

# A New System in Organooxotin Cluster Chemistry Incorporating Inorganic and Organic Spacers between Two Ladders Each Containing Five Tin Atoms

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**Abstract:** Hydrolysis of dibenzyltin dichloride in ethanol has been found to give an unprecedented carbonate anion ( $\text{CO}_3^{2-}$ )-bridged double-ladder organooxotin cluster,  $[(\text{R}_2\text{SnO})_3(\text{R}_2\text{SnOH})_2(\text{CO}_3)]_2$  (**1**,  $\text{R} = \text{C}_6\text{H}_5\text{CH}_2$ ), with five tin atoms in each ladder. With the aim of obtaining organooxotin clusters with large cavities suitable for host-guest chemistry, we used 1,1'-ferrocenedicarboxylic acid ( $\text{H}_2\text{L}_a$ ) and hexanedioic acid ( $\text{H}_2\text{L}_b$ ) to replace the carbonate anions ( $\text{CO}_3^{2-}$ ), and thereby clusters  $[(\text{R}_2\text{SnO})_3(\text{R}_2\text{SnOH})_2\text{L}_a]_2$  (**2**) and

$[(\text{R}_2\text{SnO})_3(\text{R}_2\text{SnOH})_2\text{L}_b]_2$  (**3**) were obtained. When **1** was treated with benzoic acid ( $\text{HL}_c$ ) in different stoichiometric ratios (1:4, 1:10), ladder cluster  $(\text{R}_2\text{SnO})_3(\text{R}_2\text{SnOH})_2(\text{L}_c)_2$  (**4**) and drum cluster  $[\text{RSn}(\text{O})\text{L}_c]_6$  (**5**) were obtained. Through the hydrolysis of  $\text{Cy}_2\text{SnCl}_2$  ( $\text{Cy} = \text{C}_6\text{H}_{11}$ ) and  $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SnCl}_2$ , two interesting ethanolate-modified

clusters  $[\text{Cy}_2(\text{C}_2\text{H}_5\text{O})\text{SnOSn}(\text{C}_2\text{H}_5\text{O})\text{Cy}_2]_2$  (**6**) and  $[(\text{R}_2\text{SnO})_3(\text{R}_2\text{SnOH})(\text{R}_2\text{SnOC}_2\text{H}_5)(\text{CO}_3)]_2$  (**7**) were obtained. All the tin atoms in these ladder clusters are five-coordinate surrounded by two alkyl groups and three O atoms, and have distorted trigonal-bipyramidal coordination environments with two carbon atoms and one O atom in the equatorial positions and two O atoms in the axial positions. The structures of all these compounds have been established by single-crystal X-ray diffraction analyses.

**Keywords:** bridging ligands • cluster compounds • inorganic and organic spacers • organotin

## Introduction

Organooxotin clusters have been attracting considerable attention in recent years because of their novel structures,<sup>[1]</sup> their suitability for the construction of supramolecular frameworks,<sup>[2]</sup> and their efficient catalysis of various organic reactions.<sup>[3]</sup> Several types of organooxotin cluster, such as ladder,<sup>[4a]</sup> O-capped,<sup>[4b]</sup> cube,<sup>[4c]</sup> butterfly,<sup>[4d]</sup> drum,<sup>[4e-g]</sup> football cage,<sup>[5]</sup> cyclic trimer,<sup>[6]</sup> among others, have been prepared and their structures established by X-ray diffraction analysis. Recently, more studies have been focused on ligand-bridged organooxotin clusters, such as alkyl-bridged double- and triple-ladder clusters,<sup>[7]</sup> an alkyl-bridged  $\text{Sn}_3\text{O}_3$  cluster,<sup>[8]</sup> an eighteen-tin-nuclear ladder cluster,<sup>[9]</sup> and double O-capped clusters.<sup>[10]</sup> Of these, the alkyl-bridged ladder clusters and their variants have been most widely reported; for example, the distance between the two ladders can be changed by using different alkyl spacers and the structures can be chemically modified while retaining the

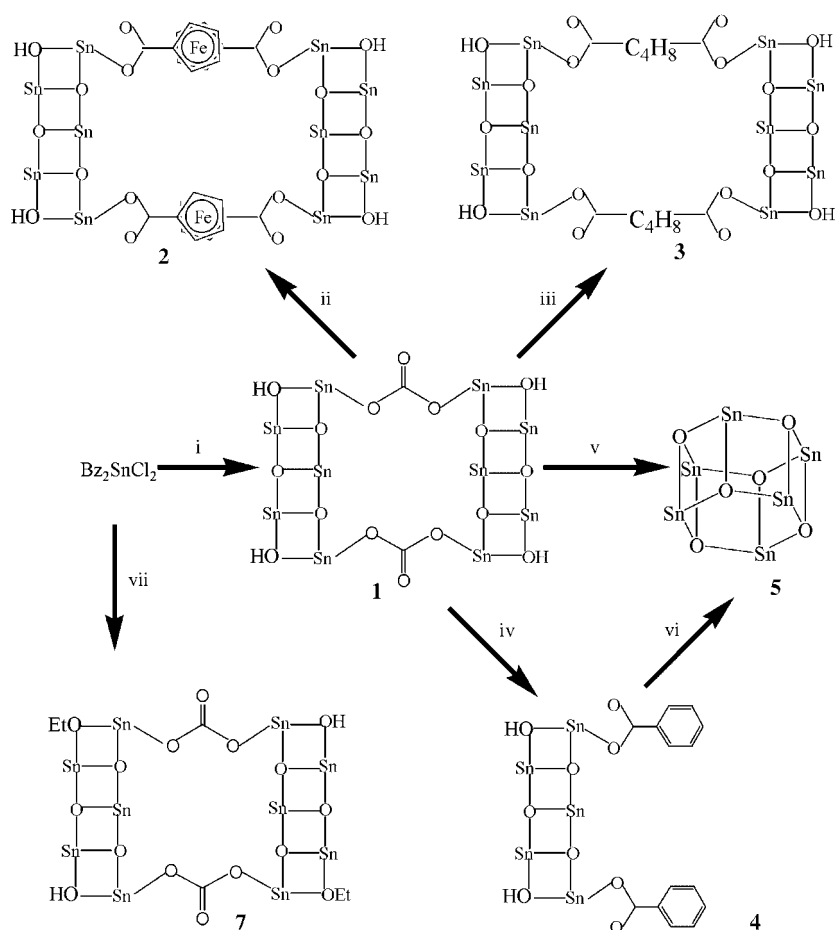
basic structural unit.<sup>[7]</sup> Syntheses of new ligand-bridged organotin-oxygen clusters can be expected to continue to attract considerable attention. As regards organooxotin cluster chemistry, reported organooxotin clusters bridged by inorganic spacers are very few.<sup>[10]</sup> Herein, we report a novel carbonate anion ( $\text{CO}_3^{2-}$ )-bridged organooxotin ladder cluster  $[(\text{R}_2\text{SnO})_3(\text{R}_2\text{SnOH})_2(\text{CO}_3)]_2$  (**1**), which was synthesized by hydrolysis of dibenzyltin dichloride in ethanol. It has been found that the inorganic  $\text{CO}_3^{2-}$  spacers can be replaced by longer organic spacers to provide organooxotin clusters with large cavities that are potentially suitable for host-guest chemistry.

