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Preparation and ^{119}Sn NMR Spectra of Coordination Compounds of Di-*t*-butyltin(IV) Derivatives

Junzo Otera,* Toru Yano, and Kazunori Kusakabe
Okayama University of Science, Ridai-cho, Okayama 700
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Di-*t*-butyltin bis(chelates) were prepared and characterized in comparison with dimethyltin analogs. ^{119}Sn NMR spectra show a six-coordinate configuration for the acetylacetonate, tropolonate, and oxinate; a nonchelating structure is partially involved in the 2-methyloxinate and dialkyldithiocarbamates. Di-*t*-butyltin dichloride gives no isolable adducts with monodentate ligands; however, the Job's continuous variation method using ^{119}Sn NMR spectra has revealed that complexations with 2 : 1 and/or 1 : 1 donor/Sn molar ratios occur in ether. It has been concluded that *t*-butyl group reduces the acceptor property of tin by means of both inductive and steric effects.

Despite extensive preparative and spectroscopic investigations on coordination compounds of dimethyltin(IV) derivatives,[1] rather few studies have been made on the other diorganotin analogs except some diphenyltin(IV) compounds, because IR and NMR spectroscopies are not so powerful means for these compounds. However, X-ray studies have revealed that the configulation was varied in some cases where methyl groups attached to tin were replaced by phenyl groups,[2] and therefore, it seems of interest to investigate other organotin analogs. *t*-Butyl group, possessing increased electron donating ability and bulkiness, seems to be appropriate for evaluating the effect of alkyl group on coordination behavior. Unfortunately, however, only a few coordination compounds of *t*-butyltin(IV) derivatives have been prepared,[3] and no systematic studies on these compounds have been made.

The most popular dimethyl- and diphenyltin(IV) compounds known so far involve diorganotin bis(chelates), $R_2Sn(Ch)_2$ (Ch=chelating ligands), and molecular complexes of diorganotin dihalides with monodentate donors. For $Me_2Sn(Ch)_2$, we have shown the usefulness of ^{119}Sn NMR spectra for elucidating the coordination about tin.[4-7] In this paper, we wish to report the preparation of di-*t*-butyltin bis(chelates), *t*-$Bu_2Sn(Ch)_2$, for which characterization was carried out by means of ^{119}Sn FT NMR spectroscopy. Interaction of *t*-Bu_2SnCl_2 with monodentate ligands in solution will also be described.

Experimental

^{119}Sn and ^{1}H NMR spectra were measured in the FT and CW modes, respectively, as reported previously.[4-7] Chemical shifts are relative to Me_4Sn and Me_4Si for ^{119}Sn and ^{1}H NMR spectra, respectively, and positive signs indicate downfield shifts from the reference. UV spectra were measured with a Hitachi Model 285 spectrophotometer equipped with 1 cm quartz cells. All the solvents were purified by standard methods. *t*-Bu_2SnCl_2 was prepared by a slightly modified Grignard method.[8] The employment of THF in place of ether as solvent resulted in an improvement of yield from 4 to 15%. Abbreviations for ligands are as follows: acac=acetylacetonate, trop=tropolonate, oxin=oxinate (or 8-quinolinolate), meox=2-methyloxinate (or 2-methyl-8-quinolinolate), mdtc and edtc=dimethyl- and diethyldithiocarbamate, DMSO=dimethyl sulfoxide, HMPA=hexamethylphosphoric triamide, DMF=*N*,*N*-dimethylformamide, and Py=pyridine.

Preparation of t-$Bu_2Sn(Ch)_2$. To a methanol solution (10 cm^3) of CH_3ONa (1 mmol) was added Hacac (100 mg, 1 mmol). After stirring for 1 h at room temperature, *t*-Bu_2SnCl_2 (152 mg, 0.5 mmol) in methanol (5 cm^3) was added to this solution. The reaction mixture was stirred for 2 h and subjected to evaporation *in vacuo*. The precipitates thus obtained were extracted with hexane (10 cm^3). After addition of a few drops of Hacac, the hexane solution was concentrated to 2 cm^3. Cooling this concentrated solution in a Dry Ice–methanol bath gave *t*-$Bu_2Sn(acac)_2$ (**1**) as colorless crystals: yield 100 mg (41%). All operations were carried out in an inert atmosphere because **1** decomposes easily in air.

t-$Bu_2Sn(trop)_2$ (**2**), *t*-$Bu_2Sn(oxin)_2$ (**3**), and *t*-$Bu_2Sn(meox)_2$ (**4**) were prepared similarly in 25—55% yields. Recrystallization of these compounds was effected from CH_2Cl_2–hexane in air.

t-$Bu_2Sn(mdtc)_2$ (**5**) and *t*-$Bu_2Sn(edtc)_2$ (**6**) were prepared by mixing mdtcNa (359 mg, 2 mmol) or edctNa (451 mg, 2 mmol) in methanol (10 cm^3) with *t*-Bu_2SnCl_2 (304 mg, 1 mmol) in CH_2Cl_2 (5 cm^3). The pure sample was obtained by recrystallization from CH_2Cl_2–hexane in yields of 308 mg (65%) and 434 mg (82%), respectively. Melting points and analytical data of the compounds thus obtained are summarized in Table 1.

