

# High Yield Synthesis and Characterization of $\text{Sn}_6(\mu_3\text{-O})_4(\mu_3\text{-OSiMe}_3)_4$ : A Novel Main Group Cluster for the Support of Multiple Transition Metal Centers

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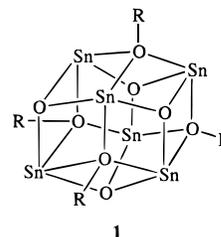
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**Abstract:** A high yielding, highly reproducible synthesis of the novel main group cluster  $\text{Sn}_6(\mu_3\text{-O})_4(\mu_3\text{-OSiMe}_3)_4$  (**2**), which involves the thermolysis of bis[bis(trimethylsilanolato)tin] (**4**) at 180 °C, is reported. Spectroscopic and chemical analyses are fully consistent with the assigned structure of **2**. A preliminary investigation of the reaction between this compound and  $\text{Fe}_2(\text{CO})_9$  reveals that the tin(II) centers of the former are capable of participating as 2e  $\sigma$ -donors in the formation of the  $\text{Fe}(\text{CO})_4$  adducts,  $[\{\text{Fe}(\text{CO})_4\} \text{Sn}_6(\mu_3\text{-O})_4(\mu_3\text{-OSiMe}_3)_4]$  (**5**) and  $[\{\text{Fe}(\text{CO})_4\}_2 \text{Sn}_6(\mu_3\text{-O})_4(\mu_3\text{-OSiMe}_3)_4]$  (**6**). The assigned structures of **5** and **6** are confirmed by spectroscopic and crystallographic analyses and the latter reveal important information regarding the influence that the steric features of **2** have on the coordination sphere of transition metal centers that are ligated to it. Space-filling models also reveal that additional complexation to **2**, **5**, and **6** is sterically permitted. Together, these findings provide an important platform upon which a variety of future studies that utilize **2** as a new class of building block for the construction of mixed p–d metal compounds and materials can be based. Single crystals of **5** are (at 25 °C) monoclinic, space group  $P2_1/n$  with  $a = 13.404(2)$  Å,  $b = 16.964(3)$  Å,  $c = 17.766(2)$  Å,  $\beta = 90.384(12)^\circ$ ,  $V = 4039.7(10)$  Å<sup>3</sup>, and  $Z = 4$  ( $D_{\text{calcd}} = 2.139$  mg m<sup>-3</sup>;  $\mu(\text{Mo K}\alpha) = 41.57$  mm<sup>-1</sup>). Single crystals of **6** ( $0.7$ )<sup>1/2</sup>C<sub>6</sub>H<sub>6</sub> are (at 23 °C) monoclinic, space group  $P2_1/n$  with  $a = 11.804(2)$  Å,  $b = 17.489(3)$  Å,  $c = 23.222(2)$  Å,  $\beta = 97.146(9)^\circ$ ,  $V = 4756(1)$  Å<sup>3</sup>, and  $Z = 4$  ( $D_{\text{calcd}} = 2.089$  mg m<sup>-3</sup>;  $\mu(\text{Mo K}\alpha) = 38.41$  mm<sup>-1</sup>).

## Introduction

The synthesis and reactivity of well-defined transition metal complexes that are ligated to soluble inorganic clusters, such as silasesquioxanes [e.g., (RSiO<sub>1.5</sub>)<sub>8</sub>] and other heterosiloxanes, have received considerable attention as a strategy through which to develop homogeneous models for heterogeneous catalysts.<sup>1</sup> In this pursuit, the potential exists for the steric and electronic features of the cluster serving as the support to interact in a synergistic fashion with the ligated transition metal center to impart favorable characteristics, such as an increased selectivity and/or reactivity in a catalytic process. For clusters that can support multiple transition metal fragments, the possibility also exists that new classes of “high density” homogeneous catalysts can be developed in which additional synergism between the transition metal centers may be present. With respect to the search for other inorganic clusters that might serve as suitable supports, the structural framework of **1** that is presented by the  $\text{Sn}_6(\mu_3\text{-O})_4(\mu_3\text{-OR})_4$  class of compound<sup>2</sup> is an intriguing one given the ability of a variety of divalent tin species to function as neutral, 2e  $\sigma$ -donors.<sup>3</sup> Indeed, two hexanuclear clusters  $[\{(\text{CO})_5\text{CrSn}\}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]$  and  $[\{\text{Cp}^*(\text{CO})_2\text{MnSn}\}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) were recently isolated that can formally be viewed as having arisen from the direct metal

