounds **1**, **2** and **3** (28–30 Hz), **10** and **11** (24 and 22 Hz); the satellites accompany the signals marked with an asterisk. [e] $^3J(Sn-CH_2) = 60$ Hz. [f] $^2J(Sn-CH_2) = 244$ Hz.. [g] In ppm from external Me_4Sn.

(as illustrated in Fig. 1), in all the derivatives except Cl_3SnQ and Br_3SnQ the presence of two types of pyrazole rings is indicated by the ^{1}H and ^{13}C spectra, and in the ^{1}H spectra the ratio of the two sets of pyrazole signals is 2 : 1. This excludes fluxionality of these compounds in chloroform or dichloromethane solution, and the sharp singlet seen in each case in the ^{119}Sn spectra (Table 3) is thus due to a single species.

In the $Cl_{3-n}R_nSnQ$ compounds the ^{119}Sn chemical shift is a linear function of n, as shown in Fig. 2a, 2b or 2c for the three cases where R is methyl, butyl or phenyl respectively. In addition, in the same Figures the data are plotted for the related

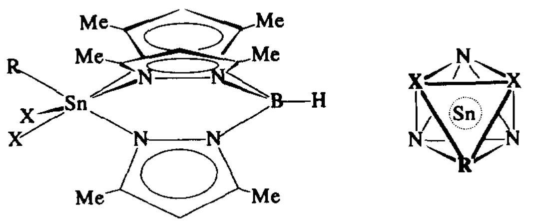

Fig. 1. Octahedral coordination around tin; on the right, the same viewed along the Sn–B–H axis.

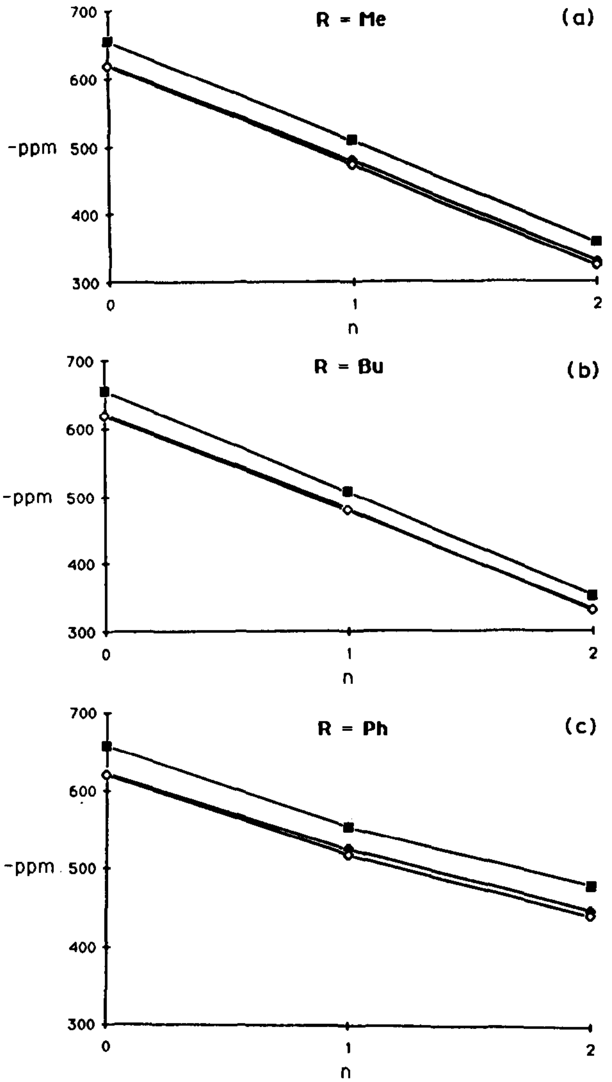

Fig. 2. Coordination between ^{119}Sn chemical shift and the number of tin-bounded R-groups for R = methyl, n-butyl, and phenyl in the compound $Cl_{3-n}R_nSnQ$; ■ = Q; ◆ = Q′; ◇ = Q″.

$Cl_{3-n}R_nSnQ'$ and $Cl_{3-n}R_nSnQ''$ complexes; while the two sets of lines are overlapping, the lines due to the Q derivatives are displaced but are still parallel to the others. Similar correlations exist if the ^{13}C chemical shift values for carbons directly attached to the tin atom are plotted in the same fashion against the number of R groups: the line obtained for the Q ligand is parallel to, but again, displaced from, the lines referring to Q′ and Q″. Such displacements correspond to higher basicity and/or greater hindrance of the ligand Q. From the linearity and parallelism observed it can be concluded that the same factors operate in the three series of complexes, involving Q, Q′ and Q″, so that the same arrangement of ligands is likely for all the compounds, with the tripodal ligand occuping a face of the octahedron. The suggestion of pentacoordination, acceptable for some compounds for which neither $^4J(Sn-H(4))$ nor $^3J(Sn-C(4))$ coupling is detected, would require the following conditions, which are not met: (1) two types of pyrazole signals in a 2 : 1 ratio for the compounds **10** and **11**; (2) a Sn–C coupling constant much lower than that observed for compounds **1**, **6** and **7**.

In conclusion, organotin(IV)- and halogenotin(IV) derivatives of a sterically demanding ligand such as Q are stable; they are non-fluxional and contain both six-coordinate tin(IV) and a tripodal ligand. Although an X-ray crystal structure is not available, inspection of molecular models suggests an explanation for the observed behaviour. Q is sterically demanding in the region of pyrazolyl rings, but in six-coordinate complex there remains some space between these rings and this is available for groups which are not bulky (methyl, linear alkyl, halide) or are flat (phenyl); correspondingly, in this cog-wheel type arrangement stable bonds are possible in spite of the sterically demanding ligand, and intramolecular movement of the ligand Q is difficult, so that fluxional behaviour is not observed.

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 this Department; molecular weight determinations were performed at Pascher's Mikroanalytisches Laboratorium, Remagen, Germany. Infrared spectra were recorded from 4000 to 250 and from 4000 to 600 cm^{-1} on a Perkin–Elmer 457 instrument and 1600 Series FTIR instrument, respectively. ^1H-, ^{13}C- and ^{119}Sn-NMR spectra were recorded on a Varian EM-390, and VX-300 spectrometers operating 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 Crison CDTM 522 conductimeter at room temperature. Melting points were taken on a IA 8100 Electrothermal Instrument.

[Hydrotris(3,5-dimethylpyrazol-1-yl)borato]methyldichlorotin(IV), 1

A dichloromethane solution (20 ml) of methyltrichlorotin(IV) (240 mg, 1 mmol) was added to a stirred suspension of potassium hydrotris(3,5-dimethyl-pyrazolyl) borate (340 mg, 1 mmol) in dichloromethane (20 ml). The filtered solution was evaporated to dryness; the residue was purified by recrystallization from dichloromethane–diethyl ether. Compounds **2–11** were obtained similarly.

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