Heteroatom Chemistry
Volume 8, Number 3, 1997

Redistribution Reactions of Diorganotin Dicarboxylates and Diorganotin Dihalides: A Convenient Method for the Preparation of Halo-Diorganotin Carboxylates

Saqib Ali,* Muhammad Danish, and Muhammad Mazhar

Department of Chemistry, Quaid-i-Azam University, 45320 Islamabad, Pakistan

Received 2 February 1996; revised 19 December 1996

ABSTRACT

Organotin compounds with the general formula $R_2(X)SnL$ *(where* $R = Me$, *Et, n-Bu, Ph;* $L =$ *the trans-3-(2-furanyl)-2-propenoate anion or the trans-3-(3-methylphenyl)-2-propenoate anion; and* $X = Cl$*) have been prepared by redistribution reactions between the* R_2SnL_2 *and* R_2SnX_2 *compounds. These compounds were characterized by elemental analyses and various spectroscopic techniques such as* ^1H, ^{13}C, ^{119}Sn *NMR, Mass, Mössbauer, and IR spectroscopies. On the basis of these spectroscopic data, it is suggested that these compounds adopt the cis-*$R_2(X)SnO_2$ *geometry. © 1997 John Wiley & Sons, Inc. Heteroatom Chem* **8***: 273–278, 1997.*

INTRODUCTION

Organotin halides are well-known starting materials for the synthesis of new organotin compounds [1]. Previously, we have synthesized and characterized organotin carboxylates of the general formulas R_3SnL, R_2SnL_2, and $[(R_2SnL)_2O]_2$ using either an organotin chloride or an organotin oxide as one of the starting materials [2–5]. In this article, we report the preparation of $R_2(X)SnL$ compounds by redistribution reactions of diorganotin carboxylates (R_2SnL_2) with diorganotin dihalides (R_2SnX_2). We have observed that each such a reaction provides a higher yield and a product of higher purity than the reaction of a diorgantin dihalide with a metallic salt of the donor ligand or by a direct reaction of the donor ligand with a diorganotin dihalide in a 1:1 molar ratio in the presence of a base [1]. These halo-diorganotin carboxylates may also be used for the preparation of mixed diorganotin carboxylates of the general formula R_2SnLL', where L and L′ are different carboxylate anions.

EXPERIMENTAL

Synthesis

General Procedure. A mixture of 0.01 mole of organic acid (LH) and 0.01 mole of organotin oxide was refluxed in dry toluene (150 mL) for 4–6 hours. Water formed during the reaction was continuously removed by use of a Dean-Stark apparatus. Toluene was then completely removed under reduced pressure provided by use of a membrane pump or a high vacuum pump. The residue was dissolved in dry dichloromethane, treated with activated charcoal, and the mixture was filtered. The filtrate was concentrated and kept at −10°C for a week. The crystalline or solid mass thus obtained was recrystallized from an appropriate solvent or mixed solvent. Yield 85–95%.

---

*Author to whom correspondence should be addressed.

© 1997 John Wiley & Sons, Inc.
1042-7163/97/030273-06

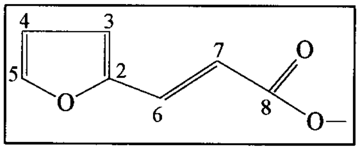
$$(R_2Sn)_2O + 2LH \rightarrow R_2SnL_2 + H_2O$$

An equimolar mixture of R_2SnL_2 (0.005 mole) and R_2SnCl_2 (0.005 mole) was refluxed in dry chloroform (100 mL) for 5–8 hours under an atmosphere of argon. The reaction mixture was then concentrated under vacuum and kept at −10°C for one to two weeks. Crystals thus formed were collected and purified by repeated crystallization from dichloromethane or a dichloromethane-hexane mixed solvent.

