

actions, and reduced solvent polarity or lower effective dielectric media have recently been discussed<sup>28</sup> for active-site cavities of enzymes, especially for carboxypeptidase A. The possibility of reducing the effective dielectric constant close to a metal ion via a nearby hydrophobic micelle offers a very subtle tool for nature, especially as the energy differences<sup>46</sup> involved are very small. For example, in the present study the maximum stability increase observed equals only 0.29 log unit, corresponding to -1.7 kJ/mol, but this leads already to a formation degree for the closed species (eq 6a) of 49%. Assuming that such a closed conformation of

a complex is the reactive species in an enzymic process, it is evident that some few percent of this species are enough for a continuous flow of the reaction, and the desired selectivity is in this way also achieved.

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## Novel Drums and Mixed-Drum Organooxotin Clusters from Carboxylic, Phosphinic, and Phosphoric Acids<sup>1,2</sup>

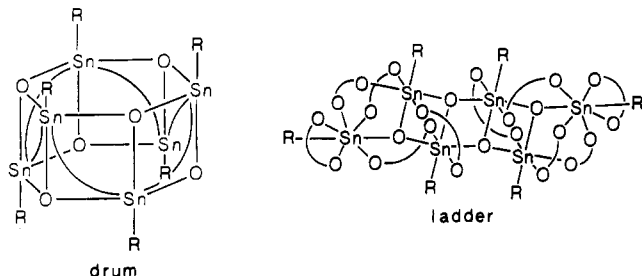
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A variety of new "drum" geometries were synthesized by a condensation reaction of an alkylstannonic acid with either a carboxylic acid or a phosphorus-based acid. The structures of  $[\text{MeSn}(\text{O})\text{O}_2\text{CMe}]_6$  (1),  $[(\text{MeSn}(\text{O})\text{O}_2\text{CMe})(\text{MeSn}(\text{O})\text{O}_2\text{P}(t\text{-Bu}))_2]_3$  (2), and  $[n\text{-BuSn}(\text{O})\text{O}_2\text{P}(\text{OPh})_2]_6$  (3) were revealed by X-ray analysis. Interestingly, the mixed-drum composition 2 resulted from the reaction of the drum formulation 1 with di-*tert*-butylphosphinic acid. Also an oxygen-capped cluster  $[(n\text{-BuSn}(\text{OH})\text{O}_2\text{P}(\text{OPh})_2)_3\text{O}][(\text{PhO})_2\text{PO}_2]$  (8) is formed when the same reaction that was used to prepare 3 is conducted at 25 °C rather than at reflux. 1 crystallizes in the rhombohedral space group  $R\bar{3}$  with  $a_H = 17.420$  (5) Å,  $c_H = 9.963$  (2) Å, and  $Z = 3$ . 2 crystallizes in the monoclinic space group  $C2/c$  with  $a = 21.495$  (4) Å,  $b = 28.032$  (6) Å,  $c = 10.013$  (2) Å,  $\beta = 95.34$  (2)°, and  $Z = 4$ . 3 crystallizes in the monoclinic space group  $P2_1/n$  with  $a = 14.252$  (3) Å,  $b = 17.346$  (2) Å,  $c = 21.987$  (3) Å,  $\beta = 91.62$  (1)°, and  $Z = 2$ . The conventional unweighted residuals were 0.023 (1), 0.036 (2), and 0.040 (3).

### Introduction

In several recent articles,<sup>1b,3-6</sup> we have identified new structural forms of organotin compounds. X-ray analysis reveals all are oxotin derivatives and possess hexacoordinated tin atoms in a four-membered stannoxane ring,  $(-\text{Sn}-\text{O}-)_2$ , as a common structural feature. "Drum" compositions  $[\text{R}'\text{Sn}(\text{O})\text{O}_2\text{CR}]_6$  and "ladders"  $[(\text{R}'\text{Sn}(\text{O})\text{O}_2\text{CR})_2\text{R}'\text{Sn}(\text{O}_2\text{CR})_3]_2$  result from the reaction of an aryl- or alkylstannonic acid with a carboxylic acid.<sup>1b,c</sup> An alternate route makes use of an organotin trichloride in reaction with a salt of the carboxylic acid.



When phosphorus-based acids are used instead of a carboxylic acid, the geometrical forms isolated are more diverse, although

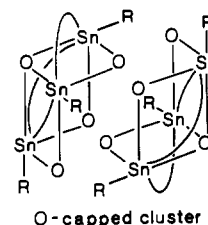
a ladder structure has not been obtained thus far with this type of ligand. We have reported a cube<sup>6</sup> and an oxygen-capped cluster<sup>5</sup> resulting from the reactions of *n*-butylstannonic acid with dicyclohexylphosphinic acid and diphenylphosphinic acid, respectively. The cube has the composition  $[n\text{-BuSn}(\text{O})\text{O}_2\text{P}(\text{C}_6\text{H}_{11})_2]_4$  while the oxygen-capped cluster exhibits the ionic formula  $[(n\text{-BuSn}(\text{OH})\text{O}_2\text{PPh}_2)_3\text{O}][\text{Ph}_2\text{PO}_2]$ . Hydrogen bonding is present between the hydroxyl groups in the cationic portion and the oxygen atoms of the phosphinate anion.

The drum and open-drum or "ladder" forms,  $[n\text{-BuSn}(\text{O})\text{O}_2\text{C}(\text{C}_6\text{H}_{11})]_6$  and  $[(n\text{-BuSn}(\text{O})\text{O}_2\text{CC}_6\text{H}_{11})_2(n\text{-BuSn}(\text{O}_2\text{CC}_6\text{H}_{11})_3)]_2$ , which contains the same organotin group and cyclohexanoate ligand, interconvert as shown by <sup>119</sup>Sr NMR.<sup>1b</sup> Hydrolytically, the drum form is more stable. The hydrolysis reaction in eq 1 illustrates this. In excess carboxylic acid, the

$$[(\text{R}'\text{Sn}(\text{O})\text{O}_2\text{CR})_2\text{R}'\text{Sn}(\text{O}_2\text{CR})_3]_2 + 2\text{H}_2\text{O} \rightarrow [\text{R}'\text{Sn}(\text{O})\text{O}_2\text{CR}]_6 + 4\text{RCO}_2\text{H} \quad (1)$$

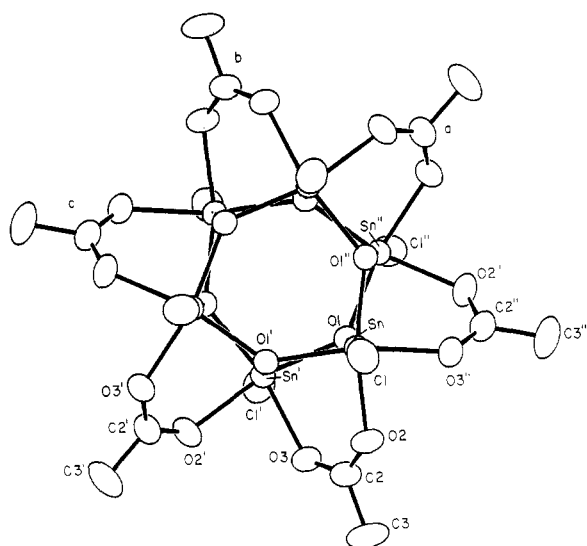
reaction may be reversed and the drum opens up, yielding the open drum or ladder.

Examination of the structural relationships among the forms that have been isolated suggests that additional oligomers in other cluster arrangements are possible. For example, the tin-oxygen framework of the oxygen-capped cluster<sup>5</sup> can be viewed as a cube with one corner removed.

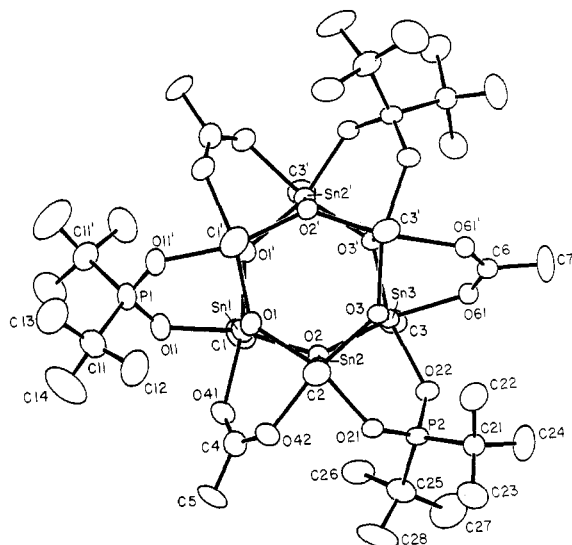


In this paper we explore further routes to these interesting new oligomeric oxotin compounds using acetate, di-*tert*-butyl-

- (1) (a) Organotin Clusters 3. (b) Part 2; Chandrasekhar, V.; Schmid, C. G.; Burton, S. D.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1987**, *26*, 1050-1056. (c) Part 1: Holmes, R. R.; Schmid, C. G.; Chandrasekhar, V.; Day, R. O.; Holmes, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 1408-1414.
- (2) Presented in part at the 195th National Meeting of the American Chemical Society Toronto, Canada, June 1988; INOR 346 and 508.
- (3) Chandrasekhar, V.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1985**, *24*, 1970-1971.
- (4) Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Shafeizad, S.; Harland, J. J.; Rau, D. N.; Holmes, J. M. *Phosphorus Sulfur* **1986**, *28*, 91-98.
- (5) Day, R. O.; Holmes, J. M.; Chandrasekhar, V.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 940-941.
- (6) Kumara Swamy, K. C.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 5546-5548.