The Job's continuous variation method[9,10] was used under the condition that the total concentration of *t*-Bu_2SnCl_2 and a ligand was 1 M (1 M=1 mol dm^{-3}) in ether. The ligands employed were distilled from CaH_2 before use.

Attempted Isolation of Adducts. *t*-Bu_2SnCl_2 (304 mg, 1 mmol) and DMSO (156 mg, 2mmol) were stirred in ether (3 cm^3) at room temperature for 30 min. After addition of 3 cm^3 hexane, the solution was cooled at −78 °C to give white precipitates, which were filtered out and dried (100 mg). The NMR spectrum of the precipitates in CCl_4 exhibited two methyl proton signals at δ=2.45 (DMSO) and 1.41 (*t*-Bu), but no reproducible results were obtained with respect to their integral ratios, which varied between 12 : 20 and 12 : 28 in

Table 1. Melting points and analytical data of *t*-$Bu_2Sn(Ch)_2$

	Ch	Mp θ_m/°C	Found (Calcd) (%) C	H	N
1	acac	101—103	50.23(50.15)	7.67(7.48)	
2	trop	166—168	55.58(55.62)	5.95(5.94)	
3	oxin	199—202	59.60(59.91)	5.77(5.80)	5.40(5.38)
4	meox	207—208	60.70(61.00)	6.04(6.58)	5.01(5.08)
5	mdtc	174—176	35.56(35.52)	6.37(6.39)	5.98(5.92)
6	edtc	100—102	40.87(40.83)	7.23(7.23)	5.38(5.29)

repeated preparations, indicating coexistence of 2 : 1 and 1 : 1 adducts. Employment of 4 equiv. DMSO also gave similar results. When other monodentate ligands were treated in an analogous manner, no adducts were obtained,only t-Bu_2SnCl_2 being recovered after cooling at −78 °C.

Results and Discussion

t-$Bu_2Sn(Ch)_2$. All chelates were prepared as analytically pure crystalline compounds from t-Bu_2SnCl_2 and sodium salts of ligand anions, and were fairly stable in air except the acetylacetonato complex, which decomposes easily on exposure to air both in the solid state and in solution. The ^1H and ^{119}Sn NMR spectral parameters of these compounds are summarized in Table 2, in which the deviations in $^3J(^{119}Sn–H)$ and $\delta(^{119}Sn)$ values from those in the corresponding dimethyltin analogs are given as Δ_1 and Δ_2. Evidently, the $^3J(^{119}Sn–H)$ value in t-$Bu_2Sn(Ch)_2$ is constantly increased by 30—40 Hz from the $^2J(^{119}Sn–H)$ value in $Me_2Sn(Ch)_2$, except for the 2-methyloxinato complex **4**

Table 2. ^1H and ^{119}Sn NMR spectral parameters of t-$Bu_2Sn(Ch)_2$ in CCl_4

Compound	$\delta(CH_3–C–Sn)$ ppm	$^3J(^{119}Sn–H)$ Hz	Δ_1[a] Hz	$\delta(^{119}Sn)$ ppm	Δ_2[b] ppm
1	1.01	130.6	31.3	−486	−120
2	1.18	111.4	39.2	−326	−134
3	1.13	107.2	36.0	−338	−105
4	1.03	109.4	20.4	−311	−83
5	1.53	119.3	35.3	−255	+89
6	1.55	119.6	35.6	−262	+76

a) $\Delta_1 = {}^3J(^{119}Sn–H)$ (t-$Bu_2Sn(Ch)_2$) $- {}^2J(^{119}Sn–H)$ ($Me_2Sn(Ch)_2$). b) $\Delta_2 = \delta(^{119}Sn)$ (t-$Bu_2Sn(Ch)_2$) $- \delta(^{119}Sn)$ ($Me_2Sn(Ch)_2$).