## Chart 1



complexation of  $\text{Sn}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$ .<sup>4</sup> In reality, however, neither of these compounds were prepared in this fashion, and instead, they were generated from the air-hydrolysis of the dianion  $[\{(\text{CO})_5\text{Cr}\}_2\text{Sn}(\text{Cl})_2]^{2-}$  and the dimanganastannacumulene  $[\text{Cp}^*\text{Mn}(\text{CO})_2=\text{Sn}=\text{Mn}(\text{CO})_2\text{Cp}^*]$ , respectively. Accordingly, an open question that remains is whether or not some, or all, of the six tin(II) centers of **1** are willing, and able, to participate in the formation of transition metal complexes. Unfortunately, efforts directed toward a settlement of this issue have been severely hampered by the lack of reliable sources for the set of known derivatives that is encompassed by  $\text{R} = \text{H, Me, and Pr}^i$  in **1**. Furthermore, at least two of these,  $\text{R} = \text{H and Me}$ , are reported to be highly insoluble in most solvents.<sup>2a,b</sup> Herein, we now present a break in this impasse that is provided by the discovery of a simple, high yielding, highly reproducible, synthesis of the new derivative,  $\text{Sn}_6(\mu_3\text{-O})_4(\mu_3\text{-OSiMe}_3)_4$  (**2**), that possesses favorable solubility characteristics. In addition,

(3) (a) Holt, M. S.; Wilson, W. L.; Nelson, J. H. *Chem. Rev.* **1989**, 89, 11. (b) Lappert, M. F.; Rowe, R. S. *Coord. Chem. Rev.* **1990**, 100, 267. (c) Veith, M.; Weidner, S.; Kunze, K.; Käfer, D.; Han, J.; Huch, V. *Coord. Chem. Rev.* **1994**, 137, 297.

(4) (a) Schiemenz, B.; Ettl, F.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1993**, 458, 159. (b) Schiemenz, B.; Antelmann, B.; Huttner, G.; Zsolnai, L. *Z. Anorg. Allg. Chem.* **1994**, 620, 1760.

<sup>†</sup> The University of Chicago.

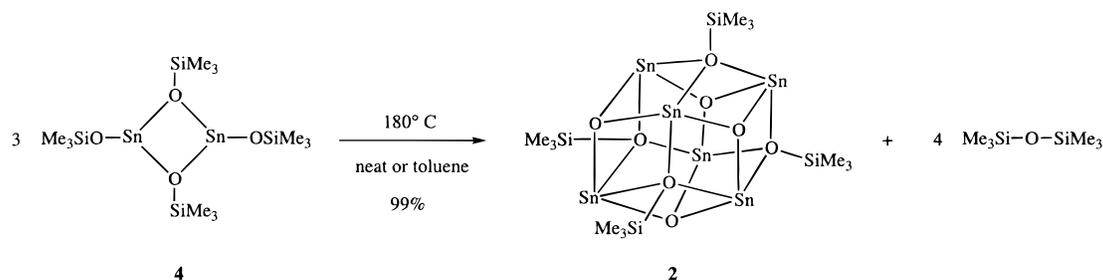
<sup>‡</sup> University of Delaware.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, January 15, 1997.

(1) Feher, F. J.; Budzichowski, T. A. *Polyhedron* **1995**, 14, 3239. (b) Calzaferri, G.; Imhof, R.; Törnroos, K. W. *J. Chem. Soc., Dalton Trans.* **1993**, 3741. (c) Ritter, U.; Winkhofer, N.; Murugavel, R.; Voigt, A.; Stalke, D.; Roesky, H. W. *J. Am. Chem. Soc.* **1996**, 118, 8580. (d) Murugavel, R.; Chandrasekhar, V.; Roesky, H. W. *Acc. Chem. Res.* **1996**, 29, 183.