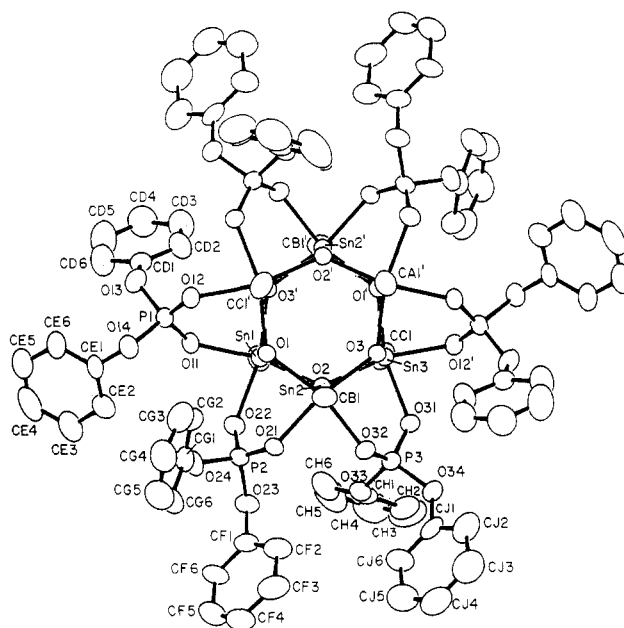
**Figure 1.** ORTEP plot of  $[\text{MeSn}(\text{O})\text{O}_2\text{CMe}]_6$  (**1**) with thermal ellipsoids at the 50% probability level. The view is down the crystallographic  $S_6$  axis. Symmetry operators: single prime,  $y, y-x, -z$ ; double prime,  $x-y, x, -z$ ; a,  $-y, x-y, z$ ; b,  $-x, -y, -z$ ; c,  $y-x, -x, z$ . Hydrogen atoms are omitted for purposes of clarity.



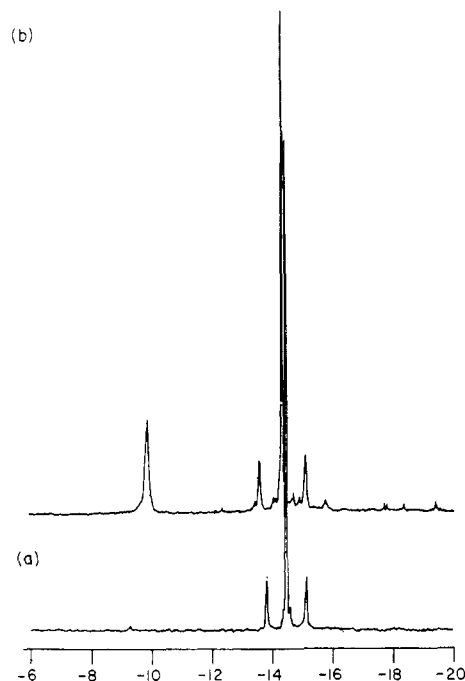
**Figure 2.** ORTEP plot of  $[(\text{MeSn}(\text{O})\text{O}_2\text{CMe})(\text{MeSn}(\text{O})\text{O}_2\text{P}(t\text{-Bu})_2)]_3$  (**2**) with thermal ellipsoids at the 50% probability levels. Primed atoms are related to unprimed ones by a crystallographic 2-fold axis ( $-x, y, 1/2-z$ ).

phosphinate, and diphenylphosphate as ligands. This range of ligand compositions was chosen to determine their influence on the ease of formation of drum clusters. Earlier work<sup>7a</sup> with acetate,

(7) (a) Lambourne, H. *J. Chem. Soc.* **1922**, 121(2), 2533–2540. (b) Lambourne, H. *J. Chem. Soc.* **1924**, 125, 2013–2015. (c) The preparation of **1** given in this paper is a modification of that reported by Lambourne.<sup>7a</sup> (d) Other stannoxane derivatives with carboxylate ligands having the composition  $\text{PhSn}(\text{O})\text{O}_2\text{CR}$ , where  $\text{R} = (\text{CH}_2)_8\text{CH}=\text{CH}_2$  and  $(\text{CH}_2)_{16}\text{Me}$ , were reported earlier: Ford, B. F. E.; Liengme, B. V.; Sams, J. R. *J. Organomet. Chem.* **1969**, 19, 53–65. Like Lambourne,<sup>7a</sup> Ford et al. favored cyclic trimeric structures but ones that contained pentacoordinated tin atoms instead of tetraordinated ones. For related derivatives,  $\text{PhSn}(\text{O})\text{O}_2\text{CR}$ , where  $\text{R} = t\text{-Bu}$ ,  $\text{CCl}_3$ , and  $\text{CF}_3$ , polymeric structures containing bridging oxygen atoms were suggested: Poller, R. C.; Ruddick, J. N. R.; Taylor, B.; Toley, D. L. B. *J. Organomet. Chem.* **1970**, 24, 341–346. More recently, Roy and Ghosh suggested linear or cyclic polymeric structures for carboxylate compositions, e.g.,  $[\text{PhSn}(\text{OH})_2\text{O}_2\text{CMe}]_n$  and  $[\text{PhSn}(\text{O})\text{O}_2\text{CMe}]_n$  (Roy, A.; Ghosh, A. K. *Inorg. Chim. Acta* **1978**, 29, L275–L277; **1977**, 24, L89–L91), and Otera et al. (Otera, J.; Yano, T.; Kunimoto, E.; Nakata, T. *Organometallics* **1984**, 3, 426–431) obtained the butyltin triphosphate  $\text{BuSn}[\text{O}_2\text{P}(\text{OBu})_2]_3$  as an oil. Further polymeric species based on a stannoxane framework are suggested for diorganotin phosphates, e.g.,  $\text{R}_2\text{Sn}[\text{O}_2\text{P}(\text{OPh})]_2$  and  $\text{R}_2\text{Sn}[\text{O}_2\text{P}(\text{OPh})_2]_2$  in the solid state: Barbieri, R.; Alonzo, G.; Herber, R. H. *J. Chem. Soc., Dalton Trans.* **1987**, 789–794.

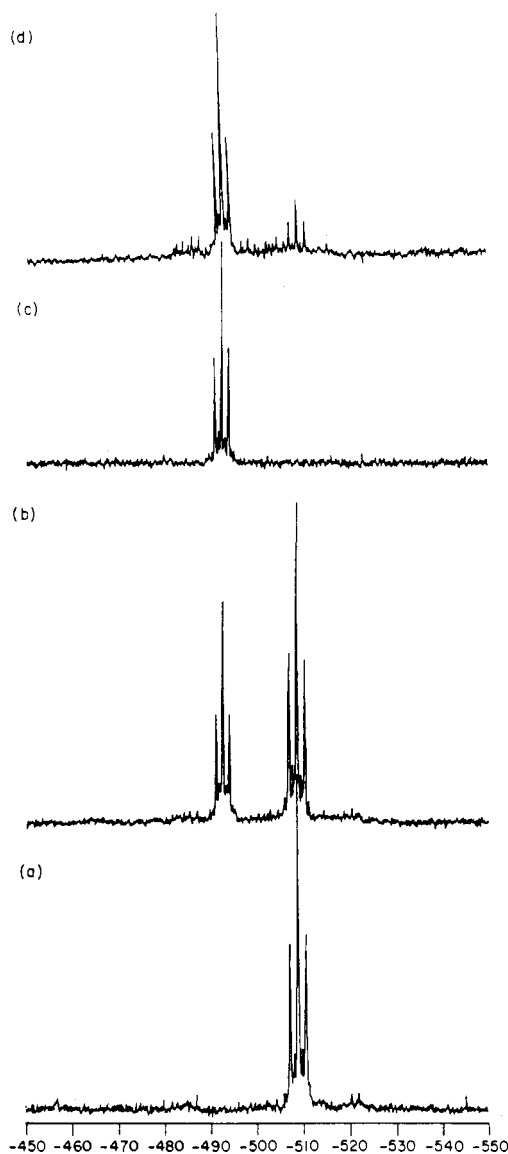


**Figure 3.** ORTEP plot of  $[n\text{-BuSn}(\text{O})\text{O}_2\text{P}(\text{OPh})_2]_6$  (**3**) with thermal ellipsoids at the 30% probability level. Primed atoms are related to unprimed ones by a crystallographic inversion center ( $-x, -y, -z$ ). Pendant atoms of the *n*-butyl groups (CA2–CA4, CA2 bonded to CA1, etc.) are omitted for purposes of clarity.



**Figure 4.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of (a) the drum  $[n\text{-BuSn}(\text{O})\text{O}_2\text{P}(\text{OPh})_2]_6$  (**3**) and (b) the oxygen-capped cluster  $[(n\text{-BuSn}(\text{OH})\text{O}_2\text{P}(\text{OPh})_2)_3\text{O}][\text{O}_2\text{P}(\text{OPh})_2]$  (**8**).

for example, suggested the formation of a trimeric ring structure on interaction with methylstannonic acid. In addition to the preparative methods previously employed,<sup>1–6</sup> the reactivity of the drum composition itself in eliciting further reaction was attempted. Reported here are the synthesis and X-ray analysis of the drum composition,  $[\text{MeSn}(\text{O})\text{O}_2\text{CMe}]_6$  (**1**), the mixed drum,  $[(\text{MeSn}(\text{O})\text{O}_2\text{CMe})(\text{MeSn}(\text{O})\text{O}_2\text{P}(t\text{-Bu})_2)]_3$  (**2**), containing both carboxylate and phosphinate ligands, and the phosphate drum,  $[n\text{-BuSn}(\text{O})\text{O}_2\text{P}(\text{OPh})_2]_6$  (**3**). The interesting interconversion between drum and oxygen-capped forms involving the latter derivative is described, which suggests the close relative stability of these cluster units. Also other drum compositions **4–7** were synthesized and their solution structures characterized by  $^{119}\text{Sn}$  NMR spectroscopy.



