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Syntheses and Characterization of Pentacoordinate Organo-Tin(IV) Complexes II

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ABSTRACT

Nine substituted benzoyl hydrazonyl, three semicarbazonyl, and four thiosemicarbazonyl tridentate ligands were synthesized. They were used to coordinate with Bu_2SnCl_2 *or* $(PhCH_2)_2SnCl_2$ *to form 18 novel tin complexes that contained pentacoordinate organotin(IV) in a heterobicyclic ring. All these complexes were characterized by MS, NMR, and IR spectroscopy elemental analyses. © 1995 John Wiley & Sons, Inc.*

The Schiff bases of hydrazones are good ligands to tin(IV), and we have synthesized and characterized the complex **1** [1]. In another previous paper [2], we have also reported the synthesis of pentacoordinate organotin(IV) complexes **2** formed from salicylaldehyde Schiff bases of amino acids. The complexes may be designated as bicyclodiazastannoxides. Apart from amino acids, the Schiff bases of substituted hydrazones, semicarbazones and thiosemicarbazones also exhibit good coordinate activity for organometallic complexes.

Now we report the preparation of organotin(IV) complexes **3** and **4** in which the ligands are benzoylhydrazone, semicarbazone, and thiosemicarbazone derivatives (X = O, S; Y = Ar, NH_2, NHPh, p-$O_2NC_6H_4$, m–$O_2NC_6H_4$, p-ClC_6H_4, o-Cl–C_6H_4, p-MeC_6H_4; R = n-Bu, $C_6H_5CH_2$) and **5** (X = O, S; Y = NHPh, NH_2, p-$CH_3OC_6H_4$). We have confirmed the structures of the bicycloazastannoxides by X-ray single-crystal diffraction [1,2,7,8]. We found that the central metal Sn(IV) in each case became pentacoordinated and was located at the central point of the bicyclic complex in which each ring contains one or two N atoms as heteroatoms.

EXPERIMENTAL

Melting points were determined on a PHMK melting point stage and are uncorrected. Elemental analyses were carried out on an automatic elemental analysis apparatus CORDER M-73. ^{1}Hnmr spectra were taken on a JNMLMX 60 MHz nuclear magnetic resonance apparatus using TMS as an internal standard and $CDCl_3$ as solvent. The IR spectra were taken on a NICOLET FT-IR 50x spectrometer using a KBr disc. The MS were obtained on a VG ANALYTIC 7070E-HF using EB of 70 eV beam. The physical data are shown in Tables 3 through 6.

All reactions were carried out under moisture-free and oxygen-free conditions. The anhydrous, inert solvents (benzene, toluene and ether) were dried after reflux with sodium and used immediately. Trimethylamine was used to condense the organotindichlorides with the ligands.

Diphenyl, dibutyl, and dibenzyl substituted dichlorostannanes were prepared according to the literature [3–5], and the ligands were also prepared by known methods [6]. The physical data of the ligands, Schiff bases, semicarbazones, and thiosemicarbazones are listed in Table 1 and of the benzoyl hydrazones in Table 2.

An example of the condensation reaction: Into 20 ml of an anhydrous benzene solution of 0.75 mmol of p-nitrobenzoyl-(salicylal)hydrazone, a solution of 0.77 mmol of Bu_2SnCl_2 and 0.8 mL of Et_3N in 10 mL of benzene was added dropwise. The reaction mixture became yellow after having been stirred for 3 hours. After filtration and condensation of the solution to 2 mL, 10 mL of petroleum ether was added in order to precipitate the crude

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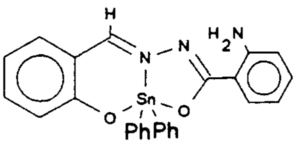

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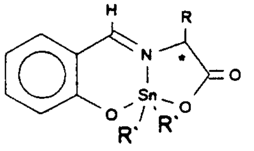

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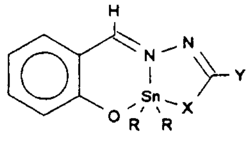