(2) (a) R = H: Howie, R.; Moser, W. *Nature* **1968**, 219, 372. (b) R = Me: Harrison, P. G.; Haylett, B. J.; King, T. J. *J. Chem. Soc., Chem. Commun.* **1978**, 112. (c) R = Pr<sup>i</sup>: Sasaki, Y.; Miyazawa, N. *Kin. Daigaku Rik. Kenk. Hokoku* **1992**, 28, 237 (*Chem. Abstr.* **1992**, 119, 18173u).

## Scheme 1

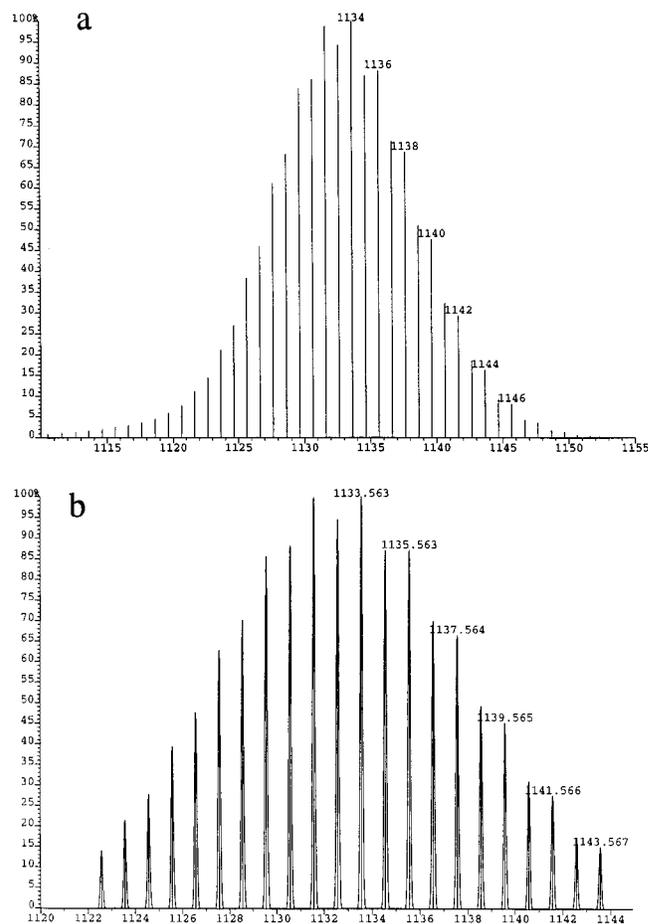


the results of a preliminary study of the reaction between **2** and diironnonacarbonyl,  $\text{Fe}_2(\text{CO})_9$  (**3**), are presented which demonstrate, through the isolation and full characterization of two  $\text{Fe}(\text{CO})_4$  adducts, that the subvalent tin centers in this  $\text{Sn}_6(\mu_3\text{-O})_4(\mu_3\text{-OR})_4$  derivative are indeed capable of serving as  $2e$   $\sigma$ -donors to transition metal centers. These data also reveal important information regarding the impact that complexation has on the framework of **2**, and on the coordination sphere of the transition metal centers that are ligated to it. Altogether then, these findings provide an important platform upon which a variety of future studies that utilize **2** as a new class of building block for the construction of mixed p-d metal compounds and materials can be based.

## Results and Discussion

The synthesis of air-sensitive **2** involves the thermally-driven self-condensation of bis[bis(trimethylsilyloxy)tin] (**4**)<sup>5</sup> that is illustrated in Scheme 1. As indicated, this process proceeds, without solvent, in virtually a quantitative yield with the only co-product being hexamethyldisiloxane (HMDS).<sup>6</sup> Thus, simply heating **4**, which is a colorless oil at room temperature, in a Schlenk flask, at ambient pressure and under an inert atmosphere of dinitrogen, produced, at 180 °C, HMDS as a distillate. Upon cooling, the colorless oil remaining as the pot material then rapidly crystallized to provide, after removing *in vacuo* any remaining HMDS, a white crystalline material that was shown by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR spectroscopy to be essentially pure **2** at this stage. Analytically pure material, however, was easily provided through recrystallization of **2** from a toluene/acetonitrile solvent mixture at  $-40$  °C to provide this compound as very thin white needles that are highly soluble in most nonpolar solvents.