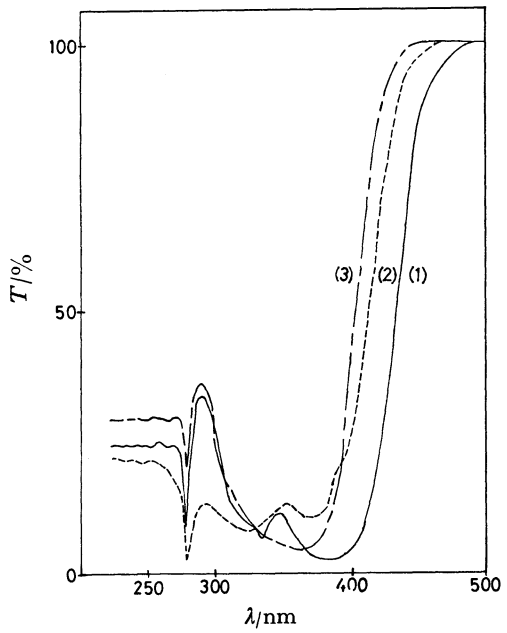

Fig. 1. UV spectra of $R_2Sn(oxin)_2$ and $R_2Sn(meox)_2$ in benzene. (1) t-$Bu_2Sn(oxin)_2$: λ_{max} 386 nm (ε 5200), (2) t-$Bu_2Sn(meox)_2$: λ_{max} 320 nm (ε 3800) and 370 nm (ε 3400), (3) $Me_2Sn(meox)_2$: λ_{max} 365 nm (ε 3900).

(*vide infra*). Since the latter value can be correlated linearly with the C–Sn–C bond angle,[4] it may be said that the $^3J(^{119}Sn–H)$ value in t-$Bu_2Sn(Ch)_2$ also increases with increasing C–Sn–C bond angle. It should be noted, however, that the $^3J(^{119}Sn–H)$ value cannot necessarily be correlated with the coordination mode.[4]

By contrast, a great discrepancy was found for Δ_2. The $\delta(^{119}Sn)$ values in t-$Bu_2Sn(Ch)_2$ shifted upfield by 105—134 ppm from those in corresponding $Me_2Sn(Ch)_2$ for the acetylacetonato **1**, tropolonato **2**, and oxinato **3** complexes. Since the chelation of ligands in these compounds is confirmed on the basis of IR spectra for **1** (ν(C=O) 1590 cm^{-1})[10] and **2** (ν(C=C) 1592 and ν(C=O) 1497 cm^{-1})[12] and UV spectrum for **3** (Fig. 1),[13] the upfield shifts mentioned above has been brought about simply by the replacement of methyl group by t-butyl group. On the other hand, the magnitude of the upfield shift is moderately reduced in the 2-methyloxinato complex **4**. As shown in Fig. 1, the UV spectrum of **4** exhibits two peaks at 320 and 370 nm assignable to nonchelating and chelating structures, respectively, while the dimethyltin counterpart gives rise to a single peak at 365 nm. As a result, the $\delta(^{119}Sn)$ value apparently reflects this coordination behavior. In $Me_2Sn(Ch)_2$, when Ch was changed from oxin to meox, $\delta(^{119}Sn)$ was shifted downfield (from −273 to −228 ppm).[6] Introduction of a methyl group into the α-position of the quinoline ring resulted in expansion of the C–Sn–C bound angle, though a slightly weakened chelation being maintained; that is, a considerable steric repulsion is operative between methyl groups attached to tin and the quinoline ring. Accordingly, a strong steric interaction between t-butyl groups and methyl groups in **4** is reasonably assumed to prevent nitrogen from coordinating to tin.

Quite surprisingly, the $\delta(^{119}Sn)$ values in the dialkyldithiocarbamato complexes **5** and **6** lie downfield relative to those in corresponding dimethyltin compounds. Since we have revealed that the $\delta(^{119}Sn)$ value in organotin chelates is shifted downfield as the coordination number of tin decreases,[7] the above results may be interpreted in terms of coexistence of a nochelating structure with the chelating structure. In general, t-$Bu_2Sn(Ch)_2$ was found to involve a fairly weak chelation as compared with $Me_2Sn(Ch)_2$.

Interactions of t-Bu_2SnCl_2 with Monodentate Ligands. Me_2SnCl_2 forms molecular complexes with various monodentate ligands with 2 : 1 and/or 1 : 1 donor/Sn stoicheometry. For example, DMSO, HMPA, and Py afford quite stable 2 : 1 adducts, while DMF gives

Table 3. ^1H and ^{119}Sn NMR spectral parameters of t-Bu_2SnCl_2 in donor solvents

Solvent	$\delta(CH_3–C–Sn)$ ppm	$^3J(^{119}Sn–H)$ Hz	$\delta(^{119}Sn)$ ppm
CCl_4	1.43	112.8	56
DMSO	1.36	125.0	−147
HMPA	1.42	122.0	−153
DMF	1.38	118.0	−99
Py	1.39	117.0	30

