~10% of the oxidized complex. The powerful one-electron-oxidants $NOBF_4$, $NOPF_6$, or NO_2BF_4 effect the complete oxidation of $(Fe(C_5H_4PPh_2)_2)Re(CO)_3Cl$ within 1–2 h in CH_2Cl_2. The slow rate of these oxidations is probably caused by the insolubility of the oxidizing agents in CH_2Cl_2. Chemically produced $(FcPPh_2)_2Re(CO)_3Cl^{2+}$ is also unstable and decomposes, yielding some $(FcPPh_2)Re(CO)_4Cl$.

The chemically oxidized complexes can, in all cases, be chemically reduced back to the neutral complexes by addition of ferrocene or cobaltocene in the case of $FcRe(CO)_5$. We investigated these oxidation and reductions quantitatively by IR spectroscopy and found that in all cases the reduced complexes could be recovered in greater than 95% yield. Even $(FcPPh_2)_2Re(CO)_3Cl$ could be chemically oxidized and reduced before significant decomposition occurred. The quantitative nature of these redox reactions permits determination of IR molar absorptivities for the oxidized complexes. These values are reported in Table I. Values obtained for IR molar absorptivities in spectroelectrochemical experiments by assuming quantitative production of oxidized complex are in reasonable (±20%) agreement. The concomitant reduction of benzoquinone to hydroquinone accompanying chemical oxidation of ferrocenyl complexes make determination of UV/vis extinction coefficients from spectra of chemically oxidized complexes difficult. We measured the UV/vis spectrum of chemically oxidized $(Fe(C_5H_4PPh_2)_2)Re(CO)_3Cl$ since the byproduct, NO, is gaseous, and it is in good agreement with the spectrum obtained in the spectroelectrochemical cell.

Conclusions

The five Re complexes containing ferrocenyl ligands shown in Scheme I have been synthesized and characterized. In each of the complexes the ferrocenyl unit(s) can be reversibly oxidized by one electron each. That the oxidation is ferrocenyl-centered is supported by the oxidation potentials of the free ligands and the observation of bands in the UV/vis similar to those for ferrocenium. The oxidized complexes have been characterized spectroscopically (IR and UV/vis) and chemically by reduction back to their neutral complexes. Peak positions in the CO stretching region of the IR spectra all shift to higher energy upon oxidation of the complexes. The shift of the Re–CO peak positions to higher energy is indicative of lowered electron density at the Re atom. The magnitude of the shift depends upon the distance or the number of bonds separating the Re atom and ferrocenyl moiety. The important point of this work is that electron density at a metal center can be predictably adjusted by oxidation of a pendant redox center.

Tuning the electron density at a metal center by oxidation of a pendant ferrocene represents a new and useful alternative to tuning by varying the substituents on cyclopentadienyl or pyridyl ligands or reduction of pendant redox ligands. Work in this laboratory is in progress to examine the effect of the oxidation state of a pendant redox ligand upon the rate or equilibrium constant of a reaction at the effected metal center and to design other redox-active ligands.

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Registry No. $FcPy^+$, 120577-84-6; FcPy, 120577-85-7; Fc, 102-54-5; Fc^+, 12125-80-3; $(dppe)Re(CO)_3Cl$, 25257-38-9; $Re(CO)_5Cl$, 14099-01-5; *fac*-$(Fe(C_5H_4PPh_2)_2)Re(CO)_3Cl$, 120577-73-3; *fac*-$(FcPy)_2Re(CO)_3Cl$, 120577-74-4; *cis*-$(FcPPh_2)Re(CO)_4Cl$, 120577-75-5; *fac*-$(FcPPh_2)_2Re(CO)_3Cl$, 120577-76-6; $FcPPh_2$, 12098-17-8; $FcRe(CO)_5$, 120577-77-7; $FcRe(CO)_5^+$, 120577-78-8; *fac*-$(Fe(C_5H_4PPh_2)_2)Re(CO)_3Cl^+$, 120577-79-9; *cis*-$(FcPPh_2)Re(CO)_4Cl^+$, 120608-47-1; *fac*-$(FcPy)_2Re(CO)_3Cl^{2+}$, 120577-80-2; *fac*-$(FcPPh_2)_2Re(CO)_3Cl^{2+}$, 120577-81-3; *fac*-$(FcPPh_2)_2Re(CO)_3Cl^+$, 120577-82-4; $Fe(C_5H_4PPh_2)_2$, 12150-46-8; $FcPPh_2^+$, 120577-83-5; FcBr, 1273-73-0; Fc_2Hg, 1274-09-5; 1,2-dibromoethane, 106-93-4; 4-bromopyridine, 1120-87-2; *cis*-(1,3-bis(diphenylphosphino)propane)dichloronickel, 55659-60-4.

Supplementary Material Available: Complete atom-labeling scheme (Figure S1) and complete listings of bond lengths and angles (Table S1), anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms (Table S2), and hydrogen atom coordinates (Table S3) for $(Fe(C_5H_4PPh_2)_2)Re(CO)_3Cl$ and complete atom-labeling scheme (Figure S2) and complete listings of bond lengths and angles (Table S5), anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms (Table S6), and hydrogen atom coordinates (Table S7) for $(FePPh_2)_2Re(CO)_3Cl$ (16 pages); listings of F_o and F_c for both compounds (Tables S4 and S8) (57 pages). Ordering information is given on any current masthead page.