$$R_2SnL_2 + R_2SnCl_2 \rightarrow 2R_2Sn(Cl)L$$

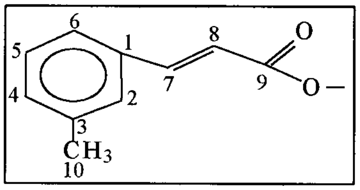
For compounds (**I**), (**II**), (**III**), and (**IV**), R = Me, Et, *n*-Bu, and Ph;

L =



For compounds (**V**) and (**VI**), R = Me and *n*-Bu;

L =



Compound (**I**) *Chlorodimethyltin*(*trans-3-*(*2-furanyl*)*-2-propenoate*). Recrystallized from dichloromethane under argon. Yield 86.5%; mp 125–126°C. Elemental analysis, calcd/found (%): $C_9H_{11}ClO_3Sn$: C, 33.49/33.45; H, 3.41/3.38.

Compound (**II**) *Chlorodiethyltin*(*trans-3-*(*2-furanyl*)*-2-propenoate*). Recrystallized from dichloromethane at −20°C under argon. Yield 95.0%, mp 61–62°C. Elemental analysis, calcd/found (%): $C_{11}H_{15}ClO_3Sn$: C, 37.66/37.68; H, 4.28/4.30.

Compound (**III**) *Chlorodibutyltin*(*trans-3-*(*2-furanyl*)*-2-propenoate*). Recrystallized from dichloromethane/hexane mixture at −20°C. Yield 95.5%, mp 48–49°C. Elemental analysis, calcd/found (%): $C_{15}H_{23}ClO_3Sn$: C, 44.28/44.23; H, 5.66/5.62.

Compound (**IV**) *Chlorodiphenyltin*(*trans-3-*(*2-furanyl*)*-2-propenoate*). Recrystallized from a chloroform/ether mixed solvent at −20°C. Yield 92.0%, mp 82–83°C. Elemental analysis, calcd/found (%): $C_{19}H_{15}ClO_3Sn$: C, 51.06/51.10; H, 3.36/3.34.

Compound (**V**) *Chlorodimethyltin*(*trans-3-*(*3-methylphenyl*)*-2-propenoate*). Recrystallized from dichloromethane under argon. Yield 90.0%, mp 124–125°C. Elemental analysis, calcd/found (%): $C_{12}H_{15}ClO_2Sn$: C, 41.62/41.61; H, 4.34/4.35.

Compound (**VI**) *Chlorodibutyltin*(*trans-3-*(*3-methylphenyl*)*-2-propenoate*). Recrystallized from dichloromethane/hexane mixed solvent at −20°C. Yield 88.0%, mp 75–76°C. Elemental analysis, calcd/found (%): $C_{18}H_{27}ClO_2Sn$: C, 50.23/50.25; H, 6.28/6.29.

Instrumentation

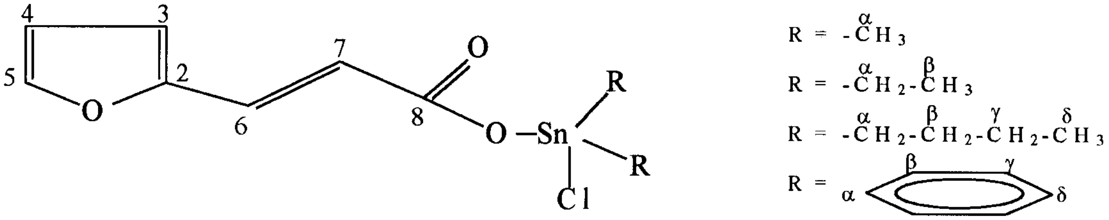
Melting points were determined in a capillary tube using an electrothermal melting point apparatus model MP-D Mitamura Riken Kogyo and are uncorrected. Infrared absorption spectra were recorded as KBr pallets on a Hitachi 270-50 spectrophotometer (Japan). Mass spectral data were measured on a MAT 8500 Finnigan spectrometer (Germany). Elemental analyses were performed at the University of Bath (UK). The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 500 spectrometer, in $CDCl_3$ solution with reference to internal Me_4Si, while ^{119}Sn NMR spectra were obtained on a Bruker 250 ARX spectrometer with Me_4Sn as an external reference. ^{119m}Sn Mössbauer spectra were obtained with a constant acceleration microprocessor-controlled spectrometer (Cryoscopic Ltd, Oxford, U.K.); the barium stannate source was used at room temperature, and samples were packed in perspex discs and cooled to −193°C. Isomeric shift data are relative to SnO_2.

