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Organometallic Tin Complexes Derived from 2-Guanidinobenzimidazole

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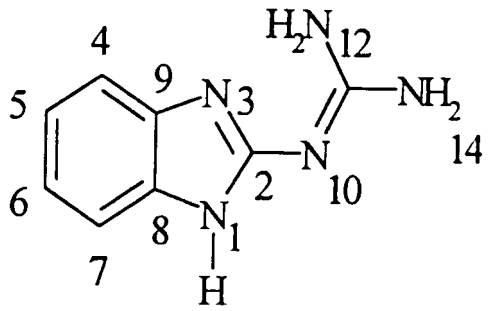
ABSTRACT: *Coordination compounds derived from 2-guanidinobenzimidazole* **1** *and* R_2SnCl_2 (**2** *R = Me,* **3** *R = Bu,* **4** *R = Ph),* R_3SnCl (**5** *R = Bu,* **6** *R = Ph), and* $SnCl_4$ **7** *were prepared and their structures investigated by* ^1H, ^{13}C, ^{119}Sn, ^{15}N *NMR, mass spectrometry (FAB or EI), infrared, and elemental analysis. The NMR data suggest pentacoordinated (***5** *and* **6***) or hexacoordinated tin atoms* **2–4** *and* **7**. *In all cases, 2-guanidinobenzimidazole acts as a bidentate ligand. In the solid state,* **2–4** *and* **7** *are associated by bridging chlorine atoms in polymeric chains.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9: 637–641, 1998

INTRODUCTION

Owing to the interest in the biological activity of 2-guanidinobenzimidazole [1,2] and antitumor or biocide activity of many organotin complexes [3–6], we decided to prepare organotin derivatives of 2-guanidinobenzimidazole **1**.



Several coordination compounds derived from organotin chlorides and imidazole [7–11], benzimidazole [12], benzothiazole [13,14], pyrazole [15,16], or bipyridine [17] have been reported. The molecular structures of some tin imidazole derivatives have been determined by X-ray diffraction studies [9,10,13–15,17]. Their chemistry is interesting because the tin atom easily becomes penta- [9,10,13,14] or hexacoordinated [11,12,15–17] by complexation with solvents or Lewis bases and also because they have a fluxional stereochemical behavior [6,12]. It is known that organotin chlorides have a strong tendency to associate in the solid state or in solution through one or two halogen bridges between two tin atoms to give a polymeric array [6–9].

2-Guanidinobenzimidazole (**1**) is a polyfunctional planar molecule with a delocalized π system. It contains five nitrogen atoms that may act as basic centers and five labile N–H groups. The basic sites

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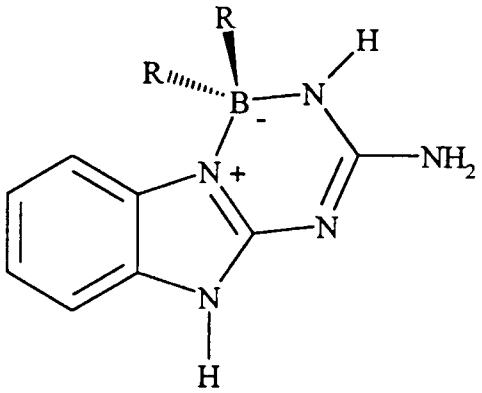
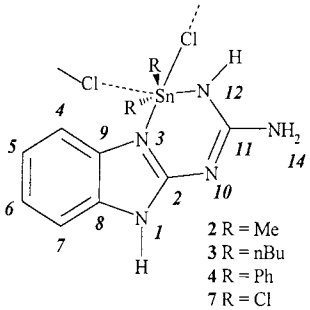
of **1** have been located using Lewis acids [18] or metallic salts [19]. Compound **1** acts as a mono- or bidentate ligand to form strong complexes [18,19]. With boron compounds, **1** gives heterocycles by coordination through the imidazolic nitrogen and substitution of one proton of the guanidinic NH_2 group [20].

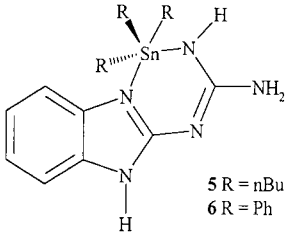


The tautomeric equilibrium of the imidazole group in **1** makes CH-4 and CH-7 and CH-5 and CH-6 equivalent in the ^{1}H- and ^{13}C-NMR spectra at room temperature [18] (Table 1). By cooling (at -60°C, in DMF solution) or by complexation, the tautomeric exchange becomes slow, and all the aromatic nuclei appear at different frequencies. Therefore, coordination to the pyridine-type nitrogen atom of the imidazole can be detected in the ^{13}C spectra by the differentiation of the aromatic carbon atoms.