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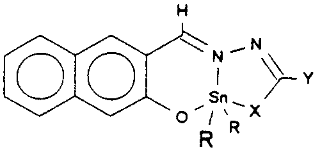

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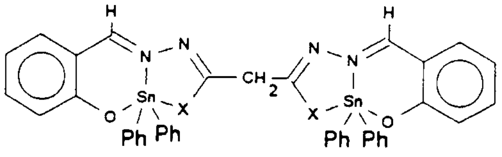

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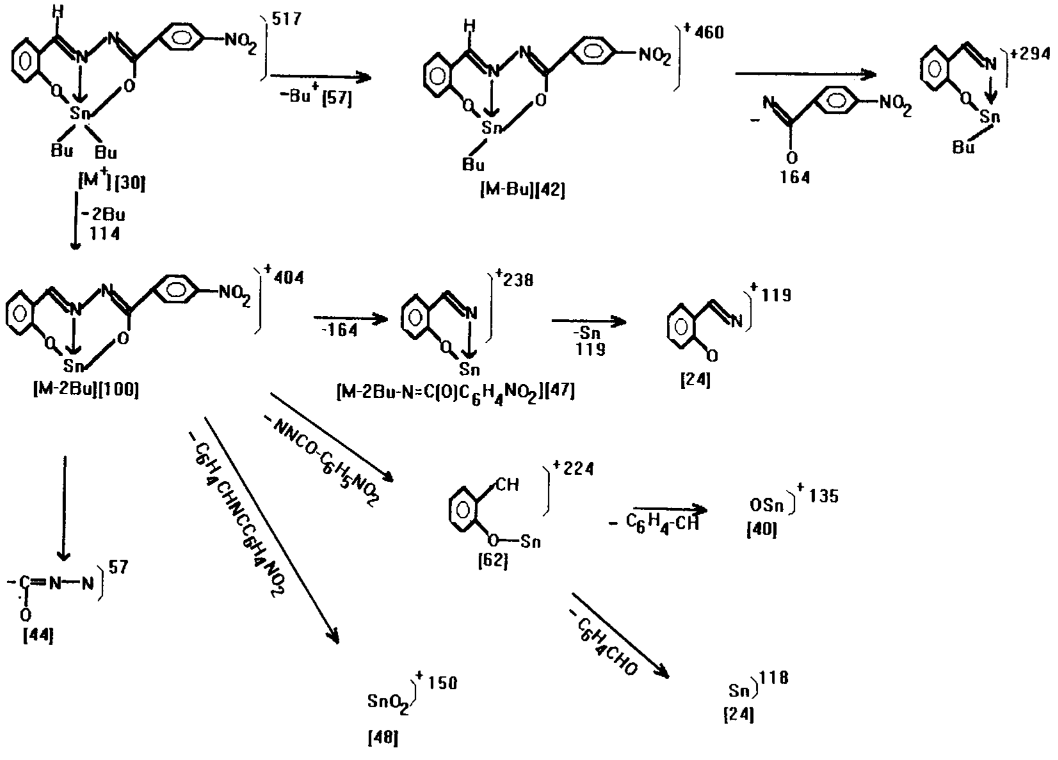


product. The solid was recrystallized from CH_2Cl_2/ligloin solution.

RESULTS AND DISCUSSIONS

The bicyclodiazastannoxides are white or brown-red solids that are stable in air and have definite melting points. When the bicyclodiazastannoxides were subjected to electron bombardment in 70 eV mass spectroscopic studies, the following typical degradation patterns were observed:

The structures of the bicyclodiazastannocides have been confirmed by X-ray crystallographic analysis [7], in one of which the double bicyclostannoxide rings are connected by a methylene bridge (**5**), and the others differ in the tin moiety, e.g., dibutyl or diphenyltin. In each case, the tin atom, surrounded by electronegative chlorine and organic ligands, exhibits a partially electron deficient state and thus becomes the target of nucleophilic attack by the Schiff bases to give the pentacoordinate complexes that involve the tin's **5–d** orbital.