**Figure 5.**  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectra of (a) the oxygen-capped cluster  $[(n\text{-BuSn}(\text{OH})\text{O}_2\text{P}(\text{OPh})_2)_3\text{O}][\text{O}_2\text{P}(\text{OPh})_2]$  (**8**) (b) partial conversion (40%) of the oxygen-capped cluster **8** to drum **3** on heating **8** in benzene for  $1/2$  h, (c) a  $\text{CDCl}_3$  solution of the crystals of the drum  $[n\text{-BuSn}(\text{O})\text{O}_2\text{P}(\text{OPh})_2]_6$  (**3**) obtained from heating the product shown in part b with toluene for 24 h, and (d) the same  $\text{CDCl}_3$  solution used in part c but after 5 days at  $25^\circ\text{C}$ , showing partial conversion of drum **3** to the oxygen-capped cluster **8**.

## Experimental Section

Chemicals were obtained from Aldrich, Fisher Scientific, and Alfa and used without further purification. Methylstannonic acid was prepared according to the procedure given by Lambourne.<sup>7a,b</sup> Di-*tert*-butylphosphinic acid was prepared by literature methods.<sup>8</sup> *n*-Butylstannonic acid was a gift from Koriyama Kasei Co., Ltd. (Koriyama, Japan) and was purified by using excess KOH in  $\text{CHCl}_3$  to remove a small amount of  $n\text{-BuSn}(\text{OH})\text{Cl}_2$  and/or  $n\text{-BuSn}(\text{OH})_2\text{Cl}$  suspected<sup>1b</sup> as a contaminant. Solvents used were of HPLC grade (Fisher Scientific). Further purification was done according to standard procedures.<sup>9</sup>

$^1\text{H}$ ,  $^{31}\text{P}$ , and  $^{119}\text{Sn}$  NMR spectra (proton decoupled) were recorded on a Varian X-L 300 FT/NMR spectrometer equipped with a multinuclear broad-band probe and operated at 300, 121.4, and 11.862 MHz, respectively. Resonances are referenced vs tetramethylsilane ( $^1\text{H}$ ), tetramethyltin (external standard,  $^{119}\text{Sn}$ ), and 85% orthophosphoric acid (external standard,  $^{31}\text{P}$ ). Infrared spectra were recorded by using KBr windows on a Perkin-Elmer Model 180 spectrometer.

**Hexameric Methyloxotin Acetate**  $[\text{MeSn}(\text{O})\text{O}_2\text{CMe}]_6$  (**1**).<sup>7c</sup> Methylstannonic acid (3.88 g, 23.2 mmol) was dissolved in 20 mL (349 mmol)

of glacial acetic acid. To this was added 15 mL of methanol, and the solution was refluxed. Within 3 h, a white precipitate appeared. After several additional hours, a white amorphous solid was isolated; mp  $315^\circ\text{C}$  dec (lit.<sup>7a</sup> mp  $280^\circ\text{C}$  dec) (yield 3.75 g, 77%). Cubical crystals were obtained for X-ray analysis from a reaction mixture, which was set aside for several weeks. Infrared spectra of the amorphous solid and crystalline material were identical. IR (Nujol) ( $\text{cm}^{-1}$ ): 1525, 1595 ( $\nu_{\text{COO}}$ ); 623 ( $\nu_{\text{Sn-O}}$ ). Due to insolubility, no NMR spectra were recorded except in phenol where decomposition is indicated.  $^{119}\text{Sn}$  NMR (phenol) (ppm): -473.2 (s), -480.8 (s), -490.4 (s), -498.9 (s). Anal. Calcd for  $\text{C}_{18}\text{H}_{36}\text{O}_{18}\text{Sn}_6$ : C, 17.26; H, 2.94. Found: C, 17.47; H, 2.90.

**Trimeric (Methyloxotin acetate)methyloxotin Di-*tert*-butylphosphinate**  $[(\text{MeSn}(\text{O})\text{O}_2\text{CMe})(\text{MeSn}(\text{O})\text{O}_2\text{P}(t\text{-Bu})_2)]_3$  (**2**). A mixture of  $[\text{MeSn}(\text{O})\text{O}_2\text{CMe}]_6$  (**1**) (1.365 g, 6.54 mmol), di-*tert*-butylphosphinic acid (0.969 g, 5.45 mmol), toluene (100 mL), and methanol (15 mL) were heated under reflux for 5 h, during which time about 10 mL of the solvent was removed by using a Dean-Stark apparatus. A homogeneous solution resulted. Removal of solvent by a rotovaporator afforded a residue, which was dissolved in dichloromethane (30 mL). Removal of the latter solvent slowly at room temperature yielded **2** as needles, mp  $> 370^\circ\text{C}$  (yield 1.23 g, 70% based on **1**).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) (ppm): 2.02 (s, *Me-C*(acetyl)), 1.20 (d, *t-Bu-P*,  $^3J(\text{P-H}) = 14.0$  Hz), 0.55 (*Me-Sn*,  $^2J(^{119}\text{Sn-H}) = 120$  Hz).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ) (ppm): 63.1 (s with  $^{119}\text{Sn}$  satellites,  $^2J(\text{Sn-O-P}) = 122$  Hz).  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ ) (ppm): -470.7 (d,  $^2J(\text{Sn-O-P}) = 125$  Hz). Anal. Calcd for  $\text{C}_{36}\text{H}_{81}\text{O}_{18}\text{P}_3\text{Sn}_6$ : C, 26.89; H, 5.07. Found: C, 26.89; H, 5.19.

**Hexameric *n*-Butyloxotin Diphenyl Phosphate**  $[n\text{-BuSn}(\text{O})\text{O}_2\text{P}(\text{OPh})_2]_6$  (**3**). To *n*-butylstannonic acid (1.00 g, 4.79 mmol) in 200 mL of dry benzene was added diphenylphosphoric acid (1.20 g, 4.80 mmol). The reaction mixture was heated under reflux for 4 h. The water formed was removed by azeotropic distillation with the use of a Dean-Stark apparatus. Removal of solvent in vacuo yielded a solid. It was redissolved in hot benzene (20 mL) and hexane (8 mL) and kept in the refrigerator. Crystals suitable for X-ray diffraction were obtained; mp  $245\text{--}247^\circ\text{C}$  (yield 1.6 g, 74.7%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) (ppm): multiplets centered at 7.2, 7.1, 7.0, 1.7, 1.4, 1.3, 0.8.  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ ) (ppm): -492.7 (t,  $^2J(^{119}\text{Sn-O-P}) = 162.5$  Hz). Elemental analysis agreed with the formula  $[n\text{-BuSn}(\text{O})\text{O}_2\text{P}(\text{OPh})_2]_{1/2} \cdot \text{C}_6\text{H}_6$ . Anal. Calcd for  $\text{C}_{99}\text{H}_{117}\text{O}_{30}\text{P}_6\text{Sn}_6$ : C, 44.29; H, 4.39. Found: C, 44.43; H, 4.44.

The preparation of additional drum compounds followed the general procedure given for **3**. The analytical and spectroscopic data for these materials are listed below.

**Hexameric *n*-Butyloxotin *p*-Chlorobenzene**  $[n\text{-BuSn}(\text{O})\text{O}_2\text{CC}_6\text{H}_4\text{Cl-p}]_6$  (**4**). Mp:  $329^\circ\text{C}$  dec (yield 62.3%). IR (Nujol) ( $\text{cm}^{-1}$ ): 1575, 1520 ( $\nu_{\text{COO}}$ ); 540 ( $\nu_{\text{Sn-O}}$ ). Anal. Calcd for  $\text{C}_{66}\text{H}_{78}\text{O}_{18}\text{Cl}_6\text{Sn}_6$ : C, 38.04; H, 3.77. Found: C, 37.92; H, 3.81.

**Hexameric *n*-Butyloxotin Cyclobutanoate**  $[n\text{-BuSn}(\text{O})\text{O}_2\text{C}(\text{C}_4\text{H}_7)]_6 \cdot 2\text{C}_6\text{H}_6$  (**5**). Mp:  $275^\circ\text{C}$  (yield 81.9%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) (ppm): 7.37 (s); multiplets centered at 3.00, 2.15, 1.70, 1.60, 1.30, and 0.80. IR (Nujol) ( $\text{cm}^{-1}$ ): 1575, 1525 ( $\nu_{\text{COO}}$ ); 605 ( $\nu_{\text{Sn-O}}$ ). Anal. Calcd for  $\text{C}_{66}\text{H}_{108}\text{O}_{18}\text{Sn}_6$ : C, 41.69; H, 5.72. Found: C, 41.16; H, 5.53.