RESULTS AND DISCUSSION

NMR Spectroscopy

Multinuclear NMR data are presented in Tables 1–3 and 5. Different resonances due to protons have been assigned on the basis of their intensity and multiplicity patterns. The aromatic carbon resonances were assigned by the comparison of experimental chemical shifts with those calculated by the incremental method [7]. Usually the substitution of chloride for a carboxylate group results in an increase in the magnitude of coupling constants $|^1J[^{119/117}Sn\text{–}^{13}C]|$ and $|^2J[^{119/117}Sn\text{–}^1H]|$, which is considered to be due to its high electronegativity [8]. In the present case, however, the electronegativity of both the oxygen and chloride substituents are to be considered. The cumulative effect of these two highly electronegative groups on tin increases its Lewis acidity, which facilitates chelation through the carbonyl oxygen and results in a change in the geometry from tetrahedral to trigonal bipyramidal. Thus, an increase in the

TABLE 1 ^{1}H NMR Data of Chlorodiorganotin(*trans* 3-(2-furanyl)-2-propenoates)[a–e]



	I	II	III	IV
Proton	*R = methyl*	*R = ethyl*	*R = n-butyl*	*R = phenyl*
3	6.63 (d, 3.5)	6.61 (d, 3.4)	6.60 (d, 3.5)	6.63 (d, 3.4)
4	6.46 (dd, 2.4, 2.4)	6.45 (dd, 1.8, 1.8)	6.43 (dd, 1.8, 1.8)	6.43 (dd, 1.8, 1.8)
5	7.49 (d, 2.0)	7.48 (d, 1.6)	7.45 (d, 1.6)	7.48 (d, 1.5)
6	7.50 (d, 16.0)	7.50 (d, 16.0)	7.49 (d, 16.0)	7.50 (d, 16.0)
7	6.29 (d, 16.0)	6.30 (d, 16.0)	6.29 (d, 16.0)	6.30 (d, 16.0)
α	1.10	1.70	1.60–2.10	—
	(s) ^{2}J[75.0]	(m) ^{2}J[61.0]	(m) ^{2}J[n.o.]	—
β	—	1.35	1.39–1.20	7.78
	—	(t) ^{3}J[130.0]	(m) ^{3}J[n.o.]	(m) ^{3}J[n.o.]
γ	—	—	1.39–1.20 (m)	7.64 (m)
δ	—	—	0.90 (t, 7.0)	7.66 (m)

[a] In $CDCl_3$ at 298 K (40%).

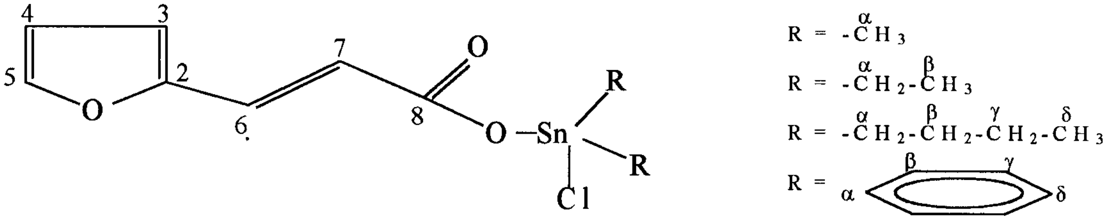
[b] Chemical shift (δ) in ppm $^{3}J(^{1}H–^{1}H)$ in Hz, $^{n}J[^{119/117}Sn–^{1}H]$ in Hz.