## Results and Discussion

To classify new tin-oxygen clusters, we have studied the hydrolysis of diorganotin dichlorides in detail, and have synthesized a series of new ladder clusters. All the reactions are summarized in Scheme 1. In contrast to the previously reported ladder cluster  $[(\text{RSn}(\text{O})\text{O}_2\text{CR}')_2\text{RSn}(\text{O}_2\text{CR}')_3]_2$ , which was synthesized by partial hydrolysis of an organotin tricarboxylate,<sup>[11]</sup> the hydrolysis of dibenzyltin dichloride in ethanol in the presence of atmospheric  $\text{CO}_2$  afforded an unprecedented compound **1**, which proved to be soluble in a wide range of organic solvents, including  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and benzene. Crystals of **1** suitable for an X-ray diffraction

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Scheme 1. Syntheses of compounds **1**, **2**, **3**, **4**, **5**, and **7**. i) NaOH, atmospheric CO<sub>2</sub>, reflux in EtOH for 12 h; ii) H<sub>2</sub>L<sub>a</sub>, reflux in benzene for 6 h; iii) H<sub>2</sub>L<sub>b</sub>, reflux in benzene for 6 h; iv) 4 equiv C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>H, reflux in benzene for 6 h; v) 10 equiv C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>H, reflux in benzene for 6 h; vi) 3 equiv C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>H, reflux in benzene for 6 h; vii) NaOH, EtONa, and hyponone; reflux in EtOH for 12 h.

study were obtained by recrystallization from acetone. Upon exposure to air, these crystals became opaque within minutes, indicating a loss of solvent.

Selected metric parameters for all the structures are listed in Table 1. The structure of **1** is shown in Figure 1; it consists of two novel Sn<sub>5</sub>O<sub>5</sub> ladders connected by two CO<sub>3</sub><sup>2-</sup> ions. This situation is reminiscent of that in a previously reported double O-capped organooxotin cluster, in which two O-capped organooxotin clusters are bridged by four HPO<sub>3</sub><sup>2-</sup> ligands.<sup>[10]</sup> The five tin atoms are almost coplanar, with the largest deviation from the Sn<sub>5</sub>O<sub>5</sub> ladder plane being 0.1701 Å. Each of the ladders consists of five tin centers held together by three μ<sub>3</sub>-oxygen atoms. According to their different coordination environments, the ten tin atoms can be divided into three types. The four tin atoms Sn1, Sn1A, Sn5, Sn5A, which are each bonded to one μ<sub>3</sub>-oxygen atom, one μ<sub>2</sub>-oxygen atom, and one oxygen atom derived from the carbonate, can be regarded as type 1. The four tin atoms Sn2, Sn2A, Sn4, Sn4A, which are each bonded to two μ<sub>3</sub>-oxygen atoms and one μ<sub>2</sub>-oxygen atom, can be regarded as type 2. The two tin atoms Sn3, Sn3A, which are each bonded to three μ<sub>3</sub>-oxygen atoms, can be regarded as type 3. All of the tin atoms are five-coordinated by two benzyl

groups and three O atoms, resulting in a *cis*-R<sub>2</sub>SnO<sub>3</sub> trigonal-bipyramidal coordination environment with the two benzyl groups and one O atom in equatorial positions [C17, C27, O2 for Sn1; C37, C47, O2 for Sn2; C57, C67, O3 for Sn3; C77, C87, O4 for Sn4; C97, C107, O4 for Sn5] and the other two O atoms in axial positions [O1, O6 for Sn1; O1, O3 for Sn2; O2, O4 for Sn3; O3, O5 for Sn4; O5, O7A for Sn5]. The O<sub>ax</sub>-Sn-O<sub>ax</sub> angles range from 146.92(9) to 152.79(9)° [O6-Sn1-O1 152.79(9)°, O3-Sn2-O1 149.15(9)°, O4-Sn3-O2 147.18(9)°, O3-Sn4-O5 146.92(9)°, O7A-Sn5-O5 150.58(9)°] and thus deviate considerably from 180°, which indicates that the structure is distorted trigonal-bipyramidal. The average Sn-O bond length is 2.117 Å, and the longest and shortest Sn-O bond lengths are Sn1-O1 (2.234(2) Å) and Sn5-O4 (2.015(2) Å), respectively. The separation between the two ladders is approximately 6 Å. The <sup>119</sup>Sn NMR spectrum of compound **1** (see Supporting Information) shows three reso-

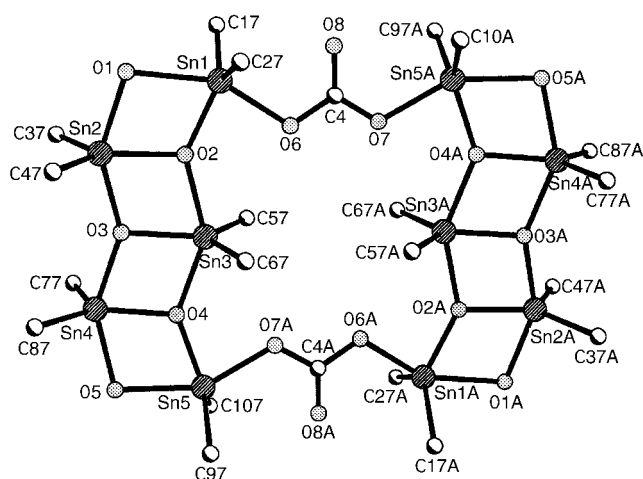


Figure 1. Framework of [(R<sub>2</sub>SnO<sub>3</sub>)(R<sub>2</sub>SnOH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>] (**1**). Benzyl groups have been omitted for clarity except for the carbon atoms bonded to tin atoms.

nances at  $\delta = -304.7, -244.5, -242.6$  ppm, which can be attributed to three kinds of five-coordinate tin centers according to the literature.<sup>[1b,12]</sup>