**Hexameric *n*-Butyloxotin Cyclopropanoate**  $[n\text{-BuSn}(\text{O})\text{O}_2\text{C}(\text{C}_3\text{H}_5)]_6$  (**6**). Mp:  $320^\circ\text{C}$  dec (yield 86.7%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) (ppm): multiplets centered at 1.60, 1.35, 1.17, 0.95, and 0.78.  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ ) (ppm): -488.14. IR (Nujol) ( $\text{cm}^{-1}$ ): 1570, 1530 ( $\nu_{\text{COO}}$ ); 610 ( $\nu_{\text{Sn-O}}$ ). Anal. Calcd for  $\text{C}_{48}\text{H}_{84}\text{O}_{18}\text{Sn}_6$ : C, 34.70; H, 5.10. Found: C, 34.51; H, 4.85.

**Hexameric *n*-Butyloxotin Benzoate**  $[n\text{-BuSn}(\text{O})\text{O}_2\text{CC}_6\text{H}_5]_6$  (**7**). Mp:  $335\text{--}342^\circ\text{C}$  (yield 85.4%).  $^{119}\text{Sn}$  NMR ( $\text{C}_6\text{H}_6$ ) (ppm): -488.3. Anal. Calcd for  $\text{C}_{66}\text{H}_{84}\text{O}_{18}\text{Sn}_6$ : C, 42.22; H, 4.51. Found: C, 42.12; H, 4.43.

Benzoate **7** was redissolved in benzene and stored in a refrigerator for 2 days. A viscous solution resulted, which yielded a glassy substance on evaporation of the solvent; mp  $318\text{--}323^\circ\text{C}$ .  $^{119}\text{Sn}$  NMR ( $\text{C}_6\text{H}_6$ ) (ppm): -488.7, -518.2, -520.1, -525.5, -554.2. Anal. Calcd for  $\text{C}_{66}\text{H}_{84}\text{O}_{18}\text{Sn}_6$ : C, 42.22; H, 4.51. Found: C, 41.92; H, 4.28.

**Preparation of the Oxygen-Capped Cluster**  $[(n\text{-BuSn}(\text{OH})\text{O}_2\text{P}(\text{OPh})_2)_3\text{O}][\text{O}_2\text{P}(\text{OPh})_2]$  (**8**) and Its Conversion to the Drum  $[n\text{-BuSn}(\text{O})\text{O}_2\text{P}(\text{OPh})_2]_6$  (**3**). A solution of diphenyl phosphate (1.02 g, 4.07 mmol) and *n*-butylstannonic acid (0.847 g, 4.07 mmol) in benzene was allowed to stand at  $25^\circ\text{C}$  for 48 h. Removal of the solvent at a temperature below  $20^\circ\text{C}$  was followed by addition of diethyl ether (20 mL) to the residue. Insoluble material (0.2 g), which formed after keeping the solution at  $25^\circ\text{C}$  for 48 h, was filtered off. Removal of the solvent at  $20^\circ\text{C}$  afforded the oxygen-capped cluster **8** as an oil (1.5 g, 95% based on phosphate used). Attempts to purify this material from traces of water and other impurities have not been successful; however, NMR ( $^1\text{H}$ ,  $^{31}\text{P}$ ,  $^{119}\text{Sn}$ ) data suggested that it is almost pure ( $\sim 96\%$ ); cf. Figures 4 and 5.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) (ppm): 7.9 (3 H, s, *OH*, disappears on  $\text{D}_2\text{O}$  exchange), 6.9–7.5 (40 H, m,  $\text{OC}_6\text{H}_5$ ), 1.0–1.9 (18 H, m,  $\text{SnCH}_2\text{-CH}_2\text{-CH}_2$ ), 0.72 (9H, t,  $\text{CH}_3$ ,  $^3J = 7.1$  Hz).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ) (ppm): -14.33 [3 P, s with  $^{117,119}\text{Sn}$  satellites, bridging  $(\text{PhO})_2\text{PO}_2$ ,  $^2J(^{117,119}\text{Sn-}$

(8) Mason, G. W.; Lewey, S. J. *Inorg. Nucl. Chem.* **1974**, *36*, 911–915.

(9) Vogel, A. I. *Textbook of Practical Organic Chemistry*; Longman: London, 1978.

**Table I.** Atomic Coordinates in Crystalline [MeSn(O)<sub>2</sub>CMe]<sub>6</sub> (1)<sup>a</sup>

atom <sup>b</sup>	x	y	z	B <sub>equiv</sub> , <sup>c</sup> Å <sup>2</sup>
Sn	0.03723 (1)	-0.10413 (1)	0.11685 (2)	2.280 (5)
O1	0.0315 (1)	-0.0897 (1)	-0.0914 (3)	2.41 (5)
O2	-0.0221 (2)	-0.2448 (2)	0.0840 (3)	3.38 (6)
O3	-0.1148 (2)	-0.2693 (2)	-0.0867 (3)	3.06 (6)
C1	0.0393 (3)	-0.1167 (3)	0.3283 (4)	3.8 (1)
C2	-0.0770 (3)	-0.2937 (2)	-0.0039 (4)	3.26 (9)
C3	-0.0973 (3)	-0.3875 (3)	-0.0103 (5)	5.0 (1)

<sup>a</sup>Numbers in parentheses are estimated standard deviations. <sup>b</sup>Atoms are labeled to agree with Figure 1. <sup>c</sup>Equivalent isotropic thermal parameters are calculated as  $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$ .

**Table II.** Selected Distances (Å) and Angles (deg) for [MeSn(O)<sub>2</sub>CMe]<sub>6</sub> (1)<sup>a</sup>

Distances			
Sn-O1	2.098 (2)	Sn-O3''	2.162 (3)
Sn-O1'	2.094 (2)	Sn-C1	2.120 (4)
Sn-O1''	2.081 (2)	O2-C2	1.263 (4)
Sn-O2	2.155 (2)	O3-C2	1.254 (6)
Angles			
O1-Sn-O1'	77.7 (1)	O1''-Sn-O3''	85.6 (1)
O1-Sn-O1''	78.00 (9)	O1''-Sn-C1	101.5 (1)
O1-Sn-O2	87.8 (1)	O2-Sn-O3''	79.5 (1)
O1-Sn-O3''	88.6 (1)	O2-Sn-C1	93.2 (1)
O1-Sn-C1	177.6 (2)	O3''-Sn-C1	93.7 (2)
O1'-Sn-O1''	103.9 (1)	Sn-O1-Sn'	100.4 (1)
O1'-Sn-O2	87.0 (1)	Sn-O1-Sn''	99.97 (9)
O1'-Sn-O3''	161.2 (1)	Sn'-O1-Sn''	133.0 (1)
O1'-Sn-C1	100.2 (1)	Sn-O2-C2	130.1 (3)
O1''-Sn-O2	159.6 (1)	Sn'-O3-C2	130.6 (2)

<sup>a</sup>Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 1.

O-P) = 181.2, 188.7 Hz), -9.55 (1 P, s free (PhO)<sub>2</sub>PO<sub>2</sub><sup>-</sup>). <sup>119</sup>Sn NMR (CDCl<sub>3</sub>) (ppm): -508.81 (t, <sup>2</sup>J(Sn-O-P) = 189.2 Hz, <sup>2</sup>J(<sup>119</sup>Sn-O-<sup>117</sup>Sn) = 202 Hz).

A portion of the above oil **8** (0.8 g) was heated under reflux in benzene (40 mL) for 1/2 h with azeotropic removal of water. The <sup>119</sup>Sn NMR (CDCl<sub>3</sub>) spectrum of the residue after stripping off all the solvent from the reaction mixture showed that 40% of the oxygen-capped cluster **8** was converted to the drum **3** (Figure 5). Further heating of this material in toluene (50 mL) for 2 h with azeotropic removal of water followed by concentrating the residue to ~10 mL gave colorless crystals of the drum (0.5 g, 65%) **3**, identified by its NMR spectra (Figure 4a). <sup>1</sup>H NMR (CDCl<sub>3</sub>) (ppm): 7.0-7.2 (m, OC<sub>6</sub>H<sub>5</sub>). 1.0-1.5 (m, SnCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 0.79 (t, <sup>3</sup>J = 7.2 Hz). <sup>31</sup>P NMR (CDCl<sub>3</sub>) (ppm): -14.47 (<sup>2</sup>J(Sn-O-P) = 159.8 Hz). <sup>119</sup>Sn NMR (CDCl<sub>3</sub>) (ppm): -492.67 (t, <sup>2</sup>J(Sn-O-P) = 162.6 Hz).

**X-ray Studies.** All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ( $\lambda = 0.71073$  Å) at an ambient temperature of  $23 \pm 2$  °C. Details of the experimental procedures have been described previously.<sup>10</sup>

Crystals were mounted in thin-walled glass capillaries, which were sealed as a precaution against moisture sensitivity. Data were collected by using the  $\theta$ - $2\theta$  scan mode with  $3^\circ \leq 2\theta_{\text{MoK}\alpha} \leq 55^\circ$  for **1** and  $3^\circ \leq 2\theta_{\text{MoK}\alpha} \leq 43^\circ$  for **2** and **3**.

The structures were solved by use of Patterson and difference Fourier techniques and were refined by full-matrix least squares.<sup>11</sup> For **1** and **2**, all computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs. For **3** computational procedures have been described previously.<sup>10</sup>

**X-ray Study for [MeSn(O)<sub>2</sub>CMe]<sub>6</sub> (1).** The colorless crystal used for the X-ray study was polyfaceted and approximately spherical with a diameter of 0.24 mm.