At the present time, it has not been possible to obtain single crystals of **2** that are suitable for crystallographic analysis; however, spectroscopic and chemical analyses are fully consistent with the assigned structure. For instance, chemical analysis supports the  $\text{Sn}_6\text{O}_4(\text{OSiMe}_3)_4$  formulation while mass spectroscopy (electron impact) provides a strong parent molecular ion in the range of  $m/z$  1122–1146 (relative intensity: 100%) that possesses an isotope cluster pattern that is also consistent with the expected composition as shown in Figure 1. In addition, at 20 °C, the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR spectra of **2** all appear to support the  $T_d$  symmetry of the proposed structure on the basis that only a single resonance is observed. However, it is important to note that in the  $^{119}\text{Sn}$  NMR spectrum there is a noticeable lack of evidence for  $^2J(^{119}\text{Sn}-^{117}\text{Sn})$



**Figure 1.** (a) A partial mass spectrum (electron impact) of **2** showing the parent ion in the  $m/z$  1122–1146 range. (b) A simulated isotope cluster pattern expected for the  $\text{C}_{12}\text{H}_{36}\text{O}_{12}\text{Si}_4\text{Sn}_6$  composition.

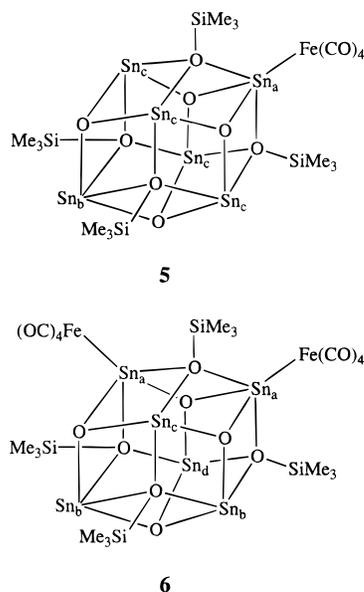
coupling between tin atoms that share a common oxygen bridge, even down to  $-80$  °C.<sup>7</sup> For comparison, in the bridged dimeric structure of **4**, the rapid exchange between terminal and bridging trimethylsilyloxy groups that is observed at 20 °C is largely frozen out at  $-50$  °C where  $^2J(^{119}\text{Sn}-^{117}\text{Sn})$  coupling satellites ( $J = 234$  Hz) in the  $^{119}\text{Sn}$  NMR spectrum can now clearly be distinguished. Together, these observations tend to suggest that while **2** is probably not undergoing dissociation in solution, the framework of this compound might be susceptible to fluxional structural distortions, such as  $T_d \leftrightarrow D_{2d} \leftrightarrow T_d$  interconversions. Finally, regarding **2**, vibrational spectroscopy (IR; KBr pellet) reveals only a small number of modes and these can be assigned to the following:  $\nu_{\text{C-H}}$  (vs,  $2947\text{ cm}^{-1}$ ),  $\delta_{\text{CH}_3}$  (vs, 1255),  $\nu_{\text{Si-O}}$

(5) The best method for the preparation of **4** in high yield (98%) is via a novel one-step carbon dioxide metathesis route that starts with commercially available bis[bis(trimethylsilyloxy)tin], see: Sita, L. R., Babcock, J. R.; Xi, R. *J. Am. Chem. Soc.* **1996**, *118*, 10912.

(6) It has previously been reported that thermolysis of **4** in solution proceeds with loss of HMDS to provide a product of composition,  $(1/x) \cdot [\text{Sn}_2\text{O}(\text{OSiMe}_3)_2]_x$ . The reported  $^{119}\text{Sn}$  NMR chemical shift of this material is close to that recorded for **2**,  $-136$  and  $-138$  ppm, respectively, see: duMont, W. W.; Grenz, M. *Z. Naturforsch.* **1983**, *38B*, 113.

(7) Due to the occurrence of the two  $I = 1/2$  isotopes of tin,  $^{119}\text{Sn}$  and  $^{117}\text{Sn}$ , that have relatively high natural abundances, 8.58% and 7.61%, respectively, it is routinely possible to observe  $^nJ(^{119}\text{Sn}-^{117}\text{Sn})$  coupling satellites between magnetically equivalent tin atoms in a structure, see: Sita, L. R. *Adv. Organomet. Chem.* **1995**, *38*, 189 and references cited therein.