Contribution from the General Electric Company, Silicone Products Division,[1]
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Asymmetric Distannoxane Dimers

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Solutions of difunctional tetrabutyldistannoxane pairs containing identical and mixed substitutions, $[Bu_2SnX]_2O$ plus $XBu_2SnOSnBu_2Y$ (X, Y = CH_3CO_2, Cl, CH_3O, C_6H_5O), respectively, were examined by ^{119}Sn NMR spectroscopy. In all cases, the resulting eight-line spectra suggest that the two starting compounds are in equilibrium with the three possible distannoxane dimers. Each dimer is associated in a "ladder" or "staircase" geometry; the mixed species comprise four chemically nonequivalent tin atoms. In contrast, there was, with one exception (X = Cl, Y = $MeCO_2$), no spectral evidence for the stable formation of dimers formed from a pair of symmetrically disubstituted species, $\{[Bu_2SnX]_2O\cdot[Bu_2SnY]_2O\}$. An irreversible ligand conproportionation reaction of the two compounds resulted in the quantitative formation of 2 equiv of $XBu_2SnOSnBu_2Y$.

Introduction

Condensed organotin species, particularly the tetraalkyldistannoxanes, are well-known moisture cure catalysts for room-temperature-vulcanized (RTV) silicone elastomers.[2] Each year in fact, organotin reagents such as these are utilized to cross-link literally tons of linear siloxane polymer. This report presents ^{119}Sn NMR data that can be employed to successfully identify the composition and structure of a mixture of active silicone RTV cure catalysts in solution. The NMR data has additional significance in light of recent reports by Otera et al. describing the use of distannoxanes as catalysts for urethane polymerization[3] and

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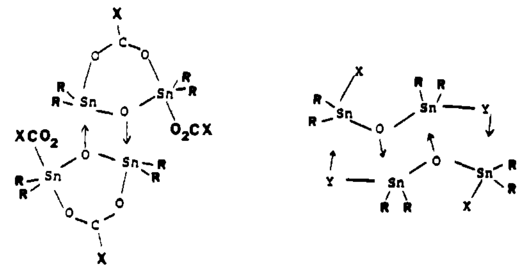
(1) Initial experiments were conducted at the General Electric Corporate Research and Development Center, 1 River Road, Schenectady, NY 12345.

(2) Chadha, R. J; Panda, K. C. U.S. Pat. 3,664,997.

(3) Otera, J.; Yano, T.; Okawara, R. *Organometallics* **1986**, *5*, 1167.



$\{[R_2Sn(O_2CX)]_2O\}_2$

Ref. 7a. R = CH_3; X = CH_2Cl
b. R = CH_3; X = CF_3
c. R = vinyl; X = CF_3
d. R = n-C_4H_9; X = CCl_3
e. R = CH_3 X = CH_3

$(XR_2SnOSnR_2Y)_2$

Ref. 5a. R = CH_3, C_2H_5; X,Y = Cl
b. R = CH_3; X,Y = Cl
c. R = $CH(CH_3)_2$; X,Y = Cl
6. R = CH_3; X,Y = NCS
8. R = n-C_4H_9; X,Y = N_3
9. R = CH_3; X,Y = $OSiMe_3$
10a. R = $CH(CH_3)_2$; X = Cl; Y = OH
10a. R = CH_2SiMe_3; X = Cl, Y = OH
b. R = C_6H_5; X = Cl; Y = OH

Figure 1. Dimeric "staircase" and "ladder" structures of tetraalkyl- and tetraaryldistannoxanes.

other organic transformations.[4]

Several X-ray crystal structural analyses performed over the last 25 years have shown the predominant solid-state structure adopted by many 1,3-disubstituted tetraalkyldistannoxanes, $XR_2SnOSnR_2Y$ (X = Y = Cl,[5] NCS,[6] RCO_2,[7] N_3,[8] $OSiMe_3$;[9] X = Cl, Y = OH[10]), to be the so-called "ladder" or "staircase" geometry originally proposed by Okawara et al.[11] (Figure 1). Throughout this time period, a series of physicochemical techniques have provided convincing evidence that the integrity of these centrosymmetric dimers was maintained in solution. For example, vapor-phase osmometry studies conducted by Alleston and co-workers[12] and cryoscopic measurements of Okawara and Maeda[13] demonstrated that, particularly in nonpolar solvents, $[(C_4H_9)_2Sn(O_2CCH_3)]_2O$ (I) was present as a dimer at even moderate solution concentrations. In agreement with the solid-state structure of the dicarboxylate-substituted tetraalkyldistannoxanes depicted in Figure 1, the infrared spectrum of I in cyclohexane displayed carbonyl absorbances that were assigned to both terminally bound and symmetric, bridging ligands.