**Crystal Data:** [MeSn(O)<sub>2</sub>CMe]<sub>6</sub>, rhombohedral space group  $R\bar{3}$ , hexagonal setting ( $C_{3i}$ -No. 148),<sup>12</sup>  $a_{\text{H}} = 17.420$  (5) Å,  $c_{\text{H}} = 9.963$  (2)

(10) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076-3081.

(11) The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w^{1/2} = 2F_o(Lp)/\sigma_l$ . Mean atomic scattering factors were taken from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 72-98. Real and imaginary dispersion corrections were taken from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 149-150.

**Table III.** Atomic Coordinates in Crystalline [(MeSn(O)<sub>2</sub>CMe)(MeSn(O)<sub>2</sub>P(*t*-Bu)<sub>2</sub>)]<sub>3</sub> (2)<sup>a</sup>

atom <sup>b</sup>	x	y	z	B <sub>equiv</sub> , <sup>c</sup> Å <sup>2</sup>
Sn1	0.06187 (3)	0.26222 (2)	0.35468 (6)	3.85 (2)
Sn2	0.09012 (3)	0.19486 (2)	0.10938 (6)	3.29 (1)
Sn3	0.06100 (3)	0.12596 (2)	0.35530 (6)	3.07 (1)
P1	0.000	0.3661 (1)	0.250	6.3 (1)
P2	0.1915 (1)	0.1086 (1)	0.2064 (3)	3.62 (5)
O1	0.0348 (3)	0.2536 (2)	0.1506 (6)	3.9 (1)
O2	0.0952 (3)	0.1936 (2)	0.3187 (6)	3.4 (1)
O3	0.0352 (3)	0.1357 (2)	0.1499 (6)	3.3 (1)
O11	0.0472 (3)	0.3372 (2)	0.3347 (7)	5.6 (2)
O21	0.1692 (3)	0.1494 (2)	0.1142 (6)	3.7 (1)
O22	0.1475 (3)	0.0958 (2)	0.3095 (6)	3.8 (1)
O41	0.1541 (3)	0.2860 (3)	0.3078 (7)	4.9 (2)
O42	0.1669 (3)	0.2467 (3)	0.1183 (6)	4.7 (2)
O61	0.0363 (3)	0.0507 (2)	0.3362 (6)	3.9 (1)
C1	0.0851 (6)	0.2634 (4)	0.566 (1)	6.1 (3)
C2	0.0770 (5)	0.1970 (4)	-0.102 (1)	5.1 (3)
C3	0.0847 (5)	0.1222 (4)	0.5684 (9)	4.9 (3)
C4	0.1839 (5)	0.2771 (4)	0.210 (1)	5.0 (3)
C5	0.2446 (5)	0.3022 (4)	0.202 (1)	6.5 (3)
C6	0.000	0.0310 (5)	0.250	4.3 (3)
C7	0.000	-0.0233 (5)	0.250	8.2 (5)
C11	0.0416 (6)	0.4008 (5)	0.127 (1)	8.9 (4)
C12	0.0672 (7)	0.3645 (5)	0.041 (1)	9.7 (4)
C13	-0.0027 (8)	0.4365 (5)	0.051 (2)	12.6 (5)
C14	0.0962 (9)	0.4291 (7)	0.204 (2)	14.9 (6)
C21	0.1968 (5)	0.0567 (4)	0.095 (1)	4.3 (2)
C22	0.1313 (6)	0.0535 (4)	0.018 (1)	6.9 (3)
C23	0.2489 (6)	0.0623 (5)	0.001 (1)	7.2 (3)
C24	0.2080 (7)	0.0102 (4)	0.180 (1)	8.1 (4)
C25	0.2650 (5)	0.1274 (4)	0.298 (1)	5.7 (3)
C26	0.2471 (5)	0.1656 (5)	0.400 (1)	6.8 (3)
C27	0.3004 (6)	0.0855 (6)	0.373 (1)	10.5 (5)
C28	0.3083 (6)	0.1527 (6)	0.202 (1)	9.4 (4)

<sup>a</sup>Numbers in parentheses are estimated standard deviations.

<sup>b</sup>Atoms are labeled to agree with Figure 2. <sup>c</sup>Equivalent isotropic thermal parameters are calculated as  $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$ .

Å,  $Z = 3$ , and  $\mu_{\text{MoK}\alpha} = 4.31$  mm<sup>-1</sup>. A total of 1453 independent reflections ( $+h, +k, \pm l$ ) were measured. An empirical absorption correction based on  $\psi$  scans was applied to the data (from 0.839 to 1.00 on  $I$ ).

The seven independent non-hydrogen atoms were refined anisotropically. The six independent hydrogen atoms (located on a difference Fourier synthesis, regularized, and riding) were included in the refinement with isotropic thermal parameters fixed at 1.3 times the equivalent isotropic thermal parameter of the bonded carbon atom. The final agreement factors<sup>13</sup> were  $R = 0.023$  and  $R_w = 0.034$  for the 1259 reflections having  $I \geq 2\sigma_I$ .

**X-ray Study for [(MeSn(O)<sub>2</sub>CMe)(MeSn(O)<sub>2</sub>P(*t*-Bu)<sub>2</sub>)]<sub>3</sub> (2).** The colorless crystal used for the X-ray study was cut from a larger lath and had dimensions of  $0.18 \times 0.23 \times 0.35$  mm.

**Crystal Data:** [(MeSn(O)<sub>2</sub>CMe)(MeSn(O)<sub>2</sub>P(*t*-Bu)<sub>2</sub>)]<sub>3</sub>, monoclinic space group  $C2/c$ , ( $C_{2h}$ -No. 15),<sup>14</sup>  $a = 21.495$  (4) Å,  $b = 28.032$  (6) Å,  $c = 10.013$  (2) Å,  $\beta = 95.34$  (2)°,  $Z = 4$ , and  $\mu_{\text{MoK}\alpha} = 2.60$  mm<sup>-1</sup>. A total of 3438 independent reflections ( $+h, +k, \pm l$ ) were measured. An empirical absorption correction based on  $\psi$  scans was applied to the data (from 0.843 to 1.00 on  $I$ ).

The 33 independent non-hydrogen atoms were refined anisotropically. Hydrogen atoms were omitted from the refinement. The final agreement factors<sup>13</sup> were  $R = 0.036$  and  $R_w = 0.057$  for the 2568 reflections having  $I \geq 3\sigma_I$ .

**X-ray Study for [*n*-BuSn(O)<sub>2</sub>P(OPh)<sub>2</sub>]<sub>6</sub> (3).** The colorless crystal used for the X-ray study was an irregular lump with rounded edges, which had maximum dimensions of  $0.23 \times 0.30 \times 0.34$  mm.

**Crystal Data:** [*n*-BuSn(O)<sub>2</sub>P(OPh)<sub>2</sub>]<sub>6</sub>, monoclinic space group  $P2_1/n$ , alternate setting of  $P2_1/c$  ( $C_{2h}$ -No. 14),<sup>15</sup>  $a = 14.252$  (3) Å,  $b = 17.346$  (2) Å,  $c = 21.987$  (3) Å,  $\beta = 91.62$  (1)°,  $Z = 2$ , and  $\mu_{\text{MoK}\alpha} = 1.529$  mm<sup>-1</sup>. A total of 6220 independent reflections ( $+h, +k, \pm l$ ) were measured. No corrections were made for absorption.

Sixty of the 69 independent non-hydrogen atoms were refined anisotropically. The nine pendant atoms of the three independent *n*-Bu groups

(12) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I, p 252.

(13)  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2}$ .

(14) Reference 12; p 101.

(15) Reference 12; p 99.

**Table IV.** Selected Distances (Å) and Angles (deg) for [(MeSn(O)O<sub>2</sub>CMe)(MeSn(O)O<sub>2</sub>P(*n*-Bu)<sub>2</sub>)<sub>3</sub>]<sub>2</sub> (2)<sup>a</sup>