Table 1. Selected bond lengths [Å] and angles [°] for 1–6.<sup>[a]</sup>

Compound 1									
C4–O8	1.237(4)	C4–O7	1.304(4)	C4–O6	1.315(4)	Sn2–O1	2.133(2)	Sn1–O1	2.234(2)
Sn1–O2	2.017(2)	Sn2–O2	2.029(2)	Sn3–O2	2.154(2)	Sn3–O3	2.058(2)	Sn2–O3	2.099(2)
Sn4–O3	2.123(2)	Sn5–O4	2.015(2)	Sn4–O4	2.030(2)	Sn3–O4	2.135(2)	Sn4–O5	2.127(3)
Sn5–O5	2.215(2)	Sn1–O6	2.094(2)	Sn5–O7 A	2.113(2)				
O8–C4–O7	123.5(3)	O8–C4–O6	122.0(3)	O7–C4–O6	114.5(3)	Sn2–O1–Sn1	101.29(9)	Sn1–O2–Sn2	113.17(10)
Sn1–O2–Sn3	142.03(11)	Sn2–O2–Sn3	104.80(10)	Sn3–O3–Sn2	105.76(10)	Sn3–O3–Sn4	105.71(10)	Sn2–O3–Sn4	148.41(11)
Sn5–O4–Sn4	112.87(10)	Sn5–O4–Sn3	140.84(11)	Sn4–O4–Sn3	106.27(10)	Sn4–O5–Sn5	101.82(10)	C4–O6–Sn1	112.1(2)
C4–O7–Sn5 A	118.2(2)	O2–Sn1–O6	81.05(9)	O2–Sn1–O1	71.75(9)	O6–Sn1–O1	152.79(9)	O2–Sn2–O3	75.47(9)
O2–Sn2–O1	73.71(9)	O3–Sn2–O1	149.15(9)	O3–Sn3–O4	73.53(9)	O3–Sn3–O2	73.68(9)	O4–Sn3–O2	147.18(9)
O4–Sn4–O3	74.35(9)	O4–Sn4–O5	73.37(9)	O3–Sn4–O5	146.92(9)	O4–Sn5–O7 A	78.81(9)	O4–Sn5–O5	71.78(9)
O7 A–Sn5–O5	150.58(9)								
Compound 2									
C211–O9	1.233(8)	C211–O8	1.311(8)	C212–O7	1.213(8)	C212–O6	1.318(8)	Sn2–O1	2.134(5)
Sn1–O1	2.241(4)	Sn2–O2	2.026(4)	Sn1–O2	2.033(4)	Sn3–O2	2.142(4)	Sn3–O3	2.034(4)
Sn4–O3	2.121(4)	Sn2–O3	2.127(4)	Sn5–O4	2.022(4)	Sn4–O4	2.036(4)	Sn3–O4	2.141(4)
Sn4–O5	2.138(5)	Sn5–O5	2.225(4)	Sn5–O6	2.148(4)	Sn1 A–O8	2.163(4)	Sn1–O8 A	2.163(5)
O9–C211–O8	122.8(6)	O7–C212–O6	123.2(6)	Sn2–O1–Sn1	100.79(18)	Sn2–O2–Sn1	112.3(2)	Sn2–O2–Sn3	105.38(19)
Sn1–O2–Sn3	141.7(2)	Sn3–O3–Sn4	105.67(18)	Sn3–O3–Sn2	105.67(19)	Sn4–O3–Sn2	148.6(2)	Sn5–O4–Sn4	112.1(2)
Sn5–O4–Sn3	142.9(2)	Sn4–O4–Sn3	104.91(17)	Sn4–O5–Sn5	100.98(18)	C212–O6–Sn5	107.6(4)	C211–O8–Sn1 A	106.7(4)
O2–Sn1–O8 A	81.73(17)	O2–Sn1–O1	72.21(16)	O8 A–Sn1–O1	153.72(17)	O2–Sn2–O3	74.66(16)	O2–Sn2–O1	74.63(17)
O3–Sn2–O1	149.23(16)	O3–Sn3–O4	74.51(16)	O3–Sn3–O2	74.17(16)	O4–Sn3–O2	148.66(15)	O4–Sn4–O3	74.91(16)
O4–Sn4–O5	74.25(16)	O3–Sn4–O5	149.07(16)	O4–Sn5–O6	81.29(17)	O4–Sn5–O5	72.62(16)	O6–Sn5–O5	153.32(17)
Compound 3									
C211–O11	1.222(7)	C211–O12	1.312(7)	C216–O14	1.223(8)	C216–O13	1.293(7)	C311–O22	1.191(7)
C311–O21	1.323(7)	C316–O24	1.221(7)	C316–O23	1.286(7)	Sn2–O1	2.142(4)	Sn1–O1	2.232(4)
Sn1–O2	2.024(3)	Sn2–O2	2.029(3)	Sn3–O2	2.155(3)	Sn3–O3	2.046(3)	Sn2–O3	2.107(3)
Sn4–O3	2.117(3)	Sn5–O4	2.022(3)	Sn4–O4	2.033(4)	Sn3–O4	2.139(3)	Sn4–O5	2.118(4)
Sn5–O5	2.218(4)	Sn7–O6	2.165(4)	Sn6–O6	2.225(4)	Sn6–O7	2.009(4)	Sn7–O7	2.037(3)
Sn8–O7	2.119(3)	Sn8–O8	2.068(4)	Sn7–O8	2.111(4)	Sn9–O8	2.120(4)	Sn10–O9	2.011(4)
Sn9–O9	2.016(4)	Sn8–O9	2.126(4)	Sn9–O10	2.173(4)	Sn10–O10	2.210(5)	Sn1–O12	2.133(4)
Sn6–O13	2.101(4)	Sn5–O21	2.127(4)	Sn10–O23	2.142(4)	Sn2–O1–Sn1	100.44(15)	Sn1–O2–Sn2	112.10(16)
Sn1–O2–Sn3	142.30(18)	Sn2–O2–Sn3	104.63(14)	Sn3–O3–Sn2	105.77(15)	Sn3–O3–Sn4	105.77(15)	Sn2–O3–Sn4	148.26(18)
Sn5–O4–Sn4	112.55(16)	Sn5–O4–Sn3	141.72(18)	Sn4–O4–Sn3	105.43(15)	Sn4–O5–Sn5	102.10(15)	Sn7–O6–Sn6	101.39(15)
Sn6–O7–Sn7	114.18(16)	Sn6–O7–Sn8	139.65(17)	Sn7–O7–Sn8	105.56(15)	Sn8–O8–Sn7	104.76(16)	Sn8–O8–Sn9	104.53(15)
Sn7–O8–Sn9	150.36(18)	Sn10–O9–Sn9	114.14(18)	Sn10–O9–Sn8	138.5(2)	Sn9–O9–Sn8	106.14(16)	Sn9–O10–Sn10	100.89(17)
C211–O12–Sn1	108.4(4)	C216–O13–Sn6	124.9(4)	C311–O21–Sn5	109.8(3)	C316–O23–Sn10	117.0(4)	O2–Sn1–O12	80.45(14)
O2–Sn1–O1	72.58(14)	O12–Sn1–O1	152.85(14)	O2–Sn2–O3	75.49(13)	O2–Sn2–O1	74.46(14)	O3–Sn2–O1	149.90(14)
O3–Sn3–O4	74.03(13)	O3–Sn3–O2	74.07(13)	O4–Sn3–O2	148.05(13)	O4–Sn4–O3	74.77(13)	O4–Sn4–O5	73.64(14)
O3–Sn4–O5	148.20(14)	O4–Sn5–O21	82.13(14)	O4–Sn5–O5	71.70(14)	O21–Sn5–O5	153.67(14)	O7–Sn6–O13	78.22(15)
O7–Sn6–O6	71.80(14)	O13–Sn6–O6	149.58(15)	O7–Sn7–O8	75.20(14)	O7–Sn7–O6	72.56(14)	O8–Sn7–O6	147.67(14)
O8–Sn8–O7	74.39(14)	O8–Sn8–O9	74.04(15)	O7–Sn8–O9	148.43(14)	O9–Sn9–O8	75.24(14)	O9–Sn9–O10	72.82(16)
O8–Sn9–O10	147.45(16)	O9–Sn10–O23	78.51(15)	O9–Sn10–O10	72.10(15)	O23–Sn10–O10	150.61(15)		
Compound 4									
C217–O12	1.208(17)	C217–O11	1.315(15)	C227–O14	1.200(16)	C227–O13	1.329(16)	C237–O16	1.237(15)
C237–O15	1.295(14)	C247–O18	1.22(3)	C247–O17	1.30(3)	Sn2–O1	2.123(12)	Sn1–O1	2.232(9)
Sn1–O2	1.991(8)	Sn2–O2	2.042(8)	Sn3–O2	2.164(9)	Sn3–O3	2.037(8)	Sn4–O3	2.077(10)
Sn2–O3	2.150(10)	Sn5–O4	2.017(7)	Sn4–O4	2.029(7)	Sn3–O4	2.144(7)	Sn4–O5	2.132(9)
Sn5–O5	2.238(9)	Sn7–O6	2.176(8)	Sn6–O6	2.224(9)	Sn7–O7	2.032(8)	Sn6–O7	2.045(7)
Sn8–O7	2.111(7)	Sn8–O8	2.035(7)	Sn7–O8	2.106(6)	Sn9–O8	2.145(6)	Sn9–O9	2.035(9)
Sn10–O9	2.046(9)	Sn8–O9	2.132(9)	Sn10–O10	2.148(9)	Sn9–O10	2.169(9)	Sn1–O11	2.152(9)
Sn5–O13	2.140(9)	Sn6–O15	2.161(8)	Sn10–O17	2.136(12)	Sn2–O1–Sn1	102.3(5)	Sn1–O2–Sn2	114.5(4)
Sn1–O2–Sn3	141.1(4)	Sn2–O2–Sn3	104.1(3)	Sn3–O3–Sn4	106.9(4)	Sn3–O3–Sn2	104.8(4)	Sn4–O3–Sn2	148.3(4)
Sn5–O4–Sn4	112.6(3)	Sn5–O4–Sn3	142.7(4)	Sn4–O4–Sn3	104.7(3)	Sn4–O5–Sn5	100.7(4)	Sn7–O6–Sn6	100.2(4)
Sn7–O7–Sn6	111.7(3)	Sn7–O7–Sn8	105.8(3)	Sn6–O7–Sn8	142.5(4)	Sn8–O8–Sn7	105.9(3)	Sn8–O8–Sn9	104.7(3)
Sn7–O8–Sn9	149.2(4)	Sn9–O9–Sn10	110.2(4)	Sn9–O9–Sn8	105.2(4)	Sn10–O9–Sn8	144.6(5)	Sn10–O10–Sn9	101.6(3)
C217–O11–Sn1	106.9(8)	C227–O13–Sn5	107.4(8)	C237–O15–Sn6	111.5(7)	C247–O17–Sn10	124.5(13)	O2–Sn1–O11	80.8(3)
O2–Sn1–O1	70.9(4)	O11–Sn1–O1	151.7(4)	O2–Sn2–O1	72.3(3)	O2–Sn2–O3	75.5(3)	O1–Sn2–O3	147.6(3)
O3–Sn3–O4	73.4(3)	O3–Sn3–O2	75.3(3)	O4–Sn3–O2	148.6(3)	O4–Sn4–O3	75.0(3)	O4–Sn4–O5	74.3(3)
O3–Sn4–O5	149.2(3)	O4–Sn5–O13	81.6(3)	O4–Sn5–O5	72.2(3)	O13–Sn5–O5	153.9(3)	O7–Sn6–O15	80.1(3)
O7–Sn6–O6	73.2(3)	O15–Sn6–O6	153.2(3)	O7–Sn7–O8	74.2(3)	O7–Sn7–O6	74.5(3)	O8–Sn7–O6	148.6(3)
O8–Sn8–O7	74.0(3)	O8–Sn8–O9	75.1(3)	O7–Sn8–O9	148.8(3)	O9–Sn9–O8	74.8(3)	O9–Sn9–O10	74.0(3)
O8–Sn9–O10	148.6(3)	O9–Sn10–O17	88.5(4)	O9–Sn10–O10	74.2(3)	O17–Sn10–O10	161.6(4)		