## Chart 2



(vs, 850), and  $\nu_{\text{Sn-O}}$  (vs, 570).<sup>8</sup> In addition, a solution of this compound in pentane ( $c = 3.53 \times 10^{-5}$  M) exhibits an intense electronic transition at  $\lambda_{\text{max}} 230$  nm ( $\epsilon_{\text{max}} 51\,664$ ) that trails off toward the visible ( $\lambda 250$  nm,  $\epsilon 15\,590$ ;  $\lambda 270$  nm,  $\epsilon 2900$ ).

The mechanism by which **2** is produced is of significant interest given that this is such a high yielding process, and that it might be amenable to the syntheses of other transition and main group metal oxo complexes by similar routes.<sup>9</sup> Interestingly, monitoring the thermolysis of **4** by <sup>1</sup>H NMR (300 MHz, toluene-*d*<sub>8</sub>) spectroscopy revealed that the production of **2** also occurs quite cleanly in solution at 180 °C with no detectable amounts of either side products or intermediates ever being observed. It can be pointed out, however, that the structurally characterized crystalline compound,  $\text{Pb}_4(\mu_4\text{-O})(\mu\text{-OSiPh}_3)_6$ , was previously isolated from a solution decomposition of  $[\text{Pb}(\text{OSiPh}_3)_2]_2$  that involves elimination of hexaphenyldisiloxane.<sup>9a</sup> Papiernik *et al.*<sup>10</sup> also speculate that the isostructural complex,  $\text{Pb}_4(\mu_4\text{-O})(\mu\text{-OPr}^i)_6$ , is an intermediate in the pathway leading to the production of  $\text{Pb}_6(\mu_3\text{-O})_4(\mu_3\text{-OPr}^i)_4$ ,<sup>11</sup> a lead analog of **1**. Accordingly, it is tempting to speculate, at this time, the intermediacy of the similar complex  $\text{Sn}_4(\mu_4\text{-O})(\mu\text{-OSiMe}_3)_6$  in the formation of **2**. Positive proof for this, however, awaits further study.

In order to obtain further support for the assigned structure of **2**, and to begin an assessment of its ability to function as a support for transition metal fragments, the chemical reactivity of this  $\text{Sn}_6(\mu_3\text{-O})_4(\mu_3\text{-OR})_4$  derivative with diironnonacarbonyl (**3**) was investigated. Similar studies with other divalent tin compounds have previously led to the formation of a number of  $\text{Fe}(\text{CO})_4$  adducts of tin(II) complexes.<sup>3</sup> Accordingly, stirring a suspension of either 1 or 2 equiv of **3** in a toluene solution of **2** for 48 h led to product mixtures containing the mono- $\text{Fe}(\text{CO})_4$  adduct **5** and the bis- $\text{Fe}(\text{CO})_4$  adduct **6**, both of which were isolated in pure form through fractional crystallization from acetonitrile/toluene solvent mixtures at  $-40$  °C. From an <sup>1</sup>H

NMR analysis of the initial crude product mixture, use of 2 equiv of **3** provides a 2.5:1 ratio of **6** to **5** for a combined yield of 66%. NMR spectroscopy also reveals the presence of another major  $\text{Fe}(\text{CO})_4$  adduct, tentatively assigned as the “para” isomer of **6** (23% yield), but due to its solubility characteristics, it has not yet been possible to isolate this compound in pure form through crystallization.