The two distinct tin chemical environments that are observed in the X-ray crystal structure of many symmetrically disubstituted tetraalkyldistannoxanes were also found in their NMR solution spectra. For example, the ^{119}Sn magnetic resonance spectra of $[(C_4H_9)_2SnCl]_2O$ (II), originally reported by Alleston[12a] in 1963 and later refined by Davies,[14] consisted of two well-defined peaks separated by approximately 1000 Hz. The frequency of these absorbances, −94 ± 5 and −145 ± 5 ppm, were consistent with a geometry in which both tin atoms occupied pentacoordinate environments. The downfield resonance was assigned to exocyclic tin atoms, reflecting an additional bond to the electron-withdrawing chloride ligand. The advent of high-field FT instruments has enabled Otera and co-workers to resolve the ^{119}Sn NMR $CDCl_3$ spectra of a series of 1,3-disubstituted tetraalkyldistannoxanes containing alkoxy, carboxy, halo, and isothiocyanate ligands. In all cases, except the isothiocyanates, the observed resonance pair suggested that the solution structure of the distannoxanes is that of a centrosymmetric dimer comprised of four tin atoms in two five-coordinate chemical environments.

In this paper, ^{119}Sn NMR spectroscopy is employed to continue the structural investigation of solvated 1,3-disubstituted tetraalkyldistannoxane species. For the first time, spectral evidence is provided to suggest the reversible formation of asymmetric distannoxane dimers comprising dissimilar monomeric units as well as the ligand-exchange reactions that result in their formation.

Experimental Section

Experiments were either carried out in a Vacuum Atmospheres MO-40-1H drybox or performed by employing standard Schlenk techniques. Sealed vials of deuterated benzene, packaged by Aldrich, were opened, used, and stored in the drybox. NMR spectra were recorded on Varian spectrometers: XL-300, ^{119}Sn = 111.8 MHz; XL-200, ^{119}Sn = 74.6 MHz. Tetramethyltin served as an internal reference.

The tetrabutyldistannoxanes $[Bu_2Sn(O_2CMe)]_2O$,[13] $[Bu_2Sn(O_2CCF_3)]_2O$, and $[Bu_2Sn(OC_6H_5)]_2O$[16] were synthesized in toluene by the well-known reactions of $Bu_2Sn(O)$ plus $MeCO_2H$, CF_3CO_2H, and C_6H_5OH, respectively. Water was removed by azeotropic distillation. Telomerization of $Bu_2Sn(O)$ plus Bu_2SnCl_2 and $Bu_2Sn(OMe)_2$ was employed to prpare $[Bu_2SnCl]_2O$[12] and $[Bu_2Sn(OMe)]_2O$,[17] respectively. The commercially available mononuclear tin compounds required pretreatment prior to use; $Bu_2Sn(OMe)_2$ was vacuum-distilled and Bu_2SnCl_2 recrystallized from hexane.

Preparation of $(MeCO_2)Bu_2SnOSnBu_2(OMe)$. Acetic acid (0.34 g, 0.0056 mol) was added dropwise to a rapidly stirred solution of $[Bu_2Sn(OMe)]_2O$ (3.18 g, 0.0056 mol) in methylene chloride (50 mL). Methanol and solvent were removed in vacuo on a rotovap, leaving a pale yellow oil. This yellow impurity was separated from the distannoxane by crystallization of the latter compound from hexane at −45 °C. Alternatively, addition of $[Bu_2Sn(O_2CMe)]_2O$, (100 g, 0.17 mol) to $[Bu_2Sn(OMe)]_2O$ (92.5 g, 0.17 mol) in hexane afforded, following recrystallization, $(MeCO_2)Bu_2SnOSnBu_2(OMe)$ in greater than 80% yield. Anal. Calcd for $(CH_3CO_2)Bu_2SnOSnBu_2(OCH_3)$: C, 39.90; H, 7.35. Found: C, 40.02; H, 7.38.

Preparation of $(MeCO_2)Bu_2SnOSnBu_2(OH)$. A qualitative amount of $(MeCO_2)Bu_2SnOSnBu_2(OMe)$ was taken up in 95/5 v/v THF/H_2O. Any volatile material was subsequently removed by rotovap, leaving a fine white powder. No methoxy resonances were observed in the ^1H NMR spectrum of this compound in $CDCl_3$. Anal. Calcd for $(CH_3CO_2)Bu_2SnOSnBu_2(OH)$: C, 38.75; H, 7.19. Found: C, 38.88; H, 7.08. ν_{OH} = 3305 cm^{-1}.

Preparation of $ClBu_2SnOSnBu_2(OMe)$. A heterogeneous mixture of $[Bu_2SnCl]_2O$ (25 g, 0.045 mol), Et_3N (6.27 mL, 0.045 mol), and CH_3OH (300 mL) was brought to reflux for 30 min. Upon cooling of the solution, large white crystals of $ClBu_2SnOSnBu_2(OCH_3)$ were deposited. These crystals were filtered and washed with CH_3OH. Mp: 72–76 °C.[18]