Distances			
Sn1-O1	2.086 (6)	Sn3-O3	2.097 (5)
Sn1-O1'	2.089 (6)	Sn3-O3'	2.082 (6)
Sn1-O2	2.094 (6)	Sn3-O22	2.131 (6)
Sn1-O11	2.131 (7)	Sn3-O61	2.181 (6)
Sn1-O41	2.184 (7)	Sn3-C3	2.150 (9)
Sn1-C1	2.13 (1)	Sn3-O2	2.079 (6)
Sn2-O1	2.094 (6)	O11-P1	1.499 (7)
Sn2-O2	2.089 (6)	O21-P2	1.519 (6)
Sn2-O3	2.097 (6)	O22-P2	1.507 (7)
Sn2-O21	2.122 (6)	O41-C4	1.25 (1)
Sn2-O42	2.195 (7)	O42-C4	1.28 (1)
Sn2-C2	2.11 (1)	O61-C6	1.238 (8)
Angles			
O1-Sn1-O1'	77.0 (2)	O3-Sn2-O21	89.1 (2)
O1-Sn1-O2	78.1 (2)	O3-Sn2-O42	161.9 (2)
O1-Sn1-O11	89.8 (3)	O3-Sn2-C2	101.1 (3)
O1-Sn1-O41	90.0 (2)	O21-Sn2-O42	78.4 (2)
O1-Sn1-C1	173.6 (4)	O21-Sn2-C2	94.2 (3)
O1'-Sn1-O2	104.2 (2)	O42-Sn2-C2	92.9 (4)
O1'-Sn1-O11	88.5 (3)	O2-Sn3-O3	76.9 (2)
O1'-Sn1-O41	162.0 (2)	O2-Sn3-O3'	104.0 (2)
O1'-Sn1-C1	99.6 (4)	O2-Sn3-O22	89.7 (2)
O2-Sn1-O11	159.8 (3)	O2-Sn3-O61	162.7 (2)
O2-Sn1-O41	84.9 (2)	O2-Sn3-C3	99.5 (3)
O2-Sn1-C1	97.6 (4)	O3-Sn3-O3'	77.7 (2)
O11-Sn1-O41	78.9 (3)	O3-Sn3-O22	89.8 (2)
O11-Sn1-C1	95.6 (4)	O3-Sn3-O61	90.0 (2)
O41-Sn1-C1	94.3 (4)	O3-Sn3-C3	175.0 (3)
O1-Sn2-O2	78.0 (2)	O3'-Sn3-O22	158.6 (2)
O1-Sn2-O3	104.1 (2)	O3'-Sn3-O61	83.8 (2)
O1-Sn2-O21	159.4 (2)	O3'-Sn3-C3	100.0 (3)
O1-Sn2-O42	84.8 (2)	O22-Sn3-O61	78.9 (2)
O1-Sn2-C2	98.6 (3)	O22-Sn3-C3	93.6 (3)
O2-Sn2-O3	76.7 (2)	O61-Sn3-C3	94.2 (3)
O2-Sn2-O21	90.0 (2)	Sn1-O1-Sn1'	101.4 (3)
O2-Sn2-O42	90.1 (2)	Sn1-O1-Sn2	100.0 (2)
O2-Sn2-C2	175.2 (3)	Sn1'-O1-Sn2	131.9 (3)
Sn1-O2-Sn2	99.8 (2)	Sn1-O11-P1	132.4 (4)
Sn1-O2-Sn3	132.5 (3)	Sn2-O21-P2	132.3 (4)
Sn2-O2-Sn3	101.9 (2)	Sn3-O22-P2	131.9 (4)
Sn2-O3-Sn3	101.0 (2)	Sn1-O41-C4	130.6 (7)
Sn2-O3-Sn3'	132.4 (3)	Sn2-O42-C4	129.3 (7)
Sn3-O3-Sn3'	100.3 (2)	Sn3-O61-C6	128.7 (7)

<sup>a</sup> Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 2.

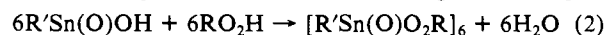
were refined isotropically, with two half-occupied positions for atom CA4. Hydrogen atoms were omitted from the refinement. The final agreement factors<sup>13</sup> were  $R = 0.040$  and  $R_w = 0.052$  for the 4759 reflections having  $I \geq \sigma_I$ .

## Results

The atom-labeling scheme for **1** is shown in the ORTEP plot of Figure 1. Atomic coordinates are given in Table I and selected bond lengths and angles are given in Table II. The corresponding information for **2** and **3** is given in Figures 2 and 3 and in Tables III-VI. Anisotropic thermal parameters and additional bond lengths and angles for **1-3** and hydrogen atom parameters for **1** are provided as supplementary material. All three compounds have the tin-oxygen framework of the "drum" formulation<sup>3</sup> exhibiting hexacoordinated tin atoms. The sides of the drum comprise six four-membered (-Sn-O)<sub>2</sub> stannoxane rings, each of which is spanned by a ligand group that forms a bridge between two tin atoms.

## Discussion

**Synthesis.** Both the drum-containing acetate ligands [MeSn(O)O<sub>2</sub>CMe]<sub>6</sub> (**1**) and the drum with phosphate ligands [*n*-BuSn(O)O<sub>2</sub>P(OPh)<sub>2</sub>]<sub>6</sub> (**3**) were synthesized by a condensation reaction of the organostannonic acid with the ligand acid (eq 2).



$R' = \text{Me}$ ,  $R = \text{MeC}$  (**1**);  $R' = n\text{-Bu}$ ,  $R = \text{P(OPh)}_2$  (**3**)

**Table V.** Atomic Coordinates in Crystalline [*n*-BuSn(O)O<sub>2</sub>P(OPh)<sub>2</sub>]<sub>6</sub> (**3**)<sup>a</sup>

atom <sup>b</sup>	10 <sup>4</sup> x	10 <sup>4</sup> y	10 <sup>4</sup> z	<i>B</i> <sub>equiv.</sub> <sup>c</sup> Å <sup>2</sup>
Sn1	-747.1 (3)	485.9 (3)	946.9 (2)	3.9
Sn2	893.7 (3)	1235.9 (3)	131.2 (2)	3.8
Sn3	-901.6 (3)	792.3 (3)	-759.2 (2)	3.9
P1	164 (2)	-462 (1)	2142 (1)	4.8
P2	237 (2)	2118 (1)	1395 (1)	4.7
P3	-159 (2)	2579 (1)	-670 (1)	4.8
O1	694 (3)	407 (3)	812 (2)	3.8
O2	-561 (3)	1125 (3)	147 (2)	3.9
O3	560 (3)	681 (3)	-694 (2)	3.9
O11	-556 (3)	53 (3)	1867 (2)	4.7
O12	894 (4)	-749 (3)	1735 (2)	5.1
O13	-317 (4)	-1155 (4)	2480 (3)	6.5
O14	705 (4)	-55 (4)	2687 (2)	6.0
O21	882 (3)	2028 (3)	881 (2)	4.4
O22	-565 (4)	1577 (3)	1418 (2)	5.1
O23	-223 (4)	2949 (3)	1396 (3)	6.2
O24	787 (4)	2103 (4)	2022 (2)	6.2
O31	-756 (4)	1992 (3)	-987 (2)	4.9
O32	730 (4)	2305 (3)	-358 (3)	5.1
O33	-718 (4)	3021 (3)	-165 (3)	5.6
O34	72 (4)	3191 (3)	-1176 (3)	6.1
CA1	-2236 (5)	523 (6)	993 (4)	5.8
CA2	-2582 (11)	669 (10)	1625 (8)	13.0
CA3	-3801 (17)	918 (14)	1608 (11)	17.1
CA4A	-4157 (3)	1201 (3)	1231 (2)	19.3
CA4B	-3854 (2)	281 (2)	1569 (1)	11.1
CB1	2387 (5)	1265 (5)	65 (4)	5.6
CB2	2809 (10)	2085 (8)	274 (6)	10.0
CB3	3864 (14)	2056 (12)	252 (9)	16.5
CB4	4073 (15)	2801 (13)	651 (10)	18.4
CC1	-2398 (6)	802 (6)	-709 (5)	6.4
CC2	-2920 (12)	1222 (9)	-1129 (7)	12.6
CC3	-4058 (12)	1094 (10)	-1026 (7)	13.0
CC4	-4522 (18)	1693 (16)	-1325 (12)	22.8
CD1	-1230 (6)	-1440 (5)	2396 (4)	5.3
CD2	-1597 (7)	-1620 (7)	1835 (5)	7.6
CD3	-2486 (8)	-1956 (8)	1803 (5)	9.6
CD4	-2995 (8)	-2101 (8)	2331 (6)	10.0
CD5	-2602 (9)	-1902 (10)	2888 (6)	11.4
CD6	-1700 (7)	-1560 (8)	2925 (5)	8.8
CE1	212 (7)	206 (6)	3195 (4)	6.1
CE2	-190 (8)	921 (7)	3161 (5)	7.6
CE3	-696 (9)	1184 (8)	3662 (6)	9.9
CE4	-739 (10)	703 (10)	4172 (6)	11.6
CE5	-327 (12)	-15 (9)	4192 (5)	11.8
CE6	182 (10)	-264 (7)	3683 (5)	9.6
CF1	359 (7)	3605 (5)	1466 (5)	6.8
CF2	1033 (7)	3774 (6)	1034 (6)	8.8
CF3	1613 (11)	4421 (7)	1151 (7)	11.1
CF4	1466 (11)	4885 (7)	1676 (6)	10.5
CF5	710 (11)	4721 (7)	2059 (6)	10.6
CF6	130 (9)	4072 (6)	1958 (5)	8.5
CG1	1781 (6)	1994 (6)	2111 (4)	5.8
CG2	2180 (7)	1318 (6)	1939 (5)	7.0
CG3	3157 (9)	1239 (8)	2062 (6)	9.7
CG4	3657 (8)	1849 (9)	2358 (6)	9.7
CG5	3212 (9)	2513 (8)	2504 (6)	10.5
CG6	2236 (8)	2641 (7)	2383 (5)	8.6
CH1	-1689 (6)	3117 (5)	-200 (5)	6.0
CH2	-2115 (8)	3451 (6)	-715 (6)	8.5
CH3	-3106 (9)	3559 (8)	-723 (8)	12.0
CH4	-3598 (9)	3370 (9)	-224 (8)	12.1
CH5	-3168 (9)	3024 (11)	308 (7)	12.1
CH6	-2139 (8)	2872 (7)	333 (5)	8.8
CJ1	700 (7)	3814 (6)	-1108 (5)	6.5
CJ2	1291 (8)	3381 (8)	-1590 (6)	9.6
CJ3	1917 (10)	4544 (10)	-1557 (8)	12.1
CJ4	1890 (9)	5052 (8)	-1054 (7)	10.5
CJ5	1298 (11)	4926 (8)	-590 (7)	11.7
CJ6	677 (10)	4289 (7)	-610 (6)	9.7

<sup>a</sup> Numbers in parentheses are estimated standard deviations. <sup>b</sup> Atoms are labeled to agree with Figure 3. <sup>c</sup> Equivalent isotropic thermal parameters are calculated as  $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$ .