Our aim was to investigate the coordinating behavior of **1** with organotin compounds and to prepare complexes with R_2SnCl_2 (**2–4**), R_3SnCl (**5, 6**), and $SnCl_4$ (**7**).



2 R = Me
3 R = nBu
4 R = Ph
7 R = Cl



5 R = nBu
6 R = Ph

Complexes **2–6** have been synthesized by equimolar reactions between **1** and organotin chloride reagents in the presence of Na_2CO_3, dry THF, and methanol and under a nitrogen atmosphere. Compound **7** was obtained by reaction of two equivalents of **1** with tin tetrachloride. The structures of the products were investigated by ^{119}Sn, ^{13}C, and ^{1}H NMR and by mass spectrometry. Unfortunately, we were unable to obtain suitable crystals for X-ray structure determinations of these adducts. The structures of the compounds in solution were mainly assigned from the ^{119}Sn-NMR spectra [9–11,16,17,21–23] because the tin coordination has a small effect on the chemical shifts of the coordinating heterocycles [9,10,24].

In the ^{1}H-NMR spectra, separation of the signals of NH-12 and NH-14 and the coupling of the tin atom to the NH-12 proton in compounds **2–4** and **7** indicate the bonding of NH-12 to the tin atom (Table 1). In the ^{1}H-NMR spectra, the coupling constant $^2J(^1H–^{119}Sn)$ of the tin organyl group could only be determined for compound **2** [25,26]. Separations of the signals of C-4 and C-7 for **2–4** and **7** show the coordination of the pyridine nitrogen atom of the imidazole. For these compounds, the ^{1}H-NMR data show that the coordination of the ligand is bidentate. In the ^{15}N-NMR spectra for compounds **2–4**, the N-12 and N-14 have different chemical shifts indicating the tin coordination to N-12 (Table 1).

^{13}C-NMR data clearly show the coordination of the pyridine nitrogen atom of the benzimidazole, because the spectra at room temperature (Table 2) present a clear separation of C-4 and C-7, and C-8 and C-9, respectively. Comparison with the chemical shifts of the free guanidine observed at -60°C indicates that coordination produces only a small shift at the carbon resonances, compound **5** having the less perturbed spectrum. The small effect of the tin coordination on the ^{13}C chemical shift of the ligand has been reported before [9]. For organyl groups directly bonded to the tin atom, the coordination of the 2-guanidinobenzimidazole also produces discrete effects. It is interesting to note that the corresponding tin chlorides in DMSO present stronger effects on the chemical shifts of the carbon atoms directly bonded to the tin atoms [27].

The strongest evidence of the complex formation was obtained from the ^{119}Sn chemical shifts that depend on the number and nature of the tin substituents. Comparison of the chemical shifts of the dimethyl, dibutyl, and diphenyl tin chlorides in a noncoordinating solvent such as toluene or $CDCl_3$ with the chemical shift of the complex shows that the signals are shifted around 300 ppm to lower frequencies (Table 3). The ligand coordination effect is less pronounced than that produced by DMSO coordination. The fact that compounds **3** and **4** have the same chemical shift in $CDCl_3$ and in DMSO shows that the DMSO is not coordinated to the tin atoms in this series of complexes. For tributyl and triphenyl tin chloride, the coordination with **1** shifts the signal 150 and 85 ppm to lower frequencies. The shifts correspond to a higher coordination number at the tin atom. The values of the found coupling

TABLE 1 ^{1}H and ^{15}N Chemical Shifts of the Ligand for Compounds **1–7** (*J* in Hz)

	Solvent	*H1*	*H12* ($^{2}J^{1}H^{119}Sn$)	*H14*	*H4, H7*	*H5, H6*	*N12 N14*
1 (25°C)	DMSO	11.12	6.89	6.89	7.20	6.92	−301.4
2	DMSO	[a]	5.38 (27)	6.53	7.15 7.25	7.02	−291.1 −287.5
3	$CDCl_3$	[a]	5.66	5.63	7.16 7.21	7.32	
3	DMSO	11.50	5.26 (28)	6.52	7.14 7.21	7.01	−290.9 −287.0
4	DMSO	11.78	5.73 (28)	6.74	6.22 7.16	6.65 6.92	−290.8 −287.5
5	DMSO	11.00	[a]	6.91	6.89	6.89	
6	DMSO	11.00	[a]	6.91	7.76	6.92	
7	DMSO	12.00	6.31 (31)	6.61	6.90	7.10	7.36

[a]Not observed.

