

Organotin(IV) polypyrazolylborates

II *. Tetrakis(pyrazolyl)borates

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Abstract

Reaction of tin(IV) or organotin(IV) halides with potassium tetrakispyrazolylborate, $K[B(\text{Pz}-N)_4]$, affords the monomeric species $R_n X_{3-n} \text{Sn}(\mu\text{-Pz}-N, N')_3 B(\text{Pz}-N)$ ($n = 0, 1$ or 2 ; $R = \text{Me, Et, Bu}$ or Ph ; $X = \text{Cl}$ or Br) which are not fluxional. Six-coordinate tin and one monodentate pyrazolato- N group are present in solution according to ^1H -, ^{13}C -, and ^{119}Sn -NMR spectroscopic studies.

Introduction

In continuation of our studies of tin(IV) and organotin(IV) derivatives containing either neutral poly(pyrazolyl)alkane [1] or anionic poly(pyrazolyl)borate [2] ligands, we decided to study the corresponding tetrakis(pyrazol-1-yl)borates, which are known for transition elements [3] but not for tin(IV). Such an anion has four nitrogen donor atoms, but only up to three are suitably arranged for intramolecular

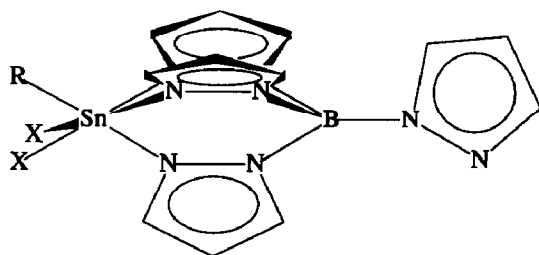


Fig. 1. Octahedral coordination around tin(IV).

* For Part I see ref. 2.

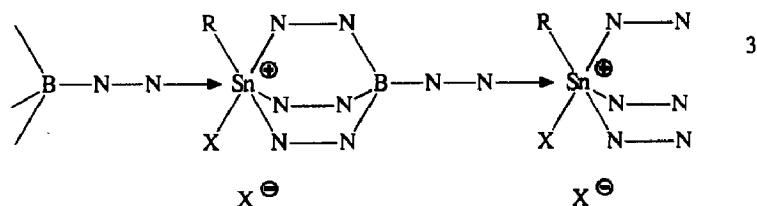
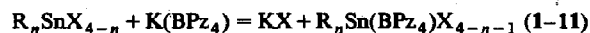


Fig. 2. Structure in which the fourth pyrazolato group takes part in an intermolecular bond (N-N: pyrazolato group).

coordination, so that the remaining donor either remains unengaged (as in Fig. 1) or takes part in an intermolecular bond, e.g. by displacing an X^- group from the coordination sphere (Fig. 2). In the former case the presence of the dangling pyrazole ring is likely to make the derivatives more soluble in organic solvents those of the $HB(Pz)_3^-$ anion. The second possibility (Fig. 2) seemed reasonable in the presence of a good Lewis acid such as Sn^{IV} , but has been ruled out by the results reported below.

Results and discussion

Interaction of potassium tetrakispyrazolylborate with organotin(IV) halides R_nSnX_{4-n} ($X = Cl, Br; n = 0, 1, 2$) in acetone gives the compounds 1-11 as colourless air-stable solids.



Compound	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	Et	Br	2
8	Bu	Cl	2
9	Ph	Cl	2
10	-	Cl	0
11	-	Br	0

The products were identified by their analytical data which are shown in Table 1 together with the melting points, yields, and specific conductivities. The conductivities show that they are non-electrolytes in acetone or dichloromethane, in which, furthermore, most of them are monomeric thus ruling out a structure such as that shown in Fig. 2. Additional support comes from the infrared spectra (Table 2), which show C-H stretching vibrations at ca. 3150 cm^{-1} , ring breathing vibrations at ca. 1500 cm^{-1} , and bands attributable to Sn-C or Sn-Cl stretching vibrations in the ranges $540-580$ and $280-330\text{ cm}^{-1}$, respectively; in addition, strong bands due to the ring out-of-plane vibrations appear at ca. 800 cm^{-1} . Apart from the absence of B-H band at ca. 2500 cm^{-1} , differences from the spectra of trispyrazolylborato analogues are quite small, so that the presence of uncoordinated pyrazolate is not immediately detectable by IR spectroscopy.