The ligand itself, glacial acetic acid, was used as a solvent in synthesizing **1**<sup>7c</sup> while benzene was used in the preparation of **3**.

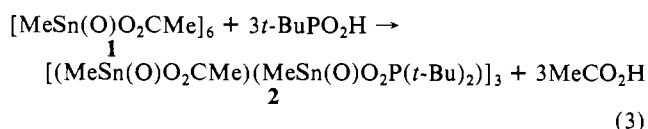
**Table VI.** Selected Bond Lengths (Å) and Bond Angles (deg) for  $[n\text{-BuSn}(\text{O})\text{O}_2\text{P}(\text{O}^-\text{Ph})_2]_6$  (**3**)<sup>a</sup>

Distances			
Sn1-Ca1	2.129 (8)	O21-Sn2	2.146 (5)
Sn1-O1	2.088 (4)	O22-Sn1	2.169 (5)
Sn1-O3'	2.119 (5)	P2-O21	1.486 (5)
Sn1-O2	2.103 (5)	P2-O22	1.481 (6)
O11-Sn1	2.167 (5)	Sn3-CC1	2.138 (8)
O12-Sn3'	2.146 (5)	Sn3-O3	2.093 (5)
P1-O11	1.478 (5)	Sn3-O2	2.116 (5)
P1-O12	1.479 (6)	Sn3-O1'	2.105 (5)
Sn2-CB1	2.138 (8)	O31-Sn3	2.151 (5)
Sn2-O2	2.084 (5)	O32-Sn2	2.153 (5)
Sn2-O1	2.101 (5)	P3-O31	1.488 (5)
Sn2-O3	2.096 (5)	P3-O32	1.501 (5)
Angles			
O1-Sn1-CA1	174.2 (3)	O2-Sn2-O21	91.0 (2)
O11-Sn1-O2	161.4 (2)	O2-Sn2-O32	89.6 (2)
O22-Sn1-O3'	160.9 (2)	O21-Sn2-O32	80.2 (2)
O3'-Sn1-O2	105.3 (2)	O21-Sn2-O1	83.5 (2)
O1-Sn1-O2	76.6 (2)	O32-Sn2-O3	86.8 (2)
O1-Sn1-O3'	76.6 (2)	Sn1-O2-Sn3	127.8 (2)
CA1-Sn1-O3'	100.1 (3)	Sn2-O2-Sn1	102.2 (2)
CA1-Sn1-O2	100.0 (3)	Sn2-O2-Sn3	102.2 (3)
CA1-Sn1-O11	93.7 (3)	Sn2-O21-P2	132.1 (3)
CA1-Sn1-O22	93.2 (3)	Sn1-O22-P2	128.3 (3)
O1-Sn1-O11	90.7 (2)	O3-Sn3-CC1	171.6 (2)
O1-Sn1-O22	91.2 (2)	O31-Sn3-O1'	158.2 (2)
O11-Sn1-O22	81.2 (2)	O12'-Sn3-O2	160.4 (2)
O11-Sn1-O3'	84.3 (2)	O2-Sn3-O1'	107.0 (2)
O22-Sn1-O2	85.6 (2)	O3-Sn3-O2	76.1 (2)
Sn3'-O1-Sn2	127.9 (2)	O3-Sn3-O1'	76.8 (2)
Sn1-O1-Sn3'	102.3 (2)	CC1-Sn3-O1'	98.8 (2)
Sn1-O1-Sn2	102.1 (2)	CC1-Sn3-O2	98.7 (2)
Sn1-O11-P1	131.3 (3)	CC1-Sn3-O31	96.1 (2)
Sn3'-O12-P1	129.9 (3)	CC1-Sn3-O12'	94.8 (2)
O2-Sn2-CB1	175.0 (2)	O3-Sn3-O31	90.2 (2)
O21-Sn2-O3	162.2 (2)	O3-Sn3-O12'	91.9 (2)
O32-Sn2-O1	158.5 (2)	O31-Sn3-O12'	78.4 (2)
O1-Sn2-O3	105.7 (2)	O31-Sn3-O2	86.2 (2)
O2-Sn2-O1	76.7 (2)	O12'-Sn3-O1'	84.6 (2)
O2-Sn2-O3	76.7 (2)	Sn2-O3-Sn1'	129.7 (2)
CB1-Sn2-O3	98.8 (2)	Sn3-O3-Sn2	102.6 (2)
CB1-Sn2-O1	102.7 (2)	Sn3-O3-Sn1'	101.7 (2)
CB1-Sn2-O21	93.8 (2)	Sn3-O31-P3	127.7 (3)
CB1-Sn2-O32	92.3 (2)	Sn2-O32-P3	125.4 (3)

<sup>a</sup> Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figure 3.

In 1922, Lambourne<sup>7a</sup> provided the preparation of a triacetyl derivative from methylstannonic acid having the empirical composition of **1**. He assigned the trimer formula  $[\text{MeSn}(\text{O})\text{O}_2\text{CMe}]_3$  based on a cryoscopic molecular weight measurement in phenol. The latter does not agree with the hexameric drum representation found by X-ray analysis. The <sup>119</sup>Sn NMR spectrum of **1** in phenol indicates that decomposition takes place; four peaks are observed rather than the one expected for a drum formulation or for the postulated cyclic trimer.<sup>7a</sup> Further, a reasonable trimer ring structure would contain pentacoordinated tin atoms instead of hexacoordinated tin that we have uniformly observed in all other related oxotin derivatives.<sup>1b,c,3-6</sup>

Somewhat surprisingly, the reaction of the acetate drum **1** with di-*tert*-butylphosphinic acid gave the mixed drum **2** in which half of the acetate ligands were replaced by phosphinate ligands (eq 3). The reaction was conducted in a toluene-methanol solvent



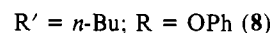
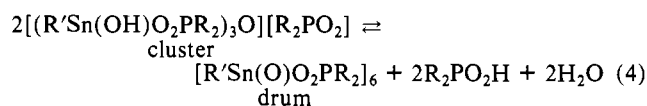
mixture (7:1). In toluene alone, no reaction occurred. Figure 2 shows the alternation of the two kinds of ligands around the outside of the drum.

In related work,<sup>6</sup> we had found that reaction of *n*-BuSn(O)OH with di-*tert*-butylphosphinic acid leads to the "cube" composition

$[n\text{-BuSn}(\text{O})\text{O}_2\text{P}(t\text{-Bu})_2]_4$ . The unique formation of the mixed-drum structure **2** here is attributed to the inability of the drum to accommodate six bulky phosphinate ligands containing *tert*-butyl groups. This is supported by the values obtained for the interligand O-Sn-O angles. In the aforementioned cube derivative<sup>6</sup> this angle averages 95.1 (2)°, whereas the O-Sn-O angle in the mixed-drum **2** averages 78.4 (2)°. The latter value is very close to 79.9 (2)° found in the drum structure **3** containing all phosphate ligands. Hence, there exists a potentially greater compression between adjacent ligands in the drum compared to the cube accompanying the approximate decrease in the interligand O-Sn-O angle of 15°.

The drum compounds are thermally quite stable with melting points above 300 °C for most derivatives,<sup>1b,c</sup> although **3**, which is the only one containing all phosphate ligands, melts the lowest, at 245-247 °C. However, the mixed-drum **2** with both carboxylate and phosphate ligands did not melt up to 370 °C.

The interesting conversion of the oxygen-capped derivative  $[(n\text{-BuSn}(\text{OH})\text{O}_2\text{P}(\text{O}^-\text{Ph})_2)_3\text{O}][(\text{PhO})_2\text{PO}_2]$  (**8**) to the drum formulation **3** on heating (Figures 4 and 5b) corresponds to the reaction in eq 4. The drum **3** on standing for 5 days at 25 °C



slowly transforms to the oxygen-capped cluster **8** (Figure 5d), showing that eq 4 is reversible. The latter conversion undoubtedly involves the slow pickup of moisture by the CDCl<sub>3</sub> solvent. The phosphate acid may come from partial hydrolytic cleavage of drum **3** corresponding to a reversal of eq 2 to the initial reactants. It is apparent that the oxygen-capped cluster is hydrolytically more stable than the drum. Although the structural relation between a drum and an oxygen-capped cluster has been discussed,<sup>5</sup> we now have provided the first experimental evidence for the existence of this transformation.

<sup>119</sup>Sn NMR Data. There is little doubt that the drum compounds, **2** and **3**, retain their structure in solution at 25 °C, at least initially. We have seen the slow transformation of drum **3** to the oxygen-capped cluster **8** at 250 °C, Figure 5d. The mixed drum **2** shows a single doublet at -470.7 ppm, the doublet due to <sup>2</sup>J(<sup>119</sup>Sn-O-<sup>31</sup>P) coupling. Although this is the expected pattern for the cubic structure of the same empirical composition,<sup>6</sup> the chemical shift normally appears at slightly lower field.<sup>16</sup> The average chemical shift value for three cubic forms that have been studied is -466 ± 5 ppm and that for five drum compounds is -488 ± 2 ppm.<sup>1b,c</sup> However, the average comprises drums that contain the *n*-butyl group attached to tin.