TABLE 2 ^{13}C-NMR Chemical Shifts for **1–7** (DMSO-d6)

	C-4	*C-7*	*C-5*	*C-6*	*C-8*	*C-9*	*C-11*	*C-2*
1, (25°C)	111.7	111.7	119.4	119.4	135.7	135.7	158.9	158.9
1(−60°C), DMF	115.4	109.4	119.9	119.9	133.0	143.1	160.0	159.5
2	112.5	110.2	121.6	121.7	131.7	137.2	162.7	156.4
3	111.9	109.7	121.1	121.2	131.2	137.1	162.3	156.4
3 $CDCl_3$	113.9	111.6	123.2	123.5	132.2	138.2	163.2	157.2
4	113.6	110.2	121.2	121.7	131.7	137.2	162.9	157.3
4 $CDCl_3$	116.1	111.4	123.6	123.6	131.7	138.2	163.2	158.2
5	115.0	109.5	119.8	119.8	132.5	143.0	159.7	159.2
6	115.4	108.2	120.0	120.0	136.9	142.7	159.6	159.2
7	114.1	110.2	121.3	122.0	131.2	136.6	162.6	157.4

TABLE 3 ^{119}Sn Data and ^{13}C Data for Tin Organyl Substituents **2–6**

			$\delta\ ^{13}C$			
	Solvent	$\delta\ ^{119}Sn$	$^{1}J(^{13}C–^{119}Sn)$	$^{2}J(^{13}C–^{119}Sn)$	$^{3}J(^{13}C–^{119}Sn)$	$^{4}J(^{13}C^{119}Sn)$
Me_2SnCl_2	toluene	+138	4.8 (452)			
Me_2SnCl_2	CD Cl_3[a]		6.7 (481)			
Me_2SnCl_2	DMSO[a]	−246	22.7(1014)			
2	DMSO	−206	7.5 (672, 703)			
Bu_2SnCl_2	$CDCl_3$	+126	26.9(421)	26.9 (43)	26.2(84)	13.4
Bu_2SnCl_2	DMSO	−208	38.1(863, 825)	28.1 (45)	26.0 (153, 147)	14.2
3	$CDCl_3$[a]	−205	27.1 (605)	28.6 (38)	14.8 (103)	
3	DMSO	−215	25.0 (646)	26.9 (40)	25.4 (92)	13.3
Ph_2SnCl_2	$CDCl_3$[a]	−26	136.8 (787)	134.9 (63)	129.7 (87)	131.8 (18)
Ph_2SnCl_2	DMSO	−406	155.0 (1549)	134.7 (71)	127.3 (125)	127.7 (23)
4	$CDCl_3$	−313	142.6	137.1 (58)	129.9 (86)	131.7
4	DMSO	−318	143.2	135.8 (58)	129.0 (84)	130.1
Bu_3SnCl	toluene	+144	16.9(325, 341)	27.8	26.9 (63)	13.4
Bu_3SnCl	DMSO	+2.0	21.5 (458)	28.2	26.7 (74)	14.1
5	DMSO	−6.0	20.9 (465)	28.3 (27)	27.0 (73)	14.1
Ph_3SnCl#	$CDCl_3$	−45	137.1 (614)	136.0 (50)	129.0 (64)	130.4
Ph_3SnCl#	DMSO	−227	143.8 (811)	136.0 (48)	128.5 (71)	129.1
6	DMSO	−125	142.7	136.6 (46)	128.9 (60)	129.6
$SnCl_4$	DMSO	−624				
7	DMSO	−576				

[a]Ref. 23.

constants $^1J(^{13}C–^{119}Sn)$ confirm the formation of the complexes. They depend significantly on the nature of the organyl substituent and on the coordination number and geometry of the tin atom. The observed values could be attributed to penta- or hexacoordinated compounds [25].

For compounds **5** and **6,** derived from tributyltin and triaryltin chloride, the elemental analyses and the NMR data allowed us to propose pentacoordinated tin heterocycles formed by substitution of the chlorine by N-12, loss of HCl, and coordination to the imidazole group. The structures are in accord with other derivatives of triphenyl [28] and trialkyl tin [29,30].

Compounds **2–4** and **7** presented complex mass spectral (FAB) data that indicate the formation of species associated by chlorine bridges; mass peaks corresponding to polymeric compounds were observed. For compounds **2–7,** the elemental analyses give evidence that one HCl molecule was lost. For compound **2,** the elemental analyses indicated that there is one benzimidazole molecule for two tin atoms.

EXPERIMENTAL

The 2-guanidinobenzimidazole and all tin (IV) chlorides were commercial reagents. All reactions were handled under a nitrogen atmosphere using dried glassware and solvents. Melting points were obtained on a Gallenkamp apparatus and are uncorrected. IR spectra were recorded on Nicolet FT-IR 740 and FT-IR-1600 Perkin Elmer spectrophotometers using KBr pellets in the 4000–400 cm^{-1} range. Mass spectra in the EI mode were recorded at 20 eV on a Hewlett-Packard HP 5989 spectrometer. Fast atom bombardment mass spectrometry (FAB mass) was performed on a Jeol SX102A instrument of inverted geometry, in a matrix of 3-nitrobenzyl alcohol and in the 0–2200 m/z range. Elemental analyses were performed by Oneida Research Services, Whitesboro, New York. NMR spectra were obtained on a Jeol 270 spectrometer, ^1H (270.05 MHz), ^{13}C (67.80 MHz), ^{15}N (27.25 MHz), ^{119}Sn (100.73 MHz), and on a Jeol 400 spectrometer, ^1H (399.78 MHz), ^{13}C (100.53 MHz), ^{119}Sn (149.05 MHz).