Table 1. (Continued)

Compound 5									
Sn1-O1	2.085(2)	Sn2A-O1	2.092(2)	Sn3-O1	2.098(2)	Sn2-O2	2.079(2)	Sn3-O2	2.081(2)
Sn1-O2	2.094(2)	Sn1-O3	2.085(2)	Sn2-O3	2.094(2)	Sn2-O1A	2.092(2)	Sn3-O3A	2.077(2)
Sn1-O1-Sn2A	132.04(11)	Sn1-O1-Sn3	99.70(9)	Sn2A-O1-Sn3	99.75(9)	Sn2-O2-Sn3	134.59(11)	Sn2-O2-Sn1	100.00(9)
Sn3-O2-Sn1	99.96(9)	Sn3A-O3-Sn1	132.85(11)	Sn3A-O3-Sn2	100.35(9)	Sn1-O3-Sn2	99.77(9)	O1-Sn1-O3	105.09(9)
O1-Sn1-O2	78.23(9)	O3-Sn1-O2	77.96(9)	O3-Sn1-Sn3	100.68(6)	O2-Sn1-Sn3	39.87(6)	Sn2-Sn1-Sn3	73.76(3)
O2-Sn2-O1A	103.59(9)	O2-Sn2-O3	78.09(9)	O1A-Sn2-O3	77.98(9)	O3A-Sn3-O2	103.17(9)	O3A-Sn3-O1	78.22(9)
O2-Sn3-O1	78.23(9)								
Compound 6									
Sn1-O1	2.160(6)	Sn2-O1	2.358(7)	Sn2-O2	1.998(6)	Sn1-O2	2.025(6)	Sn1A-O2	2.175(6)
Sn2-O3	2.020(7)	Sn1-O2A	2.175(6)						
Sn1-O1-Sn2	99.1(2)	Sn2-O2-Sn1	117.5(3)	Sn2-O2-Sn1A	135.2(3)	Sn1-O2-Sn1A	107.3(2)	O2-Sn1-O1	73.6(2)
O2-Sn1-O2A	72.7(2)	O1-Sn1-O2A	146.3(2)	O2-Sn2-O3	85.2(3)	O2-Sn2-O1	69.8(2)	O3-Sn2-O1	155.0(3)
Compound 7									
Sn1-O2	2.009(4)	Sn1-O7	2.116(4)	Sn1-O1	2.222(4)	Sn2-O2	2.023(4)	Sn2-O3	2.128(4)
Sn2-O1	2.140(4)	Sn3-O3	2.070(4)	Sn3-O2	2.123(4)	Sn3-O4	2.167(4)	Sn4-O4	2.014(4)
Sn4-O3	2.121(4)	Sn4-O5	2.127(5)	Sn5-O4	2.000(4)	Sn5-O8A	2.095(4)	Sn5-O5	2.279(4)
C1-O6	1.240(8)	C1-O8	1.298(7)	C1-O7	1.302(7)	C2-O5	1.594(16)		
O2-Sn1-O7	80.62(16)	O2-Sn1-O1	71.25(16)	O7-Sn1-O1	151.75(16)	O2-Sn2-O3	75.33(16)	O2-Sn2-O1	72.74(16)
O3-Sn2-O1	146.94(15)	O3-Sn3-O2	74.48(16)	O3-Sn3-O4	73.31(16)	O2-Sn3-O4	147.74(15)	O4-Sn4-O3	75.42(16)
O4-Sn4-O5	73.19(17)	O3-Sn4-O5	148.60(16)	O4-Sn5-O8A	80.62(16)	O4-Sn5-O5	70.18(16)	O8A-Sn5-O5	150.79(17)
O6-C1-O8	121.8(6)	O6-C1-O7	121.8(6)	O8-C1-O7	116.4(6)	Sn1-O2-Sn2	114.21(19)	Sn1-O2-Sn3	139.4(2)
Sn2-O2-Sn3	105.96(18)	Sn3-O3-Sn4	105.39(18)	Sn3-O3-Sn2	104.11(18)	Sn4-O3-Sn2	150.5(2)	Sn5-O4-Sn4	115.5(2)
Sn5-O4-Sn3	137.8(2)	Sn4-O4-Sn3	105.71(18)	C2-O5-Sn4	130.7(4)	C2-O5-Sn5	126.5(5)	Sn4-O5-Sn5	100.75(18)
C1-O7-Sn1	113.0(4)	C1-O8-Sn5A	113.9(4)						

[a] Symmetry operations: For **1**: A)  $-x+1, -y, -z+1$ ; for **2**: A)  $-x+2, -y+2, -z$ ; for **5**: A)  $-x, -y, -z+2$ ; for **6**: A)  $-x+1/2, -y+1/2, -z$ ; for **7**: A)  $-x+1, -y+1, -z+2$ .