It is felt that the presence of a methyl group instead of a *n*-butyl group lowers the chemical shift of the drum by about 15 ppm, possibly associated with a lower electron-releasing effect of the methyl group. The basis for this statement rests with an analogous observation with oligomers having the related open-drum or "ladder" formulations.<sup>1b,c</sup> Here, three resonances are seen, consistent with the presence of three pairs of different tin environments. Five of these derivatives whose X-ray structures have been investigated have *n*-butyl groups at tin. Their <sup>119</sup>Sn resonances average 524 ± 2, 549 ± 3, and 622 ± 10 ppm<sup>1b</sup> while the one open drum with a methyl group bonded to tin,  $[(\text{MeSn}(\text{O})\text{O}_2\text{CC}_6\text{H}_{11})_2\text{MeSn}(\text{O}_2\text{CC}_6\text{H}_{11})_3]_2$ , has <sup>119</sup>Sn resonances at -500.9, -527.0, and -607.4 ppm,<sup>1c</sup> respectively.

For the benzoate drum **7**, puzzling solution behavior is found. After dissolution of the pure benzoate drum, refrigeration for 2 days, and evaporation of the benzene solvent, a viscous solution remains. The viscous material shows analytical data consistent with the drum composition but a different <sup>119</sup>Sn NMR pattern. The single resonance initially present for **7** changes to a series of <sup>119</sup>Sn resonances that are indicative of a mixture of a drum and

(16) Holmes, R. R.; Kumara Swamy, K. C.; Schmid, C. G.; Day, R. O. *J. Am. Chem. Soc.*, in press.

a ladder composition.<sup>1b</sup> However, the ladder form has been independently synthesized and shows a carbon analysis of 48.45% calculated (48.23% found).<sup>1c</sup> This compares with 42.22% calculated for drum 7 and 41.92% found for the viscous material. Perhaps the drum has opened up<sup>1b</sup> and polymerized to give a chain unit that retains the empirical formula of the drum. The latter would account for the viscous nature of the solution. This suggestion, however, requires further work.

**Structural Details.** Drums 1 and 2, which contain only one type of acid residue, are cyclic hexamers with idealized  $S_6$  molecular symmetry. For 1 the crystallographic symmetry is the same as the idealized symmetry, while for 3 the crystallographic symmetry is lower, namely  $C_i$ .

The mixed drum 2, has crystallographic  $C_2$  symmetry with P1, C6, and C7 lying on the 2-fold axis, the methyl hydrogen atoms of C7 being disordered about this axis. The idealized molecular symmetry of 2 is  $D_3$  and the molecule is viewed in Figure 2 down the noncrystallographic 3-fold axis. This idealized molecular symmetry is such that all of the tin atoms as well as all of the phosphorus atoms are chemically equivalent.

The framework Sn-O bond lengths for the three drum structures 1-3 average to within  $\pm 0.01$  Å of one another, 2.091 (2)

Å for 1, 2.090 (6) Å for 2, and 2.103 (5) Å for 3. These values are similar to that reported for the corresponding cube  $[n\text{-Bu}(\text{O})\text{O}_2\text{P}(\text{C}_6\text{H}_{11})_2]_4$ ,<sup>6</sup> i.e., 2.108 (6) Å.

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**Registry No.** 1, 115270-25-2; 2, 115288-62-5; 3, 115270-27-4; 4, 115270-28-5; 5, 115270-29-6; 6, 115270-30-9; 7, 115270-31-0; 8, 115270-33-2;  $\text{CH}_3\text{Sn}(\text{O})\text{OH}$ , 753-61-7;  $\text{CH}_3\text{CO}_2\text{H}$ , 64-19-7;  $(t\text{-Bu})_2\text{PO}_2\text{H}$ , 677-76-9;  $n\text{-BuSn}(\text{O})\text{OH}$ , 2273-43-0;  $(\text{PhO})_2\text{PO}_2\text{H}$ , 838-85-7;  $\text{Cl-}p\text{-C}_6\text{H}_4\text{CO}_2\text{H}$ , 74-11-3;  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCO}_2\text{H}$ , 3721-95-7;  $\text{CH}_2\text{CH}_2\text{CHCO}_2\text{H}$ , 1759-53-1;  $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ , 65-85-0.

**Supplementary Material Available:** Listings of anisotropic thermal parameters, hydrogen atom parameters, and additional bond lengths and angles for 1 (Tables S1-S3, respectively) and anisotropic thermal parameters and additional bond lengths and angles for 2 (Tables S4 and S5, respectively) and for 3 (Tables S6 and S7, respectively) (11 pages); listings of observed and calculated structure factors for 1-3 (35 pages). Ordering information is given on any masthead page.

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## Electron Exchange by Hexakis(*tert*-butyl isocyanide)- and Hexakis(cyclohexyl isocyanide)manganese(I,II). Solvent Effect on the Rate Constant and the Volume of Activation

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The rate of electron self-exchange of  $\text{Mn}(\text{CNC}(\text{CH}_3)_3)_6^{+2+}$  and  $\text{Mn}(\text{CNC}_6\text{H}_{11})_6^{+2+}$  as the  $\text{BF}_4^-$  salts has been measured by  $^{55}\text{Mn}$  NMR line broadening as a function of pressure, temperature, and concentration in acetonitrile, bromobenzene, benzonitrile, acetone, diethyl ketone, methanol, ethanol, methylene chloride, and trimethyl phosphate, and various binary mixtures of methylene chloride, bromobenzene, and acetonitrile. The values of  $\Delta V^\ddagger$  obtained are negative and cover a range of ca. 12  $\text{cm}^3/\text{mol}$ , which is limited by ion pairing in the solvents of lower dielectric constant. The variation of the ambient pressure rate constant with solvent is qualitatively different for the  $\text{Mn}(\text{CNC}(\text{CH}_3)_3)_6^{+2+}$  reaction than was observed for the  $\text{Mn}(\text{CNC}_6\text{H}_{11})_6^{+2+}$  reaction. This is taken as further evidence for a significant influence of rather subtle differences in solvation on the molecular level that are not approximated by dielectric continuum models.

### Introduction

The work presented here is a continuation of our study of electron self-exchange in the  $\text{Mn}(\text{I,II})$ -hexakis(isocyanide) system. Previous work has considered the effects of solvent, temperature, and added electrolyte concentration on the  $\text{Mn}(\text{CNC}_6\text{H}_{11})_6^{+2+}$  reaction,<sup>1</sup> the effect of varying the ligand, including both alkyl<sup>2</sup> and aryl<sup>3</sup> isocyanide ligands, as well as the temperature and electrolyte on reactions in acetonitrile, and the effect of pressure on reactions of a series of alkyl isocyanide complexes in acetonitrile.<sup>4</sup> The purpose of these studies is to provide a body of experimental data on a series of well-defined, outer-sphere electron-transfer reactions in solvents other than water and thus to test the rapidly developing theories for these superficially rather simple reactions.<sup>5,6</sup> The  $\text{Mn}(\text{I,II})$ -hexakis(isocyanide) system is appealing for a broadly based and thorough study because the

electron self-exchange rate constants can be evaluated directly from  $^{55}\text{Mn}$  or  $^1\text{H}$  NMR line broadening, a series of complexes with both aryl and alkyl ligands can be synthesized that are substitution inert in both oxidation states, the complexes are soluble and stable in a variety of solvents over a large range of temperature, and physical measurements on the complexes are starting to provide information on properties useful in the theoretical analysis of their reactivity.<sup>7,8</sup>

We are especially interested in pursuing measurements of the volumes of activation for these reactions under a variety of conditions. Relatively few measurements of volumes of activation for electron-transfer reactions have been made<sup>9-17</sup> compared to

- (1) Nielson, R. M.; Wherland, S. *Inorg. Chem.* **1984**, *23*, 1338.
- (2) Nielson, R. M.; Wherland, S. *J. Am. Chem. Soc.* **1985**, *107*, 1505.
- (3) Nielson, R. M.; Wherland, S. *Inorg. Chem.* **1986**, *25*, 2437.
- (4) Nielson, R. M.; Hunt, J. P.; Dodgen, H. W.; Wherland, S. *Inorg. Chem.* **1986**, *25*, 1964.
- (5) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437.
- (6) Cannon, R. D. *Electron Transfer Reactions*; Butterworths: London, 1980.

- (7) Nielson, R. M.; Wherland, S. *Inorg. Chem.* **1985**, *24*, 1803.
- (8) Nielson, R. M.; Wherland, S. *Inorg. Chem.* **1985**, *24*, 3458.
- (9) Stranks, D. R. *Pure Appl. Chem.* **1974**, *38*, 303.
- (10) Candlin, J. P.; Halpern, J. *Inorg. Chem.* **1965**, *4*, 1086.
- (11) van Eldik, R. *Inorg. Chem.* **1982**, *21*, 2501.
- (12) Spiccia, L.; Swaddle, T. *J. Chem. Soc., Chem. Commun.* **1985**, 67.
- (13) Spiccia, L.; Swaddle, T. *Physica B+C (Amsterdam)* **1986**, *139-140B+C*, 684.
- (14) Sasaki, Y.; Ueno, F. B.; Saito, K. *J. Chem. Soc., Chem. Commun.* **1981**, 1135.
- (15) Ueno, F. B.; Sasaki, Y.; Ito, T.; Saito, K. *J. Chem. Soc., Chem. Commun.* **1982**, 328.