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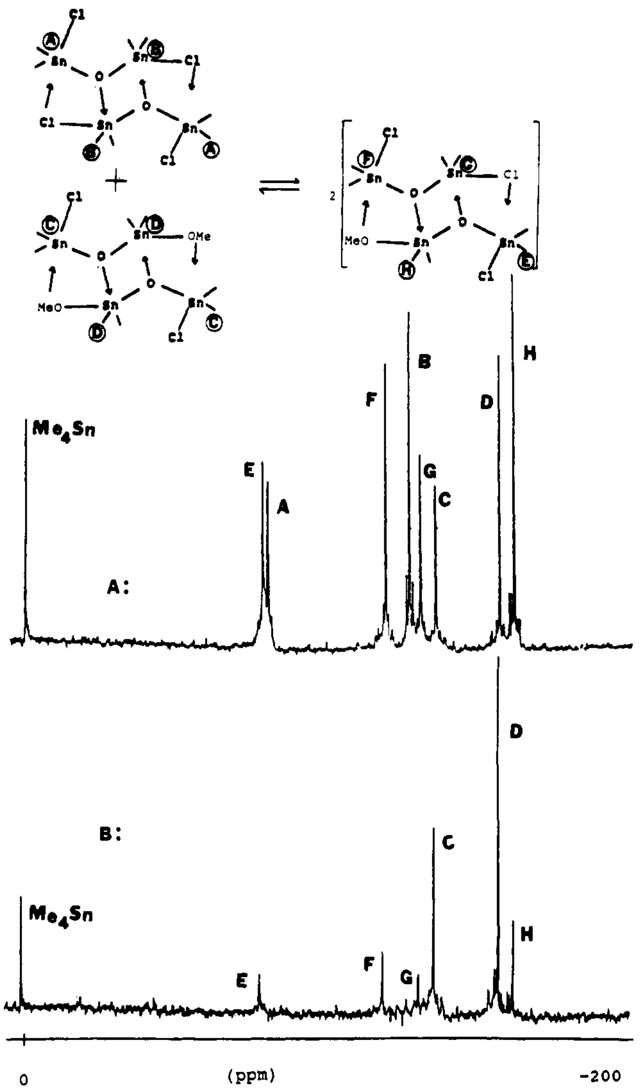


Figure 2. C_6D_6 solution ^{119}Sn NMR spectra of (a) 0.25 M/0.25 M $[Bu_2SnCl]_2O/ClBu_2SnOSnBu_2(O_2CMe)$ and (b) 0.05 M/0.25 M $[Bu_2SnCl]_2O/ClBu_2SnOSnBu_2(O_2CMe)$.

Preparation of $(MeCO_2)Bu_2SnOSnBu_2(OC_6H_5)$. A mixture of $[Bu_2Sn(O_2CMe)]_2O$ (10.3 g, 0.0172 mol) and $[Bu_2Sn(OC_6H_5)]_2O$ (11.47 g, 0.0172 mol) was gradually heated in hexane (100 mL) until a homogeneous solution resulted. The flask was then cooled to −40 °C overnight. After 15 h, crystals of the target compound were recovered in 79% yield. Anal. Calcd for $(CH_3CO_2)Bu_2SnOSnBu_2(OC_6H_5)$: C, 45.46; H, 6.95. Found: C, 45.44;, H, 6.83.

Preparation of $(CF_3CO_2)Bu_2SnOSnBu_2(OC_6H_5)$. Equimolar quantities of $[Bu_2Sn(O_2CCF_3)]_2O$ (10.21 g, 0.014 mol) and $[Bu_2Sn(OC_6H_5)]_2O$ (9.76 g, 0.0146 mol) were added to hexane (100 mL). Gentle heating was required to effect a homogeneous solution. The reaction flask was then placed in a −40 °C freezer for 15 h. Needles of $(CF_3CO_2)Bu_2SnOSnBu_2(OC_6H_5)$ were isolated in 97% yield. Anal. Calcd for $(CF_3CO_2)Bu_2SnOSnBu_2(OC_6H_5)$: C, 41.88; H, 5.96. Found: C, 41.84; H, 5.85.

The two 1,3-disubstituted tetrabutyldistannoxanes $ClBu_2SnOSnBu_2(O_2CMe)$ and $ClBu_2SnOSnBu_2(OC_6H_5)$ were prepared in C_6D_6 from the conproportionation of $[Bu_2SnCl]_2O$ plus $[Bu_2Sn(O_2CMe)]_2O$ and $[Bu_2SnCl]_2O$ plus $[Bu_2Sn(OC_6H_5)]_2O$, respectively. These compounds were not isolated.

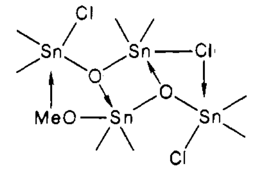
Results and Discussion

The ^{119}Sn NMR spectrum of an equimolar mixture of $ClBu_2SnOSnBu_2(OMe)$ plus $[Bu_2SnCl]_2O$ in C_6D_6 results in the eight-line spectrum displayed in Figure 2A. Two resonance pairs at −90.2, −143.1 and −152.8, −176.3 ppm are readily assigned to the reactants, $[Bu_2SnCl]_2O$ and $ClBu_2SnOSnBu_2(OMe)$, respectively. Each molecule is proposed to exist as a centrosymmetric dimer; thus, two chemical environments are observed for the four tin atoms. In each pair, the high-frequency resonance is associated with the two tin atoms found only in the exocyclic rings (A,C); the second resonance, further upfield, is assigned to the two chemically equivalent tin atoms that belong to both the exocyclic and four-membered endocyclic rings (B,D). One explanation for the four additional peaks at −88.4, −134.1, −147.2, and −181.7 ppm, which appear along with those of the starting compounds, is described by eq 1–4. In this scheme, an equilibrium