The hydrolysis of diorganotin dichlorides usually leads to various hydrolysis products with interesting structures, such as dimeric diorganotin hydroxy halides,<sup>[13a]</sup> trimeric diorganotin oxides cyclo-(R<sub>2</sub>SnO)<sub>3</sub>,<sup>[6b,c]</sup> and dimeric tetraorganodistannoxanes,<sup>[13b,c]</sup> as well as polymeric diorganotin oxides,<sup>[13d]</sup> of which the dimeric tetraorganodistannoxanes have been most extensively investigated. However, a ladder cluster containing five tin atoms has not hitherto been isolated.

Compared with the previously reported alkyl-bridged double ladder structures,<sup>[7]</sup> compound **1** contains not a dimeric tetraorganodistannoxane unit (Sn<sub>4</sub>O<sub>4</sub>) but two Sn<sub>5</sub>O<sub>5</sub> ladders, and these two ladders are connected by two carbonate anions (CO<sub>3</sub><sup>2-</sup>) in the present structure instead of the alkyl groups as previously. In the case of alkyl-bridged double-ladder clusters, the space between the two ladders can be increased by using longer alkyl chains. This led us to the question as to whether the space between the two ladder clusters could be increased by using a longer diacid dianion instead of CO<sub>3</sub><sup>2-</sup>. Based on our knowledge and experience, reaction with acid might be expected to destroy the Sn-O framework due to the basicity of the organooxotin cluster. The replacement of a weak acid by a strong acid in organooxotin cluster chemistry is rarely reported, although Holmes et al. reported a mixed-drum organooxotin cluster [(MeSn(O)O<sub>2</sub>CMe)(MeSn(O)O<sub>2</sub>P(*t*Bu)<sub>2</sub>)<sub>3</sub>]<sub>3</sub>, which was prepared by replacing the acetate anions in [MeSn(O)O<sub>2</sub>CMe]<sub>6</sub> with di-*tert*-butylphosphinate anions.<sup>[4f]</sup>

Some analogues of compound **1** have been prepared according to the above idea. [(R<sub>2</sub>SnO)<sub>3</sub>(R<sub>2</sub>SnOH)<sub>2</sub>L<sub>a</sub>]<sub>2</sub> (**2**) and [(R<sub>2</sub>SnO)<sub>3</sub>(R<sub>2</sub>SnOH)<sub>2</sub>L<sub>b</sub>]<sub>2</sub> (**3**) were obtained by treating **1**

with 1,1'-ferrocenedicarboxylic acid (H<sub>2</sub>L<sub>a</sub>) and hexanedioic acid (H<sub>2</sub>L<sub>b</sub>), respectively, in stoichiometric ratios of 1:2. In these reactions, the inorganic spacers (CO<sub>3</sub><sup>2-</sup> ions) were replaced by organic spacers (L<sub>a</sub><sup>2-</sup> or L<sub>b</sub><sup>2-</sup>). This resulted in an increase in the distance between the two ladders. The <sup>119</sup>Sn NMR spectra of compounds **2** ( $\delta = -310.7, -237.7, -233.8$  ppm) and **3** ( $\delta = -289.5, -241.2, -239.7$  ppm) are similar to that of compound **1** ( $\delta = -304.7, -244.5, -242.6$  ppm) (see Supporting Information), which proves that compounds **1**, **2**, and **3** have the same tin-oxygen framework.

The structures of **2** and **3**, in which the two ladder clusters are connected by two L<sub>a</sub><sup>2-</sup> and L<sub>b</sub><sup>2-</sup> dianions, respectively, are shown in Figure 2 and Figure 3. The structures of **2** and **3** have the same Sn-O framework as **1**. In compound **2**, the two ladders are in different planes, which are almost parallel to one another. The distance between the two planes is 3.81 Å, which is longer than the distance between the two aromatic rings of the 1,1'-ferrocenedicarboxylate dianions (L<sub>a</sub><sup>2-</sup>) (3.28 Å). The 1,1'-ferrocenedicarboxylate dianions (L<sub>a</sub><sup>2-</sup>) adopt a mutually *trans* orientation to minimize repulsions between the organic groups. The Sn-O bond lengths range from 2.022(4) to 2.241(4) Å and the O<sub>ax</sub>-Sn-O<sub>ax</sub> angles range from 148.66(15) to 153.72(17)°. The separation between the two ladders in compound **2** is at least 10 Å, which indicates that this compound constitutes a nanosized tin-oxygen cluster. An even larger organooxotin cluster can be expected to result from the use of a longer spacer. In compound **3**, the Sn-O bond lengths range from 2.009(4) to 2.232(4) Å and the O<sub>ax</sub>-Sn-O<sub>ax</sub> angles range from 147.45(16)

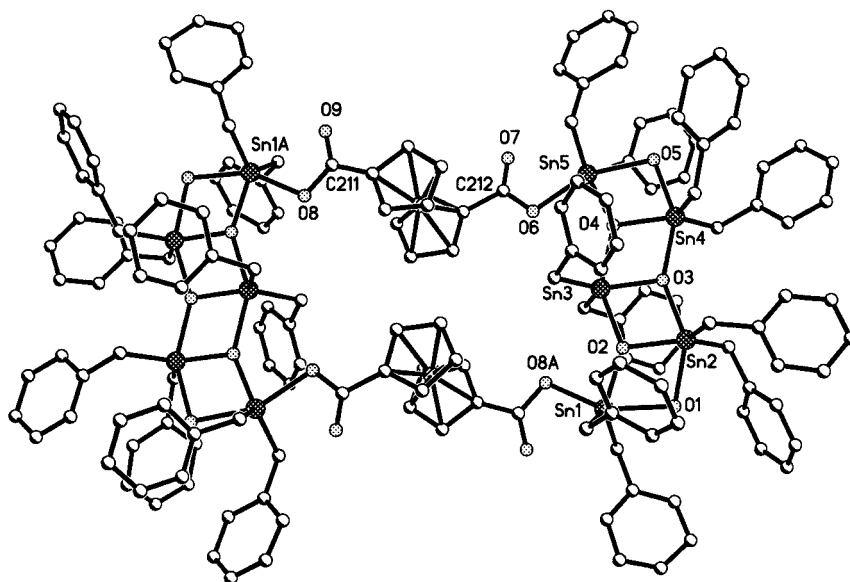


Figure 2. Molecular structure of  $[(R_2SnO)_3(R_2SnOH)_2L_c]_2$  (**2**). All H atoms have been omitted for clarity.

bond lengths range from 1.991(8) to 2.238(9) Å, and the  $O_{ax}-Sn-O_{ax}$  angles range from 147.6(3) to 161.6(4)°. Drum cluster **5** is composed of two hexameric  $Sn_3O_3$  rings, each of which adopts a puckered chair-like conformation. The Sn–O bond lengths range from 2.077(2) to 2.098(2) Å.