Table 1

Yields, analyses, and physical properties of compounds 1–11 ($L = C_{12}H_{12}N_8B$)

Compound	Yield (%)	M.p. (°C)	Elemental Analysis (Found Calcd.)			Specific conductivity ^a ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)	
			C%	H%	N%		
1	$\text{CH}_3\text{SnCl}_2\text{L}^a$	81	248–50	31.81 32.28	3.26 3.13	22.80 23.16	6.7
2	$\text{C}_4\text{H}_9\text{SnCl}_2\text{L}$	82	221–223	36.37 36.55	4.07 4.03	21.08 21.31	
3	$\text{C}_6\text{H}_5\text{SnCl}_2\text{L}^c$	84	280–282	39.28 39.61	3.22 3.14	20.26 20.53	6.3
4	$(\text{CH}_3)_2\text{SnClL}^c$	73	133–135	36.06 36.29	4.11 3.92	23.98 24.19	
5	$(\text{CH}_3)_2\text{SnBrL}$	60	124–126	32.92 33.12	3.92 3.57	21.89 22.07	3.6
6	$(\text{C}_2\text{H}_5)_2\text{SnClL}^c$	71	112–114	38.87 39.11	4.55 4.51	22.62 22.80	
7	$(\text{C}_2\text{H}_5)_2\text{SnBrL}$	63	102–104	35.42 35.87	3.94 4.14	20.46 20.91	1.4
8	$(\text{C}_4\text{H}_9)_2\text{SnClL}$	72	110–112	43.57 43.88	5.60 5.52	20.08 20.47	
9	$(\text{C}_6\text{H}_5)_2\text{SnClL}$	75	221–223	48.95 49.07	3.68 3.77	19.05 19.07	4.4
10	SnCl_3L^c	87	> 300 ^b	28.60 28.59	2.44 2.40	21.92 22.23	
11	SnBr_3L^c	78	> 300 ^b	22.46 22.61	1.95 1.90	17.30 17.58	2.0

^a Acetone solutions at room temperature and the molar concentration 1×10^{-3} ; in dichloromethane conductivity is always less than $1.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. ^b It chars without melting. ^c Monomer according to molecular weight determination by osmometry in dichloromethane.

The ^1H (Table 3), ^{13}C and ^{119}Sn (Table 4) NMR spectra were recorded for all the derivatives, and data for parent ligand and the zinc derivative $\text{Zn}(\text{BPz}_4)_2$ are included for comparison. The choice of solvent was dictated mainly by solubility, the order of preference being CDCl_3 , CD_2Cl_2 and $(\text{CD}_3)_2\text{CO}$. In any of these solvents the spectra were consistent with the proposed structures.

In the proton or ^{13}C spectra, the four pyrazole ring protons (or carbons) are equivalent in the potassium salt, in which the presence of a $\text{B}(\text{Pz})_4^-$ anion is likely, and in the zinc derivative, owing to fluxionality, but, they are not equivalent in our derivatives 1–11. In all of these compounds except for 3 and 9 two sets of signals are found: the more intense one is due to the three bridging $\text{Pz-N, N}'$ rings, and the other to the single B-Pz-N ring. As a consequence, fluxionality around the boron coordination center is ruled out. Additional evidence for this comes from inspection of some of the ^1H -NMR spectra: in the case of 10 or 11, $\text{X}_3\text{Sn}(\mu\text{-Pz-N, N}')_3\text{B}(\text{Pz-N})$ where $\text{X} = \text{Cl}$ or Br , 3J and $^4J(\text{Sn-H})$ couplings are observed for the three equivalent bridging groups, and so the presence of the remaining, monodentate, Pz-N is readily confirmed, not only in 10 and 11, but also in 1, 2, 3, or 9 through the 4-CH signal found at 6.68–6.72 ppm for all these compounds, in which the Sn must thus be six-coordinate.