$$\{[Bu_2SnCl]_2O\}_2 \rightleftharpoons 2[Bu_2SnCl]_2O \qquad (1)$$

$$\{ClBu_2SnOSnBu_2(OMe)\}_2 \rightleftharpoons 2\{ClBu_2SnOSnBu_2(OMe)\} \qquad (2)$$

$$2[Bu_2SnCl]_2O + 2\{ClBu_2SnOSnBu_2(OMe)\} \rightleftharpoons$$



(3)

$$\{[Bu_2SnCl]_2O\}_2 + \{ClBu_2SnOSnBu_2(OMe)\}_2 \rightleftharpoons 2\{[Bu_2SnCl]_2O{\cdot}\{ClBu_2SnOSnBu_2(OMe)\}\} \qquad (4)$$

is established between the dichlorodistannoxane and the chloromethoxydistannoxane dimers with 2 equiv of their respective monomers (eq 1 and 2). If the dichlorodistannoxane monomer couples with a monomer of the chloromethoxydistannoxane, then the resulting dimer (eq 3) cannot contain a center of symmetry. Since each tin atom in this ladder structure is chemically nonequivalent, four additional resonances would be observed.

Supporting evidence for the proposed distannoxane monomer/dimer equilibrium is found in the ^{119}Sn NMR spectrum obtained following the addition of a 5-fold excess of $ClBu_2SnOSnBu_2(OMe)$ to $[Bu_2SnCl]_2O$ (Figure 2B). A large excess of one reagent should drive the equilibrium summarized by eq 4 to the right such that the ^{119}Sn NMR absorbances of the dichlorodistannoxane dimer are smaller than those of the asymmetric dimer. As shown in Figure 2B, this is indeed the case. The two prominent peaks at −152.5 and −176.0 ppm are assigned to $\{ClBu_2SnOSnBu_2(OMe)\}_2$ (C, D). The two resonances of $\{[Bu_2SnCl]_2O\}_2$ are barely distinguishable from the spectral noise, while the four peaks of the asymmetric dimer (E, F, G, H) are observed clearly. Addition of 4 equiv of $[Bu_2SnCl]_2O$ to this solution results in a ^{119}Sn NMR spectrum essentially identical with that shown in Figure 2A thereby establishing reversibility. Upon further addition of $[Bu_2SnCl]_2O$, the intensity of the four peaks of the asymmetric dimer exceed those of $\{ClBu_2SnOSnBu_2(OMe)\}_2$. It must be noted that the four spectral peaks cannot be the result of a tin species formed from an exchange reaction of the labile methoxide and choride ligands as such a process is degenerate.

Although four ^{119}Sn NMR resonances must result from a distannoxane pair associated in a ladder structure without a plane or center of symmetry, peak assignment is not straightforward. The downfield resonance (E) of spectra A and B of Figure 2 at −88.4 ppm is associated with the exocyclic tin atoms possessing Bu_2SnOCl_2 coordination. A slight chemical shift difference from that observed for the exocyclic tin atoms in $\{[Bu_2SnCl]_2O\}_2$ is consistent with two bonds to the electron-withdrawing chloride ligand and the subtle effect of a Cl/OMe substitution three bonds away. The proximity of the outlying resonance at −181.7 ppm to that associated with the endocyclic tin atoms of $\{ClBu_2SnOSnBu_2(OMe)\}_2$ suggests assignment as tin atom H shown in Figure 2. The remaining two resonances (F, G) cannot be assigned absolutely.

The association of nonequivalent distannoxane units to form an asymmetric dimer is not limited to $ClBu_2SnOSnBu_2(OMe)$ and $[Bu_2SnCl]_2O$. This phenomenon appears general for tetrabutyldistannoxanes known to associate in the "ladder" or "staircase" structures and has been measured for a series of distannoxane pairs comprising $[Bu_2SnX]_2O$ plus

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Table I. ^{119}Sn Chemical Shifts of 1,3-Disubstituted Tetrabutyldistannoxane Dimers in C_6D_6[a]

dimer	chem shift, ppm
$\{[Bu_2Sn(O_2CCH_3)]_2O\}_2$	-217.1, -228.8
$\{[Bu_2SnCl]_2O\}_2$	-90.2, -143.1
$\{[Bu_2Sn(OCH_3)]_2O\}_2$	-173.9, -185.9
$\{[Bu_2Sn(OC_6H_5)]_2O\}_2$	-176.4, -177.8
$\{[Bu_2Sn(O_2CCF_3)]_2O\}_2$	-177.5, -178.6[b]
$\{ClBu_2SnOSnBu_2(O_2CCH_3)\}_2$	-158.0, -186.8
$\{ClBu_2SnOSnBu_2(OC_6H_5)\}_2$	-134.3, -171.9
$\{ClBu_2SnOSnBu_2OCH_3)\}_2$	-152.8, -176.3
$\{(CH_3CO_2)Bu_2SnOSnBu_2(OC_6H_5)\}_2$	-195.6, -203.2
$\{(CH_3CO_2)Bu_2SnOSnBu_2(OCH_3)\}_2$	-180.6, -216.0
$\{(CF_3CO_2)Bu_2SnOSnBu_2(OC_6H_5)\}_2$	-170.9, -182.5

[a] Spectra were run at 25 °C. Chemical shifts are concentration dependent and may vary 0.5 ppm from reported values. [b] Measured in $CDCl_3$.