The structural relationship and interconversion between the monoorganotin ladder cluster and the drum cluster was first reported by Holmes.<sup>[1a]</sup> The monoorganotin ladder cluster may be converted to the drum cluster through heating or hydrolysis. In this work, the conversion of the diorganotin

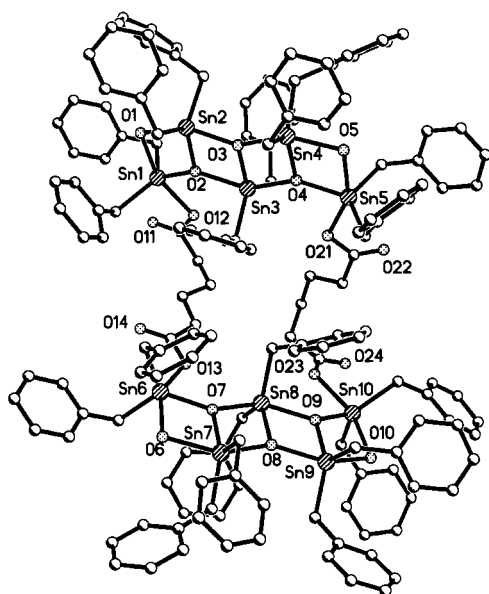


Figure 3. Molecular structure of  $[(R_2SnO)_3(R_2SnOH)_2L_c]_2$  (**3**). All H atoms have been omitted for clarity.

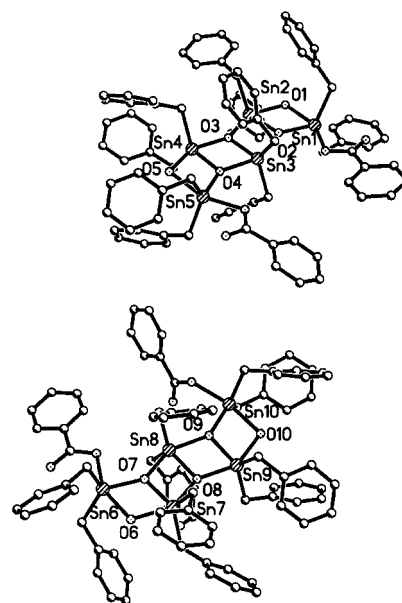


Figure 4. Molecular structure of  $(R_2SnO)_3(R_2SnOH)_2(L_c)_2$  (**4**). All H atoms have been omitted for clarity.

to 153.67(14)°. The separation between the two ladders in compound **3** is greater than 8 Å, which can vary in solution because of the flexibility of hexanedioate dianions ( $L_b^{2-}$ ).

According to the above approach, a single organooxotin ladder cluster  $(R_2SnO)_3(R_2SnOH)_2(L_c)_2$  (**4**) (Figure 4) was obtained by the reaction of **1** with benzoic acid ( $HL_c$ ) in a molar ratio of 1:4. However, when the reaction was carried out at a molar ratio of 1:10, a drum cluster  $[R_2Sn(O)L_c]_6$  (**5**) (Figure 5) was obtained through partial dealkylation of **1**. Drum clusters are generally prepared by a condensation reaction of the organostannonic acid with the ligand acid.<sup>[1]</sup> Further reaction of **4** with benzoic acid in a molar ratio of 1:3 also gave **5**. In the crystal structure of compound **4**, there are two molecules in the asymmetric unit, the Sn–O

ladder cluster to the drum cluster proceeds with an unusual Sn–C bond cleavage, which indicates that the drum structure is more stable than the ladder structure. Recently, there have been some attempts to utilize the Sn–C bond cleavage to form new organooxotin motifs.<sup>[14]</sup> To the best of our knowledge, the formation of a drum structure from a diorganotin ladder precursor has not been reported in organotin cluster chemistry.<sup>[1]</sup> The result implies that other diorganotin ladder clusters, such as dimeric tetraorganodistannoxanes, may also convert to drum clusters through Sn–C bond cleavage.

It is conceivable that hydrolysis of other diorganotin dichlorides may afford other novel carbonate-bridged ladder clusters having the same Sn–O framework as cluster **1**. In-

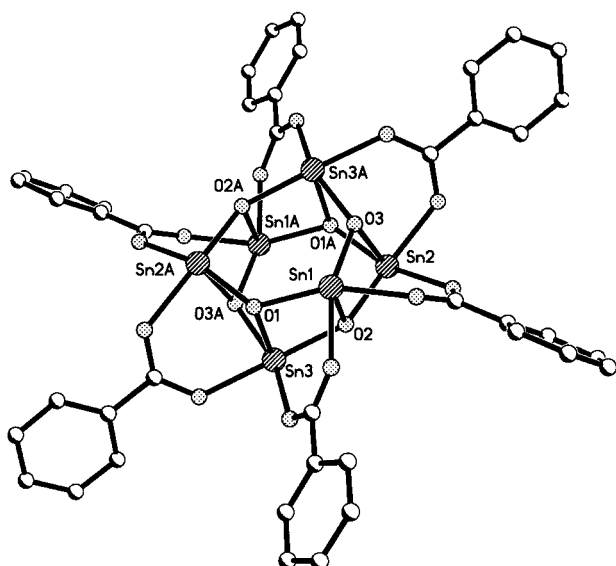


Figure 5. Molecular structure of  $[\text{R}_2\text{Sn}(\text{O})\text{L}]_6$  (**5**). All H atoms and benzyl groups have been omitted for clarity.

spired by this idea, dicyclohexyltin dichloride was hydrolyzed in ethanol according to the same method as that used for dibenzyltin dichloride. To our surprise, the hydrolysis of dicyclohexyltin dichloride afforded a dimeric tetraorganodistannoxane  $[\text{C}_6\text{H}_{11}(\text{C}_2\text{H}_5\text{O})\text{SnOSn}(\text{C}_2\text{H}_5\text{O})\text{C}_6\text{H}_{11}]_2$  (**6**; Cy =  $\text{C}_6\text{H}_{11}$ ), the structure of which is shown in Figure 6. Cluster **6** is an ethanolate-bridged ladder, in which each *exo* tin is connected to two ethanolate anions. Compound **6** is a ladder-type centrosymmetric dimer with a center of inversion at 0.25, 0.25, 0, and the  $\text{Sn}_4\text{O}_6$  structural motif is planar to within  $\pm 0.0239 \text{ \AA}$ . Each tin atom exhibits a distorted trigonal-bipyramidal geometry, with the equatorial positions being occupied by two carbon atoms and one oxygen atom, and the axial positions by two oxygen atoms. The longest Sn–O bond length in compound **6** is Sn2–O1 (2.358(7)  $\text{\AA}$ ),