Dimethyl-(2-guanidinobenzimidazole-N,N′)-stannane **2***: General Procedure for* **3–6**

To a solution of 500 mg (2.8 mmol) of 2-guanidinobenzimidazole **1** in 30 mL of dry THF, in the presence of Na_2CO_3, was added an equimolar quantity (620 mg) of Me_2SnCl_2 reagent in 10 mL of THF/methanol. The reaction mixture was handled under a nitrogen atmosphere. After 5 hours of reflux, the solution was filtered and solvent was evaporated in vacuum. A white powder was isolated, mp 185–190°C, IR (KBr), cm^{-1}: 3437, 3186 (N-H), 1684 (C=N), 1624 (N-H), 1599 (NH_2), 1537 (NH), 1193, 765 (Sn-C). MS (EI, 20 eV): M^+, 359; $[M–Me]^+$, 344, (12) 158 (100). MS (FAB): complex spectra with peaks up to mass 969. Anal. calcd for $C_{12}H_{19}N_5Sn_2Cl_2\ H_2O$: C, 25.70; H, 3.99; N, 12.49. Found: C, 25.68; H, 3.89; N, 12.47.

Dibutyl-(2-guanidinobenzimidazole-N,N′)-stannane **3**

Beige powder, mp 150–160°C, IR (KBr), cm^{-1}: 3439, 3196 (N–H), 1626 (C=N), 1600 (NH_2), 1534 (N–H), 1078, 765 (Sn–C). MS (EI, 20 eV): $[M–Bu]^+$, 386 (3); 158 (100). MS (FAB): complex spectra with peaks up to mass 1812. Anal. calcd for $C_{16}H_{26}N_5SnCl\ H_2O$: C, 41.69; H, 6.08; N, 15.20. Found: C, 41.52; H, 6.17; N, 13.62.

Diphenyl-(2-guanidinobenzimidazole-N,N′)-stannane **4**

Beige powder, mp 180–190°C, IR (KBr), cm^{-1}: 3377 (N–H), 1690 (C=N), 1617 (N–H), 1599 (NH_2), 1534 (N–H) 1072, 731, 695 (Sn–C). MS (EI, 20 eV): $[M–Ph]^+$, 406 (1); 158 (30). MS (FAB): complex spectra with peaks up to mass 2110. Anal. calcd for $C_{20}H_{18}N_5SnCl$: C, 49.68; H, 3.96; N, 14.48. Found: C, 49.62; H, 4.48; N, 14.75.

Tributyl-(2-guanidinobenzimidazole-N,N′)-stannane **5**

Beige sticky powder, mp 85–90. Anal. calcd for $C_{20}H_{35}N_5Sn$: C, 51.74; H, 7.60; N, 15.08. Found: C, 51.19; H, 7.23; N, 15.69.

Triphenyl-(2-guanidinobenzimidazole-N,N′)-stannane **6**

Colorless powder, mp 135–140°C, IR (KBr), cm^{-1}: 3423, 3190 (N–H), 1622 (N–H), 1600 ($N–H_2$), 1536 (NH_2), 1076, 730, 695 (Sn–C). MS (FAB): complex spectra with peaks up to mass 1622. Anal. calcd for $C_{26}H_{24}N_5SnCl$: C, 55.76; H, 4.11; N, 12.51. Found: C, 55.07; H, 4.70; N, 12.44.

Trichloride-(2-guanidinobenzimidazole-N,N′)-stannane **7**

A 600 mg (3.4 mmol) amount of (**1**) was dissolved in 40 mL of dry THF/CH_3OH. This solution was reacted with 200 μL (1.7 mmol) of $SnCl_4$ and refluxed for 5

hours. The solution was filtered, and the solvent was evaporated under vacuum. A slightly beige solid was obtained. THF was detected in the ^{1}H- and ^{13}C-NMR spectra, mp 140°C, IR (KBr), cm^{-1}: 3322, 3172 (N–H), 1687 (C=N), 1626 (N–H), 1593 (NH_2), 1560 (N–H). MS (FAB): M^+, 537, 539; complex spectra with peaks up to mass 1151. Anal. calcd for $C_8H_8N_5Sn_1Cl_3 1/2(OC_4H_8H_2O)$: C, 27.06; H, 2.84; N, 15.78. Found: C, 27.57; H, 3.76; N, 15.82.

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