$XBu_2SnOSnBu_2Y$, where X and Y = Cl, O_2CMe, O_2CCF_3, OMe, and OPh. The single-resonance pairs of the tetrabutyldistannoxanes investigated are shown in Table I. The four peaks that are assigned to the asymmetric dimers are tabulated in Table II.

An exception to the ubiquitous two-line spectra of all other distannoxanes employed in this study is provided by $(MeCO_2)Bu_2SnOSnBu_2(OH)$ in $CDCl_3$, which produces a plethora of broad peaks clustered between -156 and -218 ppm observed in the ^{119}Sn NMR spectrum. The complicated NMR spectrum is consistent with earlier studies that have shown that this compound does not exist as a discrete dimer in solution. Vapor-phase osmometry studies of Maeda and Okawara demonstrated that although the degree of association of $(MeCO_2)Bu_2SnOSnBu_2(OH)$ extrapolates to a dimer at zero concentration, the stannoxane becomes more highly associated in even dilute solutions.[13] These authors suggested that association of the dimers may occur through acetoxy bridges. Higher association may also result from intermolecular hydrogen bonding between the hydroxide proton and the carbonyl oxygen of an acetate ligand. Indeed, the X-ray crystal structure of $ClPh_2SnOSnPh_2(OH)\cdot 2(CH_3)_2CO$ shows that the molecule adopts a dimeric "ladder-type" configuration with the hydrogen atom of the bridging hydroxide occupied in a H-bonding interaction with the solvent of crystallization.[5d]

In contrast to $\{[Bu_2SnX]_2O\cdot XBu_2SnOSnBu_2Y\}$, dimers comprising dissimilar symmetrically disubstituted tetrabutyldistannoxanes, $\{[Bu_2SnX]_2O\cdot[Bu_2SnY]_2O\}$, were not typically detected in solution. In all but one case, an irreversible conproportionation reaction led to the quantitative formation of the "mixed-ligand" distannoxane, $XBu_2SnOSnBu_2Y$ (eq 5). These

$$[Bu_2SnX]_2O + [Bu_2SnY]_2O \rightarrow 2XBu_2SnOSnBu_2Y \quad (5)$$

$$X = O_2CMe, Cl, OPh, OMe; \; Y = Cl, OPh, OMe$$

results, which parallel the exothermic ligand conproportionation reactions reported by Davies and Harrison[19] for the better known dibutyl mononuclear analogues, provide a convenient method for the synthesis of 1,3-disubstituted tetraalkyldistannoxanes. For example, $(CF_3CO_2)Bu_2SnOSnBu_2(OPh)$, $(MeCO_2)Bu_2SnOSnBu_2(OPh)$, and $(MeCO_2)Bu_2SnOSnBu_2(OMe)$ were prepared in good yield from their parent distannoxanes, $[Bu_2Sn(OPh)]_2O$, $[Bu_2Sn(OMe)]_2O$, and $[Bu_2Sn(O_2CCX_3)]_2O$ (X = H, F). The phenoxy derivatives have not previously been reported.

^{119}Sn NMR spectral data provided strong evidence that a reversible ligand-exchange reaction occurs in the special case where $[Bu_2SnCl]_2O$ is combined with $[Bu_2Sn(O_2CMe)]_2O$.

$$\underset{\mathrm{I}}{[Bu_2Sn(O_2CMe)]_2O} + \underset{\mathrm{II}}{[Bu_2SnCl]_2O} \rightleftharpoons \underset{\mathrm{III}}{2ClBu_2SnOSnBu_2(O_2CMe)} \quad (6)$$