[c] Multiplicity is given as *s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet, n.o. = not observed.

[d] Theoretically, H^3 should give a doublet of doublets, but in the spectra, only one well-defined doublet is observed. The same is true for H^5.

[e] Resonances α–δ belong to the R groups.

TABLE 2 ^{13}C NMR Data of Chlorodiorganotin(*trans* 3-(2-furanyl)-2-propenoates)[a–c]



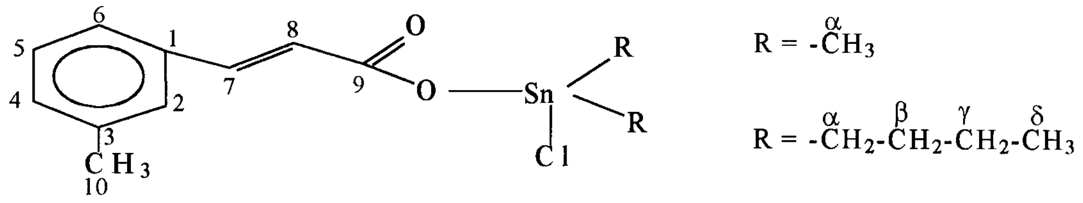
	I	II	III	IV
Carbon	*R = methyl*	*R = ethyl*	*R = n-butyl*	*R = phenyl*
2	150.5	150.6	150.6	149.0
3	115.5	115.7	115.6	115.4
4	112.8	112.4	112.3	111.9
5	144.5	144.3	145.2	144.9
6	133.6	133.4	133.3	134.9
7	113.5	113.9	114.0	113.1
8	176.5	176.3	176.5	173.1
α	6.4 ^{1}J[576.2]	18.1 ^{1}J[526.1]	25.9 ^{1}J[517.6]	138.0 ^{1}J[n.o.]
β	—	9.3 ^{2}J[40.3]	26.6 ^{2}J[32.9]	135.5 ^{2}J[n.o.]
γ	—	—	26.2 ^{3}J[94.0]	128.4 ^{3}J[n.o.]
δ	—	—	13.4	130.5

[a] In $CDCl_3$ at 298 K (40%).

[b] Chemical shift in ppm, $^{n}J[^{119/117}Sn–^{13}C]$ in Hz, n.o. = not observed.

[c] Resonances α–δ belong to R groups.

TABLE 3 ^{1}H and ^{13}C NMR Data of Chlorodiorganotin(*trans*-3-(3-methylphenyl) Cinnamates)[a–e]



	^{1}H NMR Data			^{13}C NMR Data	
Proton	V R = methyl	VI R = n-butyl	Carbon	V R = methyl	VI R = n-butyl
1	—	—	**1**	134.0	133.8
2	—	—	**2**	130.0	131.3
3	—	—	**3**	138.4	138.3
4	7.15 (d, 7.5)	7.23 (d, 7.5)	**4**	128.8	128.7
5	7.29 (t, 7.5, 7.5)	7.28 (t, 7.5, 7.5)	**5**	128.7	128.6
6	7.35 (d, 8.2)	7.30 (d, 8.1)	**6**	125.2	125.3
7	7.55 (d, 16.0)	7.75 (d, 16.0)	**7**	121.2	116.1
8	6.43 (d, 16.0)	6.44 (d, 16.0)	**8**	144.5	147.4
9	—	—	**9**	173.7	176.1
10	2.38 (s)	2.32 (s)	**10**	21.3	21.1
α	0.99 (s) ^2J[70.5]	1.73 (m)	α	5.8 ^1J[535.0]	25.7 J[500.5]
β	—	1.39–1.36 (m)	β	—	26.5 ^2J[34.1]
γ	—	1.39–1.36 (m)	γ	—	26.1 ^3J[92.2]
δ	—	0.89 (t, 7.3)	δ	—	13.3