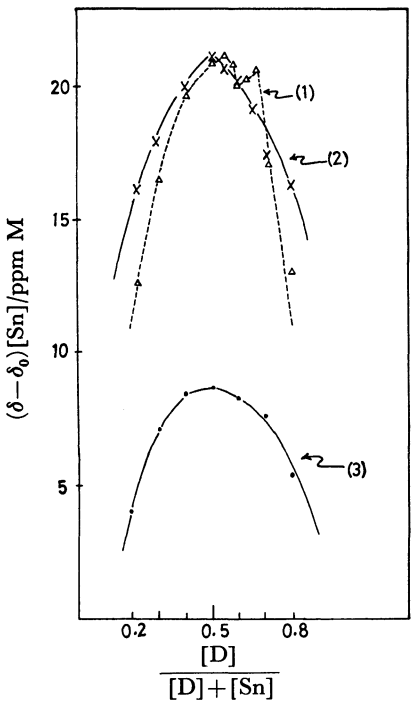

Fig. 2. Job's plots for *t*-Bu_2SnCl_2–monodentate ligand system in ether at total concentration of 1 M. (1) DMSO (2) HMPA (3) DMF.

both 2 : 1 and 1 : 1 adducts.[1b] Here we have studied the coordinating behavior of these ligands towards *t*-Bu_2SnCl_2. When *t*-Bu_2SnCl_2 and a ligand were mixed in hexane in various molar ratios, no adducts were obtained. Treatment of DMSO with *t*-Bu_2SnCl_2 in molar ratios more than 2 : 1 in ether, followed by addition of hexane and cooling at −78 °C, yielded white precipitates. The ^1H NMR spectrum, however, showed that these precipitates consisted of 2 : 1 and 1 : 1 adducts. Accordingly, we have investigated whether some kind of interaction exists in solution. In Table 3 are listed the $^3J(^{119}Sn–H)$ and $\delta(^{119}Sn)$ values of *t*-Bu_2SnCl_2 in the donor solvents. The increase in ^3J ($^{119}Sn–H$) values from that in CCl_4 indicates occurrence of donor-acceptor interactions. In line with this, the $\delta(^{119}Sn)$ values in DMSO, HMPA, and DMF shifted 150—200 ppm upfield relative to the one in CCl_4, while a slight shift was observed in Py. This is quite unexpected because Py is classified as the most favorite ligand for Me_2SnCl_2 to afford the 2 : 1 adduct.[1] In the hope of elucidating the stoichiometry of the interaction in solution, the Job's continuous variation method was applied. When hexane was employed as a solvent, $\delta(^{119}Sn)$ shifted only 10 ppm at most, so that a reliable Job's plot could not be drawn. Then, ether was used, which resulted in a shift by more than 50 ppm. Evidently, the shift was not caused by the coordination of ether since $\delta(^{119}Sn)$ of *t*-Bu_2SnCl_2 in ether (55 ppm) gave no evidence for solvation. Therefore, it can be concluded that the interaction is favored in polar medium. The Job's plots in ether are illustrated in Fig. 2. DMSO gave rise to both 2 : 1 and 1 : 1 complexations but HMPA and DMF only to the 1 : 1 stoicheometry

$$t\text{-}Bu_2SnCl_2 \overset{D}{\rightleftharpoons} t\text{-}Bu_2SnCl_2\cdot D \overset{D}{\rightleftharpoons} t\text{-}Bu_2SnCl_2\cdot 2D. \quad (1)$$

It is apparent from these findings that the acceptor property of tin is considerably reduced in *t*-Bu_2SnCl_2. Since a consultation with the molecular model showed little steric interaction for *t*-Bu_2SnCl_2–DMSO and *t*-Bu_2SnCl_2–DMF systems, the reduction of acceptor property may be attributable to the inductive effect of the *t*-butyl group. On the other hand, a significant interaction between *t*-butyl groups and *N*-methyl groups is induced on coordination of HMPA. Both *t*-Bu_2SnCl_2–DMSO and *t*-Bu_2SnCl_2–HMPA systems are comparable in stability constant for the 1 : 1 complexation, judging from the $(\delta-\delta_0)$[Sn] values in the Job's plot which are proportional to stability constants.[9] The $\delta(^{119}Sn)$ values of *t*-Bu_2SnCl_2 in these systems (Table 3) are consistent with this postulation. Therefore, the absence of the 2 : 1 complexation of HMPA is accounted for by the steric reason.

In summary, di-*t*-butyltin(IV) compounds showed various differences in coordination behavior from dimethyltin analogs. The reduced acceptor property of tin in the former compounds is primarily caused by the inductive effect of *t*-butyl groups. However, in some cases where bulky ligands are involved, it was found that the steric factor also is important.

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