Table 2
 IR data

Compound	Pz-C-H	1500-1600	< 500	Other	
K(BPz ₄)	3150 w	1505 s	335 w		
	3140 w		320 w		
Zn(BPz ₄) ₂	3150 vw	1500 m	380 w		
	3140 vw				
1	3150 w	1505 m	385 m	540 w	Sn-C
	3140 w		360 w	295 vs	Sn-Cl
	3120 w, sh		345 w		
2	3150 w, sh	1510 m	380 m	560 w	Sn-C
	3140 w		360 w, sh	540 w	
			340 w	295 vs	Sn-Cl
3	3145 w, sh	1505 w	460 w	550 w, br	Sn-C
	3130 w		380 m	310 s	Sn-Cl
4	3145 w, sh	1505 m	370 m	580 w	Sn-C
	3130 w		350 vw	280 m	Sn-Cl
	3105 w, sh		340 w		
5	3140 w, sh	1505 m	370 w	580 vw	Sn-C
	3120 w				
6	3115 w	1505 m	375 m	540 w	Sn-C
	3110 w, sh		360 w	320 w	Sn-Cl
7	3140 w	1510 s	380 m	540 w	Sn-C
	3120 w, sh		360 vw		
			340 vw		
8	3120 w, sh	1510 m	375 w	550 w	Sn-C
	3105 m			330 vw	Sn-Cl
9	3150 vw	1505 m	370 s	280 w	Sn-Cl
	3120 w		355 w		
			340 w		
10	3150 w, sh	1510 m	380 w	550 w, br	Sn-C
	3140 w		360 vw	320 vs, br	Sn-Cl
	3120 w		340 s		
	3110 w				
11	3150 w	1510 m	380 w	540 w, br	Sn-C
	3140 w				
	3110 w				

The remaining compounds, 3 and 9, give three sets of pyrazole signals in a 1 : 1 : 2 ratio, because the three bridging Pz-*N,N'* rings are inequivalent, as shown in Fig. 1. Furthermore, fluxionality around the tin atom is also ruled out. The observed ¹J(Sn-C) or ²J(Sn-H) coupling constants (which can be used as an indicator of the hybridization at Sn in the bond(s) affected [4]) show the same trend as that found for trispyrazolylborato derivatives [2], the highest values being those for the monoalkyltin derivatives.

Table 3

¹H NMR data

No.	Compound	Solvent	4-H (triplets) ^a δ ^b	3- or 5-H (doublets) ^a δ	R-Sn and ³ J(H-H) or ² J(Sn-H) ^a (starred)
	KL	(CD ₃) ₂ CO	6.10 (2.4) [4]	7.19 (2.4) [4] 7.50 (2.3) [4]	
	ZnL ₂	CD ₂ Cl ₂	6.28 (2.3) [8]	7.38 (2.2) [8] 7.79 (2.2) [8]	
1	MeSnCl ₂ L	CD ₂ Cl ₂	6.38 br [3] 6.69 (1.8) [1]	7.35 br [1] 7.98 (2.3) [6] 8.00 (2.5) 8.05 br 8.30 br [1]	Me[3] 1.36 s (118.1)* (112.8)*
2	BuSnCl ₂ L	CD ₂ Cl ₂	6.35 br [4] 6.68 br	7.37 br [1] 7.98 (1.8) [6] 8.01 (1.9) 8.30 br [1]	Bu [9] 0.95 t (7.5) (118.0)* 1.50-1.38 m 1.77-1.94 m
3	PhSnCl ₂ L	CDCl ₃	6.30 (2.0) [3] 6.36 (2.0) 6.70 (2.1) [1]	7.55 (2.0) [8] 7.58 (2.0) 7.68 (2.0) 7.95 (2.0) 8.10 (2.0) 8.45 (2.1)	Ph[5] 7.34 m 7.48 m
4	Me ₂ SnCIL	CDCl ₃	6.36 (2.0) [4] 6.39 (2.0)	7.29 (2.0) [3] 7.61 (2.0) [2] 7.97 (2.0) [3]	Me[6] 0.88 s (81.4)*
5	Me ₂ SnBrL	CDCl ₃	6.38 (1.8) [4] 6.42 (1.8)	7.31 (1.8) [2] 7.75 (1.8) [4] 7.98 (1.8) [2]	Me[6] 1.28 s(85.0)*
6	Et ₂ SnCIL	CD ₂ Cl ₂	6.32 (2.0) [4] 6.40 (2.0)	7.20 (2.0) [8] 7.54 (1.9) 7.98 (1.9)	Et[10] 1.18 t (8.0) 1.40 q (75.0)*
7	Et ₂ SnBrL	CD ₂ Cl ₂	6.36 (1.8) [4] 6.40 br	7.26 br [8] 7.60 (1.8) 8.00 br	Et[10] 1.18 t (7.80) 1.42 q (78.1)*
8	Bu ₂ SnCIL	CD ₂ Cl ₂	6.40 (2.1) [4] 6.30 (2.1)	7.11 (2.1) [4] 7.96 br [4] 8.42 br	Bu[18] 0.88 t (7.9) 1.20-1.40 m 1.50-1.60 m
9	Ph ₂ SnCIL	CDCl ₃	6.33 (2.2) [4] 6.38 (2.2) 6.72 (2.2)	7.57 (2.3) [4] 7.68 (2.3) 7.72 (2.3) 7.86 br [4] 7.98 (2.2) 8.15 (2.2) 8.48 (2.2)	Ph[10] 7.26-7.31 m 7.45-7.50 m 7.52-7.56 m