[a] In $CDCl_3$ at 298 K (40%).
[b] Chemical shift (δ) in ppm, $^3J(^1H–^1H)$ in Hz, $^nJ[^{119/117}Sn–^1H]$ in Hz.
[c] Multiplicity is given as s = singlet, d = doublet, t = triplet, m = multiplet, n.o. = not observed.
[d] Theoretically, H^4 and H^6 should give independent doublets of doublets, but only one doublet is observed for each. Similarly, for H^5 instead of a doublet of doublets, a triplet is observed.
[e] Resonances α–δ belong to the R groups.

TABLE 4 Assignment of Characteristic IR Vibrations (cm^{-1})

Compound	$\nu_{(CO2)asym}$	$\nu_{(CO2)sym}$	$\Delta\nu$	$\nu_{Sn\text{-}C}$	$\nu_{Sn\text{-}O}$	$\nu_{Sn\text{-}Cl}$
FA	1698	1416	282	—	—	—
AgFA	1650	1386	264	—	—	—
I	1642	1380	262	558	448	333
II	1639	1379	260	549	489	—
III	1644	1386	258	550	444	350
IV	1641	1380	260	586	444	345

FA = trans-3-(2-furanyl)-2-propenoic acid, and AgFA = its silver salt.

TABLE 5 Mössbauer and ^{119}Sn NMR Data[a]

	Mössbauer Parameters					
Compound	δ (mm s^{-1})	Δ (mm s^{-1})	Γ_1 (mm s^{-1})	Γ_2 (mm s^{-1})	ρ	δ ppm
I	—	—	—	—	—	−42
II	1.45	3.54	0.85	0.95	2.44	−40
III	1.52	3.72	0.82	0.83	2.45	−40
IV	—	—	—	—	—	−160
V	—	—	—	—	—	−48
VI	1.55	3.73	0.83	0.83	2.41	−54

[a] $\delta \pm 0.02$, $\Delta \pm 0.04$, $\Gamma \pm 0.02$ mm s^{-1}.

magnitude of coupling constants $|^nJ[^{119/117}Sn–^1H]|$ is observed for chlorodiorganotin carboxylates as compared to their triorganotin analogues [2,3]. This is observed in the derivatives where R = Me or Et (Tables 1 and 3), in agreement with the trigonal bipyramidal geometry due to the bidentate chelate carboxylate group. However, when R = *n*-Bu or Ph, the ^2J or ^3J couplings were not observed, even by heteronuclear shift correlation (HETCOR) experiments. Earlier data show that the magnitude of $|^1J[^{119/117}Sn–^{13}C]|$ spin–spin coupling for R_3SnL derivatives is usually less than 400 Hz and about 650 Hz for alkyl and aryl R groups, respectively [2,3]. In the present series, these values are in the range of 500–576 Hz for alkyl groups, while, for aryl groups, these coupling constants could not be observed. It has been re-

TABLE 6 Relative Abundance of Common Ions Observed at 80 eV Mono Isotopic for the Investigated Compounds

	Compound					
Ionic Species	I	II	III	IV	V	VI
$[M]^+$	—	—	—	—	—	—
$[M\text{-}Cl]^+$	50	100.0	100.0	100.0	100.0	100.0
$[M^+\text{-}R]^+$	5.5	—	—	5.0	3.5	10.0
$[M^+\text{-}RCl]^+$	—	—	—	1.5	5.5	8.6
$[M^+\text{-}ClCO_2]^+$	2.5	4.5	45.0	5.0	—	3.5
$[M^+\text{-}RClCO_2]^+$	—	—	35.0	4.3	6.0	5.5
$[M^+\text{-}R_2ClCO_2]^+$	22.0	25	—	55	—	20.0
$[M^+\text{-}LCl]^+$	4.0	15	12	10.0	52.0	11.0
$[M^+\text{-}R_2SnCl]^+$	100.0	55	80	80.5	85.0	36.0
$[M^+\text{-}R_2SnClCO_2]^+$	20.0	25	5.0	23	—	47.0
$[M^+\text{-}R_2SnClC_2H_2CO_2]^+$	60.0	—	23.0	—	50.5	50.5