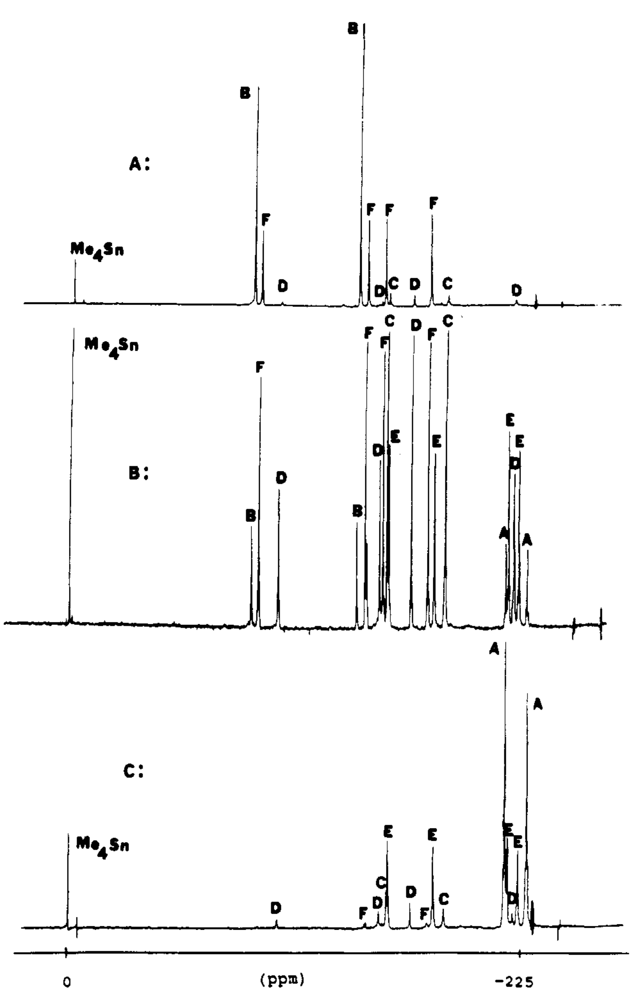

Figure 3. C_6D_6 solution ^{119}Sn NMR spectra of (a) 0.46 M/0.084 M $[Bu_2SnCl]_2O/ClBu_2SnOSnBu_2(O_2CMe)$, (b) 0.25 M/0.25 M $[Bu_2SnCl]_2O/ClBu_2SnOSnBu_2(O_2CMe)$, and (c) 0.084 M/0.46 M $[Bu_2SnCl]_2O/ClBu_2SnOSnBu_2(O_2CMe)$.

An 18-line ^{119}Sn NMR solution spectrum results from the addition of equimolar quantities of $[Bu_2SnCl]_2O$ and $[Bu_2Sn(O_2CMe)]_2O$ (Figure 3b). Two resonance pairs at -90.2, -142.8 and -218.5, -228.2 ppm indicate that the reactants, $\{[Bu_2SnCl]_2O\}_2$ (B, {II·II}) and $\{[Bu_2Sn(O_2CMe)]_2O\}_2$ (A, {I·I}), respectively, are present in solution. The remaining 14 lines can be accounted for by assuming two peaks for a symmetric, dimeric distannoxane for the product, $\{(MeCO_2)Bu_2SnOSnBu_2Cl\}_2$ (C, {III·III}), and four peaks for each of the three asymmetric dimers formed upon the three tin species participating in the equilibrium reaction (D, {I·II}; E, {I·III}; F, {II·III}). Assignment of all spectral resonances is readily accomplished by varying the reactant molar ratio. At a large molar ratio of $[Bu_2SnCl]_2O$ to $[Bu_2Sn(O_2CMe)]_2O$, the relative concentration of the three distannoxane monomeric units is [II] ≫ [III] > [I]; thus, the relative concentration of distannoxane dimers is $[\{II_2\}] \gg [\{II\cdot III\}] > [\{III_2\}] > [\{I\cdot II\}] > [\{I\cdot III\}] > [\{I_2\}]$. The ^{119}Sn NMR spectrum obtained from a 5-fold excess of $[Bu_2SnCl]_2O$ to $[Bu_2Sn(O_2CMe)]_2O$ is shown in Figure 3A. The resonances of B ({II·II}) are known; thus, the next four peaks of greatest intensity, -93.7, -146.9, -155.7, and -178.1 ppm (F), can be assigned to the asymmetric dimer {II·III}. Spectral assignment of {I·III} is similarly obtained from the ^{119}Sn NMR spectrum of a C_6D_6 solution that initially comprised $[Bu_2Sn(O_2CMe)]_2O/[Bu_2SnCl]_2O$ in a 5/1 molar ratio (Figure 3C). Under these conditions, the relative concentrations of the five distannoxane dimers follows the order $[\{I_2\}] \gg [\{I\cdot III\}] > [\{III_2\}] > [\{I\cdot II\}] > [\{II_2\}]$. The 1,3-diacetoxydistannoxane dimer (A) gives rise to an intense resonance pair at -217.0 and -228.3 ppm; thus, the four peaks at -158.9, -181.5, -218.4, and -223.8 (E) can be assigned to $\{ClBu_2SnOSnBu_2(O_2CMe)\cdot[Bu_2Sn(O_2CMe)]_2O\}$. The dramatic increase in intensity of the four resonances of {I·III} and

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(19) Davies, A. G.; Harrison, P. G. *J. Chem. Soc. C* **1967**, 298.

Table II. ^{119}Sn NMR Chemical Shifts of the Asymmetric Distannoxane Dimers {$[Bu_2SnX]_2O \cdot XBu_2SnOSnBu_2Y$}[a]

$XBu_2SnOSnBu_2Y$		$[Bu_2SnX]_2O$			
X	Y	X = Cl	X = O_2CMe	X = OC_6H_5	X = OCH_3
Cl	O_2CMe	−93.7, −146.9, −155.7, −178.1	−158.9, −181.5, −218.4, −223.8		
Cl	OC_6H_5	−87.1, −132.3, −132.7, −180.2		−135.7, −171.2, −175.4, −179.2	
Cl	OCH_3	−88.4, −134.1, −147.2, −181.7			−156.2, −172.3, −179.6, −185.6
O_2CMe	OC_6H_5		−200.8, −216.6, −219.8, −224.1	−179.8, −185.8, −193.4, −202.1	
O_2CMe	OCH_3		−200.7, −208.8, −218.0, −232.2		−171.6, −172.3, −181.6, −216.3
OC_6H_5	O_2CCF_3			−168.8, −173.6, −175.8, −184.5	

[a] All spectra accumulated at 25 °C in C_6D_6. $[Sn]_{tot}$ = 0.5 M.