Table 3 (continued)

No.	Compound	Solvent	4-H (triplets) ^a δ^b	3- or 5-H (doublets) ^a δ	R-Sn and ³ J(H-H) or ² J(Sn-H) ^a (starred)
10	SnCl ₃ L	CD ₂ Cl ₂	6.44 (2.4) [3] ^c 6.72 (2.4) [1]	7.88 (2.5) [3] 8.01 (2.6) [2] 8.24 (2.4) [3] ^d	³ J(Sn-H) 11.3 ^d ⁴ J(Sn-H) 9.2 ^c
11	SnBr ₃ L	CD ₂ Cl ₂	6.43 (2.4) [3] ^c 6.72 (2.2) [1]	7.85 (2.4) [3] 8.00 (2.2) [2] 8.30 (2.4) [3] ^d	³ J(Sn-H) 13.4 ^d ⁴ J(Sn-H) 8.4 ^c

^a Except when otherwise specified. ³J(H-H) and J(Sn-H) in hertz; in the latter case either J(¹¹⁹Sn-H) and J(¹¹⁷Sn-H) or J(^{117,119}Sn-H) are reported. ^b In ppm from internal TMS. ^c The coupling constant reported in the last column was measured on this signal. ^d Idem.

Table 4

¹³C and ¹¹⁹Sn NMR data

No.	Compound	Solvent	C-3 δ^a	C-4 δ	C-5 δ	R-Sn and J(Sn-C)	¹¹⁹ Sn - δ
	KL	(CD ₃) ₂ CO	140.5	104.1	135.2		
	ZnL ₂	CD ₂ Cl ₂	141.0	105.2	135.1		
1	MeSnCl ₂ L	CD ₂ Cl ₂	143.1 141.0 ^b	108.3 ^b 106.4	136.5 ^b 136.2	Me: 20.5	473.6
2	BuSnCl ₂ L	CD ₂ Cl ₂	143.0 ^b 141.1	108.2 ^b 106.1	136.3 136.1 ^b	Bu: 13.8 26.1 28.4 39.4 ¹ J(Sn-C) 1129, 1068	477.8
3	PhSnCl ₂ L	CDCl ₃	142.8 142.6 141.9 ^b	108.1 105.9 ^b 105.8	136.3 ^b 135.6 135.3	Ph: 133.7 129.6 128.4 135.4 129.3	519.9
4	Me ₂ SnClL	CDCl ₃	141.8	106.4 ^b 105.2	136.1 ^b 133.8	Me: 13.0	322.6
5	Me ₂ SnBrL	CDCl ₃	141.8	106.3 ^b 105.7	136.1 134.0 ^b	Me: 17.0	362.5
6	Et ₂ SnClL	CD ₂ Cl ₂	142.4	106.4 ^b 105.1	136.6 ^b 133.8	Et: 10.3 22.4 ¹ J(Sn-C) 634, 591	313.7
7	Et ₂ SnBrL	CD ₂ Cl ₂	142.5	106.3 ^b 105.2	136.6 134.0 ^b	Et: 10.7 24.7 ¹ J(Sn-C) 650, 601	329.1
8	Bu ₂ SnClL	CD ₂ Cl ₂	142.4	106.5 ^b 105.2	136.8 ^b 133.9	Bu: 13.7 26.7 27.7 30.0	329.8
9	Ph ₂ SnClL	CDCl ₃	142.3 142.1 ^b 142.0	108.1 105.9 105.8 ^b	136.2 ^b 135.5 135.3	Ph: 135.0 128.0 133.7 128.6	444.9
10	SnCl ₃ L	CD ₂ Cl ₂	143.4 142.1 ^b	108.7 106.7 ^b	137.1 ^b 136.0		618.2
11	SnBr ₃ L	CD ₂ Cl ₂	143.3 141.8 ^b	108.6 106.2 ^b	136.9 ^b 136.0		574.3