As with **2**, spectroscopic and chemical analyses of the two  $\text{Fe}(\text{CO})_4$  adducts, **5** and **6**, are fully consistent with their structural assignments. In particular, the number of resonances observed in the <sup>1</sup>H and <sup>119</sup>Sn NMR spectra of these two compounds are consistent with those anticipated on the basis of symmetry arguments that can be used to determine from these spectra both the level of complexation in an isolated adduct and its isomeric identity [e.g. the expected “ortho” and “para” isomers of the bis- $\text{Fe}(\text{CO})_4$  adduct of **2**]. An analysis of the <sup>119</sup>Sn NMR spectra for **5** and **6** also provides some additional information regarding the impact that transition metal complexation might have on the fluxionality of the  $\text{Sn}_6(\mu_3\text{-O})_4(\mu_3\text{-OR})_4$  framework. For instance, in both of these spectra, clearly defined <sup>2</sup>*J*(<sup>119</sup>Sn–<sup>117</sup>Sn) coupling satellites can be discerned for coupling between ligated tin atoms and their next nearest neighbors, with the magnitude of this coupling being on the order of 120 to 140 Hz. Coupling to more remote, non-ligated, tin atoms, however, is still not observed. These observations then suggest that transition metal complexation may serve to rigidify the  $\text{Sn}_6(\mu_3\text{-O})_4(\mu_3\text{-OSiMe}_3)_4$  framework by increasing the strength of Sn–O interactions as a consequence of the enhanced electron-deficient character of the ligated tin atoms. Finally, regarding the  $\text{Fe}(\text{CO})_4$  fragments in **5** and **6**, IR spectroscopy in solution and in the solid state, reveals only two distinct bands in the carbonyl stretching region at 2041 (m) and 1947 (s)  $\text{cm}^{-1}$ . For comparison, three bands are observed in the solution IR spectrum of the complex  $\text{Fe}(\text{CO})_4\text{-}\{\text{Sn}(\text{OAr})_2\}$  (Ar = 2,6-*Bu*<sub>2</sub>-4-Me-C<sub>6</sub>H<sub>2</sub>) at 2070 (m), 2000 (s) and 1981 (s)  $\text{cm}^{-1}$  in which the sterically encumbered stannylene fragment resides in the equatorial position of a trigonal bipyramidal (TBP)  $\text{Fe}(\text{CO})_4\text{L}$  configuration due to steric reasons.<sup>12,13</sup> We conclude from these observations that, due to the steric bulk presented by **2**, the main group cluster in **5** and **6** most likely resides in a similar equatorial position of TBP configured  $\text{Fe}(\text{CO})_4$  fragments and that no equatorial–axial interconversion at the transition metal centers is occurring in solution.<sup>14</sup>

Unequivocal proof of structure for **5** and **6** was provided by crystallographic analysis of single crystals, and as Figures 2 and 3 and Table 1 reveal, both compounds possess many similar features in the solid state. For instance, a comparison of selected bond lengths and bond angles indicates that the  $\text{Sn}_6(\mu_3\text{-O})_4(\mu_3\text{-OSiMe}_3)_4$  core units are nearly identical (see Table 1). However, it is important to note that, in each case, bonds made between siloxy oxygen atoms and ligated tin centers are significantly shorter than those made between this type of oxygen and nonligated tin atoms. It is also interesting to note that bonds made between tin and the face-bridging oxo atoms are much shorter than those between tin and the oxygen of a bridging siloxy group, and this now appears to be a common feature of  $\text{M}_6(\mu_3\text{-O})_4(\mu_3\text{-OR})_4$  derivatives where M = Sn and

(8) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley & Sons: New York, 1986.

(9) The formation of metal oxo clusters via elimination of disiloxane fragments has been observed previously, see: (a) Gaffney, C.; Harrison, P. G.; King, T. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1251. (b) Hubert-Pfalzgraf, L. G. *New J. Chem.* **1987**, 11, 663 and references cited therein.

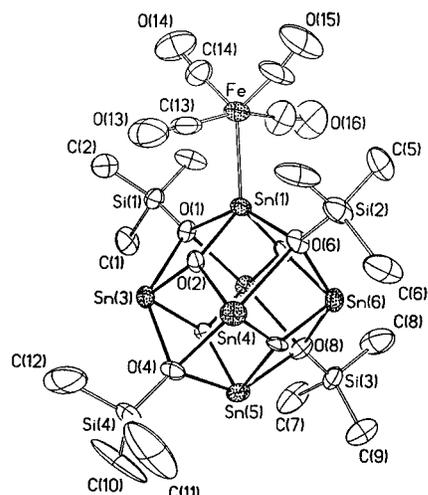
(10) Papiernik, R.; Hubert-Pfalzgraf, L. G.; Massiani, M. C. *Polyhedron* **1991**, 10, 1662.

(11) Yanovskii, A. I.; Turova, N. Y.; Turevskaya, E. P.; Struchkov, Y. T. *Koord. Khim.* **1982**, 8, 153.