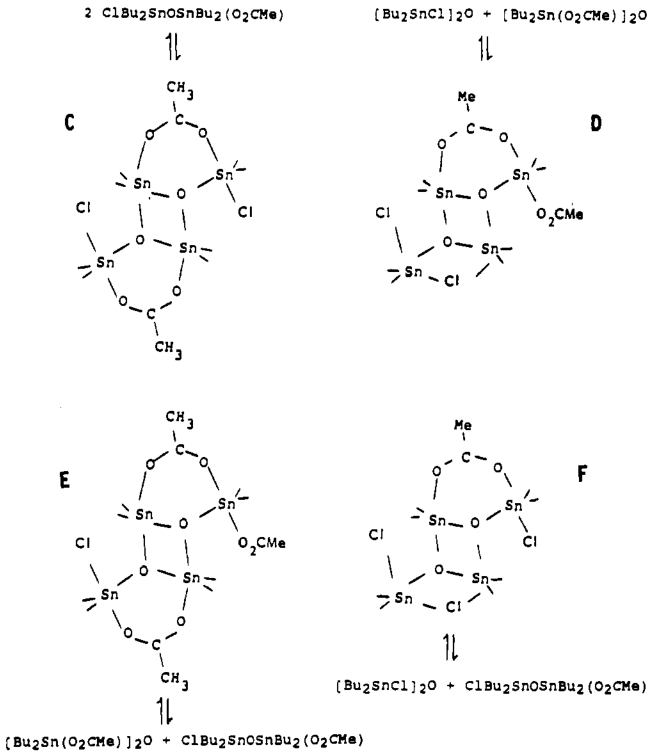

Figure 4. Proposed solution structures of (C) {$ClBu_2SnOSnBu_2(O_2CMe)$}$_2$, (D) {$[Bu_2Sn(O_2CMe)]_2O \cdot [Bu_2SnCl]_2O$}, (E) {$[Bu_2Sn(O_2CMe)]_2O \cdot ClBu_2SnOSnBu_2(O_2CMe)$}, and (F) {$[Bu_2SnCl]_2O \cdot ClBu_2SnOSnBu_2(O_2CMe)$}.

diminished intensity of the {II·III} peaks support the proposed equilibrium ligand-exchange reaction and the resulting appearance of asymmetric distannoxane dimers. The remaining six peaks present in spectra A–C of Figure 3 are assigned, again on the basis of concentration arguments, to a symmetric dimer {III_2} containing bridging carboxylate groups (Figure 4) −158.0, −186.8 ppm, (C) and the asymmetric dimer {I·II}, −107.8, −154.3, −170.1, −221.4 ppm (D). The downfield resonance, −103.8 ppm, indicative of a $SnCl_2O_3$ environment and the subtle chemical shift difference between the −221.4 peak and that assigned to the exocyclic tin atom of {$[Bu_2Sn(O_2CMe)]_2O$}$_2$ (−218.6 ppm) suggests the solution structure of {I·II} proposed in Figure 4 contains both a bridging chloride and a bridging carboxylate ligand. It must be pointed out that, empirically, one cannot distinguish {I·II} from {III_2}; thus, the Figure 4 structure may also be considered the asymmetric dimer, {$ClBu_2SnOSnBu_2(O_2CMe)$}$_2$. It is, perhaps, the inherent stability of the two six-membered heterocyclic rings of {II_2} and the poor donating ability of the chloride ligand that account for the reversibility of reaction 5.

Summary

Employment of ^{119}Sn NMR spectroscopy has again proved to be a useful tool to both identify organotin reaction products and determine their stereochemistry. For the first time, convincing evidence has been provided which demonstrates that dissimilar tetraalkyldistannoxane units reversibly couple in solution to form the now well-known "ladder" or "staircase" structure. Since, in this case, each tin atom in the structure is chemically nonequivalent, four ^{119}Sn NMR resonances are observed. By invoking a ladder structure for all possible distannoxane pairs involved in a reversible exchange process and by varying reactant molar ratios, one may successfully analyze relatively complex spectra.

Ligand conproportionation reactions were typically shown to result in the quantitative formation 1,3-disubstituted tetrabutyldistannoxanes, thus providing a convenient synthetic route to this class of compounds.

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Registry No. I, 5967-09-9; II, 10428-19-0; III, 34072-45-2; $(MeCO_2)Bu_2SnOSnBu_2(OMe)$, 2750-43-8; $[Bu_2Sn(OMe)]_2O$, 5926-85-2; $(MeCO_2)Bu_2SnOSnBu_2(OH)$, 1724-80-7; $ClBu_2SnOSnBu_2(OMe)$, 34072-42-9; $(MeCO_2)Bu_2SnOSnBu_2(OC_6H_5)$, 34072-44-1; ^{119}Sn, 14314-35-3; $[Bu_2Sn(OC_6H_5)]_2O$, 27440-74-0; $(CF_3CO_2)Bu_2SnOSnBu_2(OC_6H_5)$, 120477-31-8; $[Bu_2Sn(O_2CCF_3)]_2O$, 41311-29-9; $ClBu_2SnOSnBu_2(OC_6H_5)$, 27652-39-7.