^a In ppm from internal TMS. ^b This signal is the more intense of the two or the most intense of the three in the column.

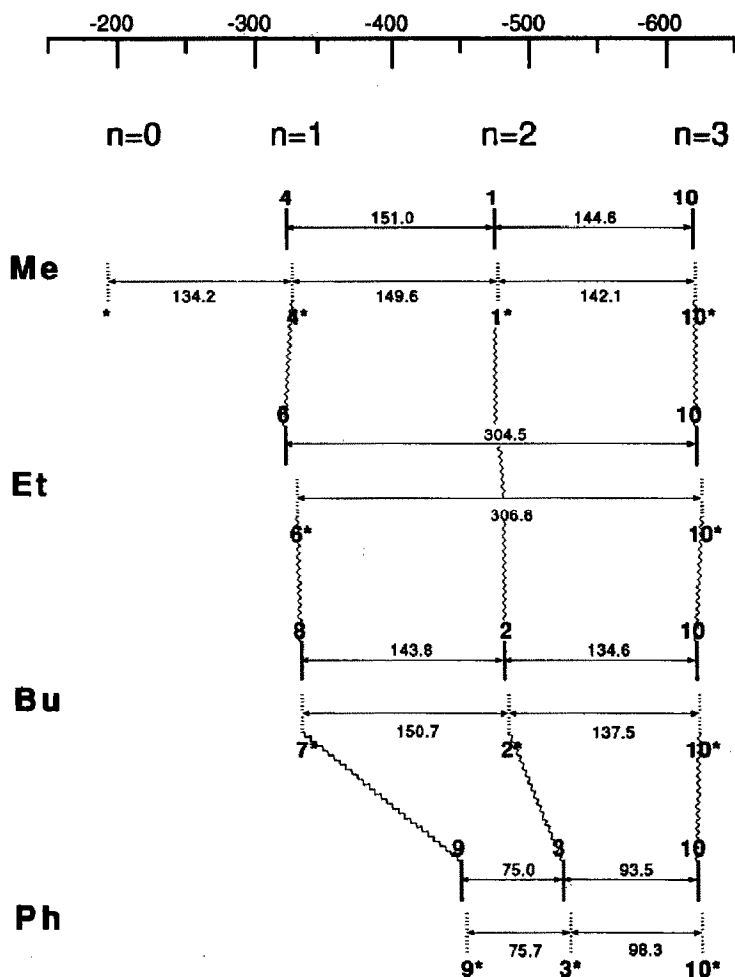


Fig. 3. Effect of substitution on the ^{119}Sn chemical shifts of $(\text{Pz})\text{B}(\text{Pz})_3\text{SnR}_{3-n}\text{Cl}_n$ (full line) and $\text{HB}(\text{Pz})_3\text{SnR}_{3-n}\text{Cl}_n$ (broken line). Data from this paper, from ref. 2 (number with asterisk) or ref. 9 (asterisk).