ported earlier that compounds in which a carboxylate anion acts as a bidentate chelate ligand are monomers in the solid state, and this chelation is retained even in solution [9,10]. In these systems, satellite signals due to $|^nJ[^{119/117}Sn\text{–}^{13}C]|$ and $|^nJ[^{119/117}Sn\text{–}^{1}H]|$ are broad, even in the case of methyl derivatives, which indicates that there is a dynamic process connected with the coordination mode of the carboxylate oxygens to the tin atom. Similarly, an increase of about 100 Hz in the magnitude of $|^1J[^{119/117}Sn\text{–}^{13}C]|$ and a high field shift of the $\delta^{119}Sn$ resonances by 165 ± 10 ppm (Tables 2 and 5), in comparison with their triorganotin analogues [2,3], also proves the increase in the coordination number of the tin atom [11,12]. However, the ^{119}Sn NMR resonance signals of these compounds are rather broad as compared to those of triorganotin carboxylates, in agreement with the dynamic process involving the carboxylate oxygens.

Infrared Spectroscopy

IR absorptions of these compounds have been assigned by comparison with those of the free acids and their silver salts. The compound formation is evidenced by the absence of a broad band at 2730–2950 cm^{-1} (ν_{OH} vibration) and the appearance of a new band at 444–482 cm^{-1} ($\nu_{Sn\text{-}O}$ vibration). There is a pronounced shifting in $\nu_{C=O}$ absorptions as compared to that of a free acid (1698 and 1416 cm^{-1}) and occurs at 1645 ± 5 and 1385 ± 5 cm^{-1} in these compounds (Table 4). The $\Delta\nu$ value [$\Delta\nu = \nu_{(CO_2)asym} - \nu_{(CO_2)sym}$] has been used as a tool for the estimation of tin–carboxylate interaction. According to the earlier reports, if this difference is comparable to that of the sodium salt of the ligand acid, then the carboxylate anion is acting as a bidentate chelate [13–16]. We here propose that, if this value is comparable to that of silver salt of the ligand acid, then the carboxylate anion is acting as a bidentate chelate. This is because silver has a greater tendency to accept a share in the electron pair from the carbonyl oxygen than does sodium.

On the basis of the $\Delta\nu$ value, it is, therefore, suggested that the bidentate chelate mode is more favorable, as this chelation is retained even in solutions of such compounds in noncoordinating solvents [9,10]. There is only one $\nu_{Sn\text{-}C}$ band in these systems, which indicates that the R groups occupy *cis* positions. Furthermore, the $\nu_{Sn\text{-}Cl}$ band is observed in the region 333–353 cm^{-1}. It was noticed that the infrared spectra of *trans*-3-(3-methylphenyl)-propenoic acid derivatives were not so informative as those of the *cis* isomers and hence are excluded from this discussion.

Mössbauer Spectroscopy

Mössbauer parameters are given in Table 5. There is an increase in IS values (1.45–1.55 mm s^{-1}) of these compounds as compared to those of R_3SnL derivatives of these ligands [1,2]. This shows that the extent of *s* electron participation is considerably reduced. On the other hand, QS (Δ) values (3.54–3.73 mm s^{-1}) are also much higher as compared to those of their R_3SnL analogs, thus indicating more imbalance in the 5p electrons. Theoretically, there must be a reduction in the IS (δ) value due to high electronegativity of chlorine and oxygen atoms attached to tin; however, the donation of a share in the electron pair through carbonyl interaction compensates for this effect, and the δ value increases. Mössbauer parameters observed for these compounds closely resemble those found for other diorganotin-halo-carboxylates

[17,18] and are in accord with a penta-coordinate trigonal bipyramidal *cis*-$R_2(X)SnO_2$ geometry.