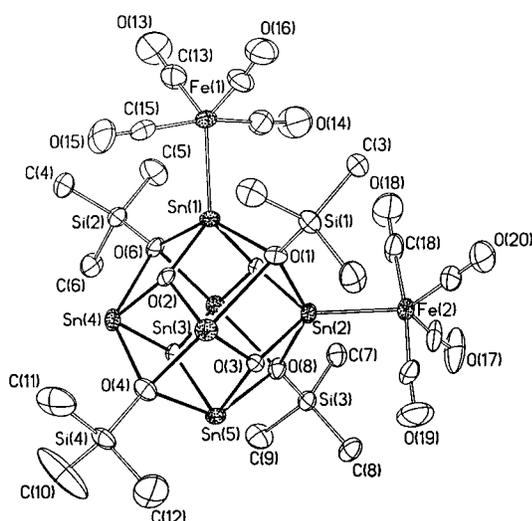
(12) Hitchcock, P. B.; Lappert, M. F.; Thomas, S. A.; Thorne, A. J.; Carty, A. J.; Taylor, N. J. *J. Organomet. Chem.* **1986**, 315, 27.

(13) Both *eq*-[ $\text{Fe}(\text{C})_4\text{L}$ ] and *ax*-[ $\text{Fe}(\text{CO})_4\text{L}$ ] TBP complexes should have four IR-active  $\nu(\text{CO})$ 's.

(14) For examples of  $\text{Fe}(\text{CO})_4\text{L}$  complexes where equatorial–axial interconversions do occur, see: Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *Inorg. Chem.* **1985**, 24, 2777 and references cited therein.



**Figure 2.** An ORTEP representation (30% thermal ellipsoids) of the molecular structure of **5**. Hydrogen atoms have been omitted for clarity.



**Figure 3.** An ORTEP representation (30% thermal ellipsoids) of the molecular structure of **6**. Hydrogen atoms have been omitted for clarity.

$\text{Pb}^{2+}$ .<sup>11</sup> Finally, the Sn–Fe bond lengths in the two adducts are very similar to those observed in other tin(II)–Fe(CO)<sub>4</sub> complexes.<sup>3</sup>

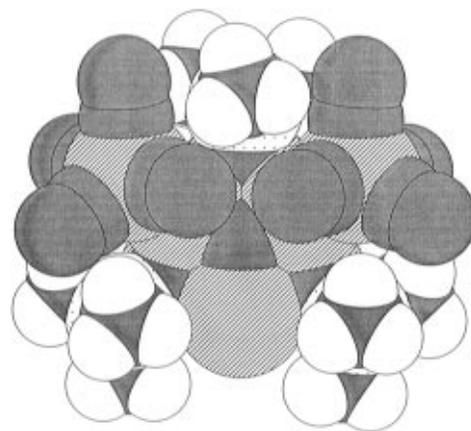
Regarding the steric influence that the main group cluster may exert on the coordination sphere of ligated transition metal centers, it is revealing that each of the Fe(CO)<sub>4</sub> fragments of **5** and **6** adopt distorted TBP geometries in which the main group cluster does in fact reside in the unusual equatorial position. In addition, in each case, the C<sub>eq</sub>–Fe–C<sub>eq</sub> angles are slightly reduced from the 120° value expected for an idealized TBP structure (see Table 1) and this is likely due to nonbonded interactions with the trimethylsilyloxy groups of the main group cluster. Interestingly, however, the axial carbonyl ligands of each Fe(CO)<sub>4</sub> fragment tilt toward the Sn<sub>6</sub>(μ<sub>3</sub>-O)<sub>4</sub>(μ<sub>3</sub>-OSiMe<sub>3</sub>)<sub>4</sub> framework.<sup>15</sup> Space-filling models of the two adducts, such as that shown in Figure 4 for compound **6**, reveal that this “umbrella” effect is easily accommodated in the observed conformations where the planes defined by C<sub>ax</sub>–Fe–C<sub>ax</sub> and O<sub>oxo</sub>–Sn–O<sub>oxo</sub> are nearly coplanar. These space-filling models are also instructive with respect to the question of how additional Fe(CO)<sub>4</sub> fragments would fit into the vacant ligation sites of **5**

(15) A similar umbrella effect has been noticed in the solid-state structures of several other tin–transition metal carbonyl complexes, see: (a) Bryan, R. F. *J. Chem. Soc. A* **1968**, 696. (b) Weidenbruch, M.; Stilter, A.; Peters, K.; v. Schnering, H. G. *Z. Anorg. Allg. Chem.* **1996**, 622, 534.