In the ^{119}Sn spectra (Table 4) only a sharp singlet is observed in each case; since the compounds are not fluxional, only one isomer is present even when more are conceivable. As shown in Fig. 3, the chemical shifts of the $\text{B}(\text{Pz})_4$ derivatives are quite similar to those of the $\text{HB}(\text{Pz})_3$ derivatives reported previously [2], and again they are roughly additive. Given the very high sensitivity of ^{119}Sn NMR spectroscopy [8], the environment around tin must be the same in all the reported compounds belonging to both of the series $\text{R}_{3-n}\text{SnCl}_n\text{L}$, where L is tris- or tetrakispyrazolylborates. In addition, the roughly constant change in the chemical shift upon substitution of halide by an alkyl (134–153 ppm) or, to a lesser degree, by a phenyl group (75–98 ppm), suggests that the coordination number around the central metal atom is always six, as already established independently for compounds 1, 2, 3, 10 and 11. Crystal structure determinations have shown [5,6] that the octahedron around tin(IV) is severely distorted, partly because of the inequivalence of the Sn–N bonds, so that in many cases (e.g. [6]) description of the geometry as skewed or trapezoidal bipyramidal would probably be more appropriate.

Evidence for distortion can be found from the proton NMR spectra of our compounds **4** and **5**, to which Lockhart's equations [4b] can be applied, although the data on which they are based do not include tridentate ligands. Use of the 2J values reported in Table 3 gives a calculated C–Sn–C angle ϑ of 133 and 137° for **4** and **5**, respectively, according to Lockhart's equations 2 and 3, respectively [4b]. Such values are in agreement with a severely distorted octahedron, but imply that an alternative coordination is also possible, namely a trigonal bipyramid, such as is found in $\text{Me}_3\text{Sn}(\text{Pz})_2\text{BH}_2$ [9]. In such a case the $(\text{Pz})_4\text{B}$ ligand would be only bidentate, and, because of its "bite", would occupy one axial and one equatorial site, so that the methyl groups would fill the remaining two equatorial sites with an expected value of ϑ of 120°, not too different from those calculated above. Such a hypothesis cannot be ruled out for **4** and **5** (or **6–9**) by examining the relative integrals (either 3:1 or 2:2) of the signals from the protons belonging to the pyrazole ligands because these signals are too close one to another. However, fortunately in the ^{13}C NMR spectra in all cases the integrals of the two sets of pyrazole ligands are clearly very different, and the difference is the same as that observed in cases such as **10** or **11**, in which integration of the proton NMR spectrum proves that three (and not two) of the four pyrazoles are equivalent.

Experimental

Concentration was always carried out under reduced pressure (water aspirator). Products were dried under vacuum to constant weight (20°C, ca. 0.1 torr). Carbon, hydrogen, and nitrogen analyses were carried out in our Department or by Mr A. Canu at the University of Sassari. Molecular weight determinations were performed at Pascher's Mikroanalytisches Laboratorium, Remagen, F.R.G.. 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. The ^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 determined with a IA 8100 Electrothermal Instrument.

PzB(μ -*Pz*)₃*SnClMe*₂, **1**

An acetone solution (20 ml) of potassium tetrakis(1-pyrazolyl)borate (640 mg, 2 mmol) was added to a stirred acetone solution (20 ml) of CH_3SnCl_3 (480 mg, 2 mmol). The solution was filtered and then evaporated to dryness. The oily residue became solid when stirred with diethyl ether, and was then washed with water (25 ml) dried at 100°C, and shown to be compound **1**. Compound **3** was obtained similarly.

PzB(μ -*Pz*)₃*SnBuCl*₂, **2**

Butyltrichlorotin(IV) (2 mmol, 0.35 ml, 590 mg) was added to an acetone solution (30 ml) of potassium tetrakis(1-pyrazolyl)borate (2 mmol, 640 mg) at room temperature. After 36 h the solution was filtered, the filtrate was evaporated to dryness, and the residue was extracted with dichloromethane. Concentration of the extract gave compound **2**. Compound **10** was obtained similarly from anhydrous tin(IV) chlo-

ride; in the case the residue was initially oily, but solidified when stirred with petroleum ether.

PzB(μ-Pz)₃SnMe₂Cl, 4

A solution of dimethyldichlorotin(IV) (440 mg, 2 mmol) and potassium tetrakis (1-pyrazolyl)borate (640 mg, 2 mmol) in acetone (60 ml) was stirred at room temperature. The solution was filtered and evaporated, and the residue extracted with dichloromethane. Compound 4 separated upon concentration of the extract. Compound 5, 8, 9, 11, 6 and 7 were obtained similarly; in the first two cases the reaction was carried out at 0°C, and the residue was initially oily but solidified when stirred with diethyl ether.

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