In the IR spectra, the complexes show the Sn–N stretch at around 410–457 cm^{1} (Tables 3 and 4) while the chemical shifts around δ 8.44–9.4 are attributable to the proton at the position alpha to the benzene ring. The IR bands of $V_{c=o}$ and $V_{c=s}$ in the ligands appear at 1440–1672 and 1030–1040 cm^{-1}, respectively. When the ligands coordinate with tin, the C–N stretching frequencies do not change much, while the C=O and C=S stretching

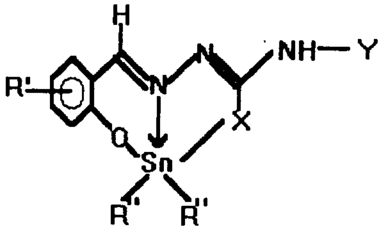
TABLE 1 Physical Data of Semicarbazones, Ar–CH=N–NH–C(X)–Y

Number	Ar	X	Y	Color	Yield (%)	MP (°C)	IR (cm^{-1}) NH_3	NH	C=X	C=N	C–O
1	o-HO–C_6H_4	O	NH_4	white	90	229–89	3492	3273, 3057	1696	1589	1269
2	o-HO–C_6H_4	S	NH_4	pale yellow	70	230	3484	3197	1030	1606	1275
3	o-HO–C_6H_4	O	NHPh	pale yellow	85	198–200		3303, 3033	1646	1606	1270
4	o-HO–C_6H_4	S	NHPh	white	68	180–1		3337, 3156	1032	1622	1270
5	2-HO-1-NaPh	O	NHPh	pale yellow	80	217		3435, 3014	1688	1598	1294
6	2-HO-1-NaPh	S	NHPh	green yellow	60	200–3		3384, 3184	1032	1622	1261
7	2-HO-1-NaPh	S	NH_2	orange	75	245–6	3451	3262, 3164	1040	1606	1278

TABLE 2 Physical Data of Benzoylhydrazones, Ar–CH=N–NH–C(X)–Y

Number	Ar	X	Y	Color	MP (°C)	Yield (%)	IR (cm^{-1}) NH	C=X	C=N
1	o-HOC_6H_4	O	C_6H_5	white	163–5	50	3271(m), 3040(w)	1671(s)	1622(s)
2	o-HOC_6H_4	O	p-$NO_2C_6H_4$	yellow	266–9	55	3214(m), 3066(m)	1655(s)	1606(s)
3	o-HOC_6H_4	O	m-$NO_2C_6H_4$	pale yellow	233	35	3230(m), 3058(m)	1659(s)	1625(s)
4	o-HOC_6H_4	O	p-ClC_6H_4	white cryst	200–2	45	3370(w), 3214(m) 3050(m)	1638(s)	1622(s)
5	o-HOC_6H_4	O	o-ClC_6H_4	pale yellow	105–8	50	3213(m), 3066(m)	1633(s)	1822(s)
6	o-HOC_6H_4	O	p-$MeOC_6H_4$	white	180–2	55	3271(w), 3156(w) 3025(w)	1639(s)	1814(s)
7	o-HOC_6H_4	O	$-CH_2-$	white	213.5–5	90	3279(m), 3066(m)	1672(s)	1614(s)
8	o-HOC_6H_4	S	p-$MeOC_6H_4$	pale yellow	194–6	70	3440(m), 3170(m)	1030(m)	1604(s)
9	2-HO-1-NaPh	S	p-$MeOC_6H_4$	yellow	156–8	75	3423(w)	1029(m)	1600(s)