Mass Spectrometry

The 80 eV monoisotopic mass fragmentations of the compounds are given in Table 6. The molecular ion peak is not observed in any of these compounds. Primary decomposition seems to be due to the loss of the chloride ion. This follows the loss of the R group or the CO_2 molecule. It has been noticed that, after elimination of the chloride ion, the fragmentation patterns for these compounds are similar to those of triorganotin carboxylates [1,4,5].

ACKNOWLEDGMENTS

We are thankful to the Pakistan Science Foundation for funding this project. K. C. Molloy, University of Bath (U.K.), and G. Kehr, University of Bayreuth (Germany), are thanked for elemental analyses, and Mössbauer and NMR measurements, respectively.

REFERENCES

[1] A. G. Davis, P. J. Smith: in G. Wilkinson, F. G. Stone, E. W. Able (eds): *Comprehensive Organometallic Chemistry, The Synthesis Reactions and Structures of Organometallic Compounds,* Pergamon, Oxford vol. 2, (1982).

[2] M. Danish, S. Ali, M. Mazhar, A. Badshah, M. I. Chaudhry, H. G. Alt, G. Kehr, *Polyhedron, 14,* 1995, 3115.

[3] M. Danish, H. G. Alt, A. Badshah, S. Ali, M. Mazhar, N. Islam, *J. Organomet. Chem., 486,* 1995, 51.

[4] M. Danish, S. Ali, M. Mazhar, A. Badshah, T. Masood, E. R. T. Tiekink, *Main Group Met. Chem., 18,* 1995, 27.

[5] A. Badshah, M. Danish, S. Ali, M. Mazhar, S. Mahmood, *Synth. React. Inorg. Met.-Org. Chem., 24,* 1994, 1155.

[6] M. Danish, A. Badshah, M. Mazhar, S. Ali, N. Islam, M. I. Chaudhry, *Tran. J. Chem. & Chem. Engg., 13,* 1994, 1.

[7] H. O. Kalinowski, S. Berger, S. Brown; *^{13}C NMR Spektroskpie,* Thieme Verlag, Stuttgart, Germany (1984).

[8] B. Wrackmeyer, G. Kehr, *Main Group Met. Chem., 16,* 1993, 305.

[9] K. C. Molloy, R. Quill, I. W. Nowell, *J. Chem. Soc. Dalton Trans.,* 1987, 101.

[10] K. C. Molloy: in F. R. Hartley (ed): *The Chemistry of Metal-Carbon Bond, Bioorganotin Compounds,* Wiley, New York, vol. 5, (1989).

[11] B. Wrackmeyer: in G. A. Webb (ed.): *Annual Report on NMR Spectroscopy, ^{119}Sn NMR Parameters,* Academic, London, vol. 6, (1985).

[12] M. Nadvornik, J. Holecek, K. Handllir, A. Lycka, *J. Organomet. Chem., 275,* 1984, 43.

[13] H. K. Sharma, S. Lata, K. K. Sharma, K. C. Molloy, P. C. Waterfield, *J. Organomet. Chem., 353,* 1988, 9.

[14] C. Vatsa, V. K. Jain, T. Kesavadas, E. R. T. Tiekink, *J. Organomet. Chem., 410,* 1991, 135.

[15] G. K. Sandhu, G. Kaur, *Main Group Met. Chem., 13,* 1990, 149.

[16] G. K. Sandhu, N. S. Boparoy, *J. Organomet. Chem., 423,* 1992, 183.

[17] A. J. Crowe, R. Hill, P. J. Smith, J. S. Brooks, R. Formstone, *J. Organomet. Chem., 204,* 1981, 47.

[18] W. D. Honnick, J. J. Zuckermann, *J. Organomet. Chem., 178,* 1979, 133.