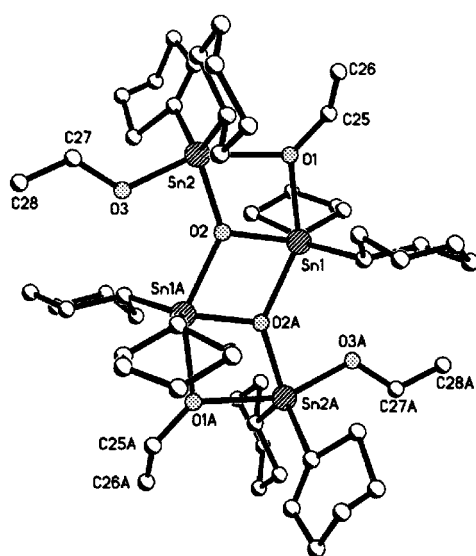


Figure 6. Molecular structure of  $[\text{R}_2(\text{C}_2\text{H}_5\text{O})\text{SnOSn}(\text{C}_2\text{H}_5\text{O})\text{R}]_2$  (**6**). All H atoms have been omitted for clarity.

and the  $\text{O}_{\text{ax}}\text{-Sn-O}_{\text{ax}}$  angles are O3–Sn2–O1 155.0(3) and O1–Sn1–O2A 146.3(2) $^\circ$ , respectively. These results indicate that the organic group on the tin atom can affect the formation of hydrolysis products as a result of electronic and steric requirements.

According to the formation of **6**, compound **1** may be chemically modified at the four corner positions, that is to say, the OH groups at the corner positions may be replaced by  $\text{R}'\text{O}^-$  groups ( $\text{R}' = \text{alkyl}$ ) through changing the conditions of hydrolysis of dibenzyltin dichloride. Somewhat at variance with our expectations, a new ethanolate-modified cluster  $[(\text{R}_2\text{SnO})_3(\text{R}_2\text{SnOH})(\text{R}_2\text{SnOC}_2\text{H}_5)(\text{CO}_3)]_2$  (**7**) was obtained by hydrolysis of dibenzyltin dichloride in ethanol in the presence of EtONa and hypnone. The most notable structural variation is that two diagonally opposite hydroxyl groups are replaced by ethanolate groups, which shows that the tin-oxygen cluster **1** can be extended from its corner positions. However, attempts to synthesize the compound modified at all four corner positions failed.

The structure of **7** is shown in Figure 7; the framework of the tin-oxygen cluster is the same as that in **1**. The Sn–O bond lengths range from 2.000(4) to 2.279(4)  $\text{\AA}$  and the  $\text{O}_{\text{ax}}\text{-Sn-O}_{\text{ax}}$  angles range from 146.94(15) to 151.75(16) $^\circ$ . The longest Sn–O bond length in compound **7** is Sn(5)–O(5) (2.279(4)  $\text{\AA}$ ), which is longer than the longest Sn–O bond length in compound **1** (2.234(2)  $\text{\AA}$ ).

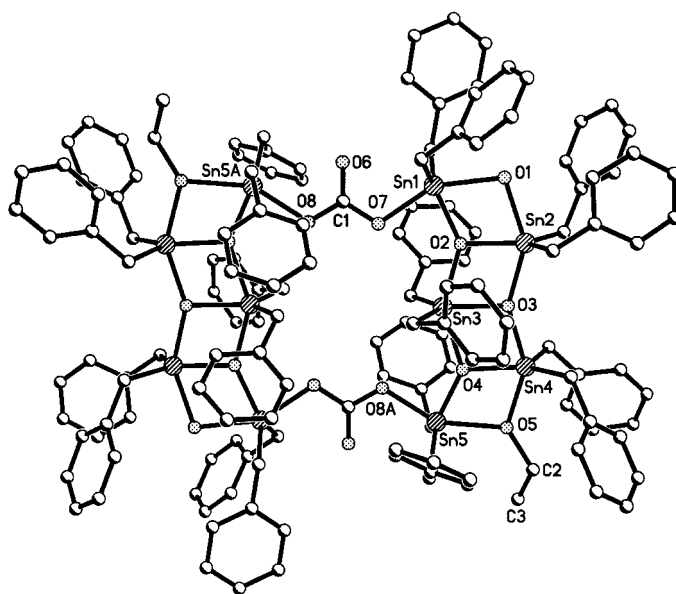


Figure 7. Molecular structure of  $[(\text{R}_2\text{SnO})_3(\text{R}_2\text{SnOH})(\text{R}_2\text{SnOC}_2\text{H}_5)(\text{CO}_3)]_2$  (**7**). All H atoms have been omitted for clarity.

## Conclusion

In summary, we have synthesized and characterized a series of unique organotin clusters incorporating inorganic and organic spacers between two ladders, each of which contains five tin atoms. The formation of a drum structure starting from a diorganotin ladder precursor has been observed for the first time. Meanwhile, the new organotin cluster has

been modified at its corner positions. The synthetic approach described herein also offers a new method for obtaining organooxotin clusters with large cavities suitable for host–guest chemistry. Moreover, access to new high-nuclear organotin oxides can be expected through the reaction of **1** with polyacids. The reactions of compound **1** with polyacids to form high-nuclear organooxotin clusters, as well as the host–guest chemistry of the organooxotin clusters, are under investigation in our laboratory.

## Experimental Section

**General procedures:** Chemicals were obtained from commercial sources and were used without further purification. 1,1'-Ferrocenedicarboxylic acid<sup>[15]</sup> and dibenzyltin dichloride<sup>[16]</sup> were prepared by literature methods.

**Physical measurements:** FT-IR spectra were recorded from samples in KBr pellets in the range 4000–400 cm<sup>-1</sup> on a Mattson Alpha-Centauri spectrometer. Elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer. <sup>119</sup>Sn NMR spectra (proton-decoupled) were recorded on a Bruker AMX-300 spectrometer operating at 111.9 MHz; resonances are referenced to tetramethyltin (external standard, <sup>119</sup>Sn).

**Synthesis of 1:** Na (0.063 g) was added to ethanol (70 mL). After heating the solution at reflux for 5 min, (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>SnCl<sub>2</sub> (0.370 g) was added. The reaction mixture was heated at reflux for 12 h, and then the resulting suspension was filtered. The solvent was slowly evaporated from the filtrate in air to give the product as colorless crystals (0.051 g, yield: 15%); elemental analysis calcd (%) for [(R<sub>2</sub>SnO)<sub>5</sub>(R<sub>2</sub>SnOH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>·2CH<sub>3</sub>COCH<sub>3</sub>]: C 52.14, H 4.61; found: C 52.03, H 4.73; <sup>119</sup>Sn NMR (CDCl<sub>3</sub>): δ = -304.7, -244.5, -242.6 ppm; FT-IR: ν̄ = 3023 (m), 1599 (s), 1546 (s), 1492 (vs), 1452 (s), 1361 (s), 1209 (m), 1055 (m), 757 (vs), 696 (vs), 612 (s), 555 (m), 519 (s), 454 cm<sup>-1</sup> (m).

**Synthesis of 2:** 1,1'-Ferrocenedicarboxylic acid (0.054 g) was added to a solution of compound **1** (0.340 g) in benzene (50 mL). After heating the reaction mixture at reflux for 6 h, the solvent was evaporated. Recrystallization of the residue from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether gave the product as red block-shaped crystals (0.272 g, yield: 70%); elemental analysis calcd (%) for [(R<sub>2</sub>SnO)<sub>5</sub>(R<sub>2</sub>SnOH)<sub>2</sub>·10H<sub>2</sub>O]: C 50.54, H 4.65; found: C 50.66, H 4.77; <sup>119</sup>Sn NMR (CDCl<sub>3</sub>): δ = -310.7, -237.7, -233.8 ppm.