TABLE 3 The Tin Complexes of the Semicarbazones



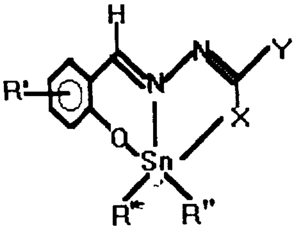
Number	R'	X	Y	FW	Color	MP (°C)	Yield (%)	Elemental Analysis C	H	N
1	H	O	H	410	pale yellow	90–92	80	46.46 (46.86)	6.11 (6.14)	10.18 (10.25)
2	H	S	H	426	yellow	40	75	44.02 (45.09)	5.45 (5.91)	9.38 (9.38)
3	H	O	Ph	488	yellow	88–90	83	54.27 (54.38)	5.98 (6.01)	8.88 (8.64)
4	H	S	Ph	502	yellow	92–94	77	52.62 (52.61)	6.01 (5.82)	8.44 (8.37)
5	3,4-benz	O	Ph	536	yellow	88–90	81	58.41 (58.23)	5.83 (5.83)	7.92 (7.94)
6	3,4-benz	S	Ph	552	yellow	oil	79	56.41 (56.54)	5.86 (5.66)	7.55 (7.61)
7	3,4-benz	S	H	476	brown red	oil	75	50.32 (50.44)	5.58 (5.71)	8.62 (8.82)
8	H	O	Ph	554	yellow	174–175	75	80.04 (60.68)	4.56 (5.44)	7.48 (7.58)

Note: R″ = Bu-*a* for numbers 1 through 7; $PhCH_2$ for number 8; for numbers 5 through 7, see **4**.

TABLE 4 The Tin Complexes of the Semicarbazones

Number	*IR* (cm^{-1})	ν_{Sn-O}	ν_{Sn-N}	1H NMR (*ppm*)
1	1597(s), 1317(m)	547(m)	416(m)	1.00–1.80(m, 18H); 4.08(s, 2H); 8.70–7.40(m, 4H); 8.34(s, 1H)
2	1605(s), 1318(w)	805(w)	420(w)	1.00–1.80(m, 18H); 5.01(s, 2H); 6.70–8.10(m, 4H); 8.54(s, 1H)
3	1605(s), 1300(m)	572(m)	424(m)	0.80–1.50(m, 18H); 8.30(s, 1H); 6.70–7.30(m, 9H); 3.42(s, 1H)
4	1597(s), 1310(s)	580(w)	416(m)	0.90–1.56(m, 18H); 6.75–7.50; (m, 10H); 8.66(s, 1H)
5	1605(s), 1310(m)	570(m)	436(m)	0.86–1.80(m, 18H); 8.26(s, 1H); 6.90–7.60(m, 11H); 9.30(s, 1H)
6	1597(s), 1310(m)	595(w)	451(w)	0.70–1.50(m, 18H); 8.15(s, 1H); 6.70–8.70(m, 11H); 9.30(s, 1H)
7	1597(s), 1310(s)	523(w)	422(m)	0.90–1.60(m, 18H); 5.01(s, 2H); 7.00–7.88(m, 8H); 9.40(s, 1H)
8	1605(s), 1300(m)	556(w)	441(m)	2.80(s, 4H); 6.80–7.30(m, 19H); 8.10(s, 1H); 3.42(s, 1H)

TABLE 5 Physical Data of the Tin Complexes of the Benzoylcarbazones



Number	*R'*	*X'*	*Y*	*R'*	*FM*	*Color*	*MP* (°C)	*Yield* (%)	*Elemental Analysis* *C*	*H*	*N*
1	H	O	C_6H_6	Bu	471	yellow	92.5–94	80	56.23 (56.08)	5.55 (5.99)	5.67 (5.95)
2	H	O	p-$NO_2C_6H_4$	Bu	516	orange	55–57	90	51.37 (51.19)	5.34 (5.27)	7.88 (8.14)
3	H	O	m-$NO_2C_6H_4$	Bu	518	orange	51–55	85	51.23 (51.19)	5.28 (5.27)	8.12 (8.14)
4	H	O	p-ClC_6H_4	Bu	508	yellow	oil	80	52.52 (52.28)	5.88 (5.38)	5.18 (5.54)
5	H	O	o-ClC_6H_4	Bu	506	pale yellow	oil	85	52.02 (52.26)	5.76 (5.38)	5.87 (5.54)
6	H	O	p-$OMeC_6H_4$	Bu	501	white	59.5–80.5	75	54.84 (55.12)	6.02 (6.03)	
7[a]	H	O	CH_2	Bu	802	yellow	92–93.5	86	49.45 (49.41)	6.01 (6.03)	6.25 (6.99)
8	H	S	p-$OMeC_6H_4$	Bu	517	orange	45–47	70	53.28 (53.40)	5.85 (5.84)	5.13 (5.41)
9	3,4-benz	S	p-$OMeC_6H_4$	Bu	567	yellow	oil	72	57.51 (57.16)	5.53 (5.68)	4.54 (4.94)
10	H	O	p-$NO_2C_6H_4$	Bz	584	brown red	155–157	80	57.45 (57.58)	3.79 (3.96)	7.12 (7.19)

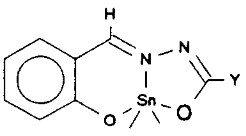
[a] $(O\text{-}C_6H_4^4CH=N-N=C-O-SnBu_2)_2CH_2$, **5**.
[b] See **4**.

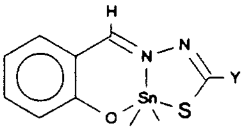
TABLE 6 Physical Data of Tin Complexes of Benzoylcarbazones (Continued)

Number	*IR* (*cm*$^{-1}$)	*Sn–O*	*Sn–N*	*NMR* (*ppm*)
1	1605(s), 1300(m)	547(w)	437(m)	0.81–1.50(m, 18H); 6.66–8.00; (m, 9H); 8.70(s, 1H)
2	1600(s), 1300(m)	555(m)	410(m)	1.01–1.80(m, 18H); 6.70–7.50; (m, 4H); 8.33(s, 4H); 8.86(s, 1H)
3	1605(s), 1300(m)	555(m)	473(m)	0.81–1.51(m, 18H); 6.70–8.30; (m, 8H); 8.9(s, 1H)
4	1805(s), 1300(w)	584(w)	485(w)	0.81–1.51(m, 18H); 6.67–8.00; (m, 8H); 8.66(s, 1H)
5	1581(s), 1300(m)	498(m)	457(m)	0.90–1.70(m, 18H); 7.00–8.00; (m, 8H); 8.66(s, 1H)
6	1605(s), 1300(m)	547(m)	482(m)	0.90–1.80(m, 18H); 3.7(s, 3H); 8.80–8.10(m, 8H); 8.20(s, 1H)
7^{a}	1605(s), 1310(w)	550(w)	457(m)	0.90–1.60(m, 36H); 3.1(s, 2H); 8.71–7.33(m, 8H); 8.66(s, 2H)
8	1605(s), 1290(w)	564(m)	457(m)	0.86–1.52(m, 18H); 3.8(s, 3H); 6.66–8.01(m, 8H); 8.80(s, 1H)
9	1605(s), 1302(m)	805(m)	425(m)	0.80–1.51(m, 18H); 3.71(s, 3H); 6.80–7.20(m, 8H); 9.61(s, 1H)
10	1605(s), 1300(m)	556(m)	441(m)	3.00(s, 4H); 7.01(s, 10H); 8.10(m, 8H); 8.50(s, 1H)

^{a}(O–C_6H_4CH=N–N=C–O–$SnBu_2)_2CH_2$.

bands in the complexes all disappear. It is likely that NH–C(O)– and NHC(S)– enol and thioenol forms coordinate with tin to form the bicyclodiazastannocides and bicyclo-stannsulfoxides:





If Y is an amino group (semicarbazone and thiosemicarbazone), the protons of the NH_2 group in complexes entry 1, 2, and 7 (Table 3) are located at high fields 4.8–5.01, and if Y is an aromatic substitute group, the proton shift is at much lower fields, 8.10–8.30.

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