**Synthesis of 3:** Hexanedioic acid (0.040 g) was added to a solution of compound **1** (0.468 g) in benzene (50 mL). After heating the reaction mixture at reflux for 6 h, the solvent was evaporated. Recrystallization of the residue from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether gave the product as colorless crystals (0.380 g, yield: 80%); elemental analysis calcd (%) for [(R<sub>2</sub>SnO)<sub>5</sub>(R<sub>2</sub>SnOH)<sub>2</sub>L<sub>6</sub>]: C 52.74, H 4.66; found: C 52.70, H 4.70; <sup>119</sup>Sn NMR (CDCl<sub>3</sub>): δ = -289.5, -241.2, -239.7 ppm.

**Synthesis of 4:** Benzoic acid (0.096 g) was added to a solution of compound **1** (0.670 g) in benzene (50 mL). After heating the reaction mixture at reflux for 6 h, the solvent was evaporated, and the residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether to give the product as colorless block-shaped crystals (0.475 g, yield: 65%); elemental analysis calcd (%) for (R<sub>2</sub>SnO)<sub>5</sub>(R<sub>2</sub>SnOH)<sub>2</sub>(L<sub>6</sub>)·0.5CH<sub>3</sub>COCH<sub>3</sub>: C 55.27, H 4.61; found: C 55.01, H 4.33.

**Synthesis of 5:** Compound **5** was prepared from **1** (0.340 g) by a procedure analogous to that used to synthesize **4**, but with a **1**:benzoic acid molar ratio of 1:10. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether gave colorless crystals (0.150 g, yield: 40%); elemental analysis calcd (%) for [R<sub>2</sub>Sn(O)L<sub>6</sub>]<sub>6</sub>·2CH<sub>2</sub>Cl<sub>2</sub>: C 45.88, H 3.40; found: C 45.44, H 3.12; <sup>119</sup>Sn NMR (CDCl<sub>3</sub>): δ = -521.8 ppm.

**Synthesis of 6:** Na (0.082 g) was added to ethanol (70 mL). After heating the solution at reflux for 5 min, Cy<sub>2</sub>SnCl<sub>2</sub> (0.356 g) was added. The reaction mixture was heated at reflux for 12 h, and then the resulting suspension was filtered. The solvent was slowly evaporated from the filtrate in air to give the product as colorless crystals (0.058 g, yield: 17%); elemental analysis calcd (%) for [Cy<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>O)SnOSn(C<sub>2</sub>H<sub>5</sub>O)Cy<sub>2</sub>]<sub>2</sub> (Cy = C<sub>6</sub>H<sub>11</sub>): C 49.74, H 8.05; found: C 49.63, H 8.10.

**Synthesis of 7:** Na (0.092 g) was added to a solution of hypnone (0.244 g) in ethanol (70 mL). After heating the solution at reflux for 5 min, (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>SnCl<sub>2</sub> (0.380 g) was added. The reaction mixture was heated at reflux for 12 h, and then the resulting suspension was filtered. The solvent was slowly evaporated from the filtrate in air to give the product as colorless crystals (0.045 g, yield: 13%); elemental analysis calcd (%) for [(R<sub>2</sub>SnO)<sub>5</sub>(R<sub>2</sub>SnOH)(R<sub>2</sub>SnOC<sub>2</sub>H<sub>5</sub>)(CO<sub>3</sub>)<sub>2</sub>]: C 52.35, H 4.57; found: C 52.30, H 4.60.

**X-ray data collection and structure refinement details:** Experimental data from the X-ray analyses are provided in Table 2. Diffraction intensities were collected on a Rigaku RAXIS-RAPID image plate diffractometer using the ω-scan technique with MoK<sub>α</sub> radiation (λ = 0.71069 Å). Absorption corrections were applied using the multiscan technique.<sup>[17]</sup> The structures were solved by direct methods using SHELXS-97<sup>[18]</sup> and refined by means of full-matrix least-squares techniques using the

Table 2. Crystal data and structure refinements for compounds **1–7**.

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>
empirical formula	C <sub>148</sub> H <sub>156</sub> O <sub>18</sub> Sn <sub>10</sub>	C <sub>164</sub> H <sub>180</sub> Fe <sub>2</sub> O <sub>28</sub> Sn <sub>10</sub>	C <sub>152</sub> H <sub>160</sub> O <sub>18</sub> Sn <sub>10</sub>	C <sub>85.50</sub> H <sub>85</sub> O <sub>9.50</sub> Sn <sub>5</sub>	C <sub>86</sub> H <sub>76</sub> C <sub>14</sub> O <sub>18</sub> Sn <sub>6</sub>	C <sub>56</sub> H <sub>108</sub> O <sub>6</sub> Sn <sub>4</sub>	C <sub>146</sub> H <sub>152</sub> O <sub>16</sub> Sn <sub>10</sub>
formula weight	3409.63	3897.68	3461.70	1857.99	2251.41	1352.18	3349.58
crystal size [mm]	0.147 × 0.286 × 0.245	0.110 × 0.272 × 0.344	0.324 × 0.447 × 0.233	0.443 × 0.319 × 0.291	0.239 × 0.294 × 0.186	0.153 × 0.194 × 0.078	0.050 × 0.112 × 0.158
crystal system	triclinic	triclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Cc</i>	<i>P</i> $\bar{1}$	<i>C2/c</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	11.8921(2)	14.226(3)	12.176(2)	28.702(6)	12.039(2)	21.977(4)	14.083(3)
<i>b</i> [Å]	15.500(3)	16.974(3)	22.275(5)	16.536(3)	13.532(3)	13.423(3)	14.731(3)
<i>c</i> [Å]	20.461(4)	19.265(4)	27.997(6)	33.268(7)	13.902(3)	22.532(5)	18.718(4)
α [°]	75.31(3)	111.21(3)	81.31(3)	90	108.42(3)	90.00	107.49(3)
β [°]	81.93(3)	102.20(3)	89.28(3)	91.28(3)	98.18(3)	108.23(3)	99.96(3)
γ [°]	82.01(3)	94.38(3)	76.45(3)	90	91.46(3)	90.00	108.47(3)
volume [Å <sup>3</sup> ]	3590.7(12)	4178.9(19)	7295(3)	15786(5)	2120.8(7)	6313(2)	3354.9(11)
<i>Z</i>	1	1	2	8	1	4	1
<i>R</i> <sub>int</sub>	0.0192	0.0330	0.0342	0.0298	0.0284	0.0731	0.0300
<i>R</i> <sub>1</sub>	0.0234	0.0449	0.0421	0.0452	0.0241	0.0544	0.0310
[ <i>I</i> > 2σ( <i>I</i> )]							
<i>wR</i> <sub>2</sub> (all data)	0.0814	0.1276	0.1350	0.1419	0.0825	0.1734	0.1060

SHELXL-97 program<sup>[19]</sup> as implemented in WINGX.<sup>[20]</sup> Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms attached to carbon were generated geometrically, while the aqua hydrogen atoms were not located. Analytical expressions of neutral-atom scattering factors were employed, with anomalous dispersion corrections incorporated therein.<sup>[21]</sup>

CCDC-232622 to CCDC-232628 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336033).

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