**Table 1.** Selected Average Bond Lengths and Bond Angles for **5** and **6**<sup>a,b</sup>

	<b>5</b>		<b>6</b>	
	Sn <sub>a</sub>	Sn <sub>b-d</sub>	Sn <sub>a</sub>	Sn <sub>b-d</sub>
Bond Lengths (Å)				
Sn–O	2.005(15)	2.087(23)	2.025(17)	2.094(18)
Sn–OR	2.335(62)	2.448(39)	2.340(41)	2.444(84)
Sn–Fe	2.472		2.463(1)	
Fe–C	1.768(42)		1.769(29)	
C–O	1.155(22)		1.146(16)	
Bond Angles (deg)				
O–Sn–OR	77.8(8)	75.1(15)	76.8(15)	74.4(19)
O–Sn–O	100.1	92.5(11)	97.9(4)	92.5(8)
RO–Sn–OR	141.4	136.3(7)	139.3(1)	134.3(4)
C <sub>ax</sub> –Fe–C <sub>ax</sub>	163.1		170.9(25)	
C <sub>eq</sub> –Fe–C <sub>eq</sub>	111.0		114.2(43)	
C <sub>ax</sub> –Fe–C <sub>eq</sub>	94.7(19)		92.4(14)	

<sup>a</sup> Tin atoms are labeled according to the figures. <sup>b</sup> Numbers in parentheses are the standard deviations in the average values.



**Figure 4.** A view of the space-filling (CPK) model for **6** that reveals how the two Fe(CO)<sub>4</sub> fragments are arranged.

and **6**, and as Figure 4 reveals, analysis of these models supports the conclusion that complexation of additional Fe(CO)<sub>4</sub> fragments to **2**, **5**, and **6** should be sterically permitted. It is reasonable to assume, therefore, that the isolation of “higher density” Fe(CO)<sub>4</sub> adducts of **2** should be possible.

## Conclusion

In summary, a high-yielding, highly reproducible, synthesis of the main group cluster **2** is reported, and the favorable solubility characteristics of this new Sn<sub>6</sub>(μ<sub>3</sub>-O)<sub>4</sub>(μ<sub>3</sub>-OR)<sub>4</sub> derivative now permit, for the first time, extensive investigations of the physical properties and chemical reactivity of this novel system to be conducted. In addition, with the demonstration that **2** can participate in the formation of well-defined transition metal complexes, new lines of study are now open that are centered on utilizing this novel main group cluster as the fundamental building block for the construction of a variety of new mixed p–d metal compounds and materials. Questions that remain to be pursued in these studies are whether or not electronic effects can be transmitted through the Sn–O bonded framework of **2** and whether this transmission then gives rise to directing effects and/or communication between complexed transition metal centers. Along these lines, we are now in the process of (1) determining the highest level of complexation that can be achieved for **2**, (2) utilizing complexes such as **5** and **6** for the synthesis of heterobimetallic transition metal adducts, and (3) generating catalytically active adducts that possess multiple reaction centers. The results of these investigations will be reported in due course.

## Experimental Section

Manipulations were performed under an inert atmosphere of dinitrogen by using standard Schlenk techniques or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. Elemental analyses were performed by Oneida Research Services, Inc.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR were recorded at 500, 125, and 186 MHz, respectively, using either benzene- $d_6$  or toluene- $d_8$  as the solvent and tetramethyltin as an external reference for the  $^{119}\text{Sn}$  NMR spectra. Infrared spectra were recorded either in the solid state using KBr pellets or in solution using dichloromethane as the solvent. Bis[bis(trimethylsilylanolato)tin] (**4**) was prepared according to the literature procedure<sup>5</sup> and diironnonacarbonyl (**3**) was used as obtained from Aldrich.

**Preparation of  $\text{Sn}_6(\mu_3\text{-O})_4(\mu_3\text{-OSiMe}_3)_4$  (**2**).** A sample of 12.33 g of **4** was placed into a 50-mL round bottom Schlenk flask that was then equipped with a short-path distillation head and a 25-mL receiver flask. The material was then heated with an oil bath to a temperature of 180 °C whereupon colorless HMDS was produced as a distillate. After 20 min, the heating bath was removed and the pot material allowed to cool whereupon it rapidly crystallized. A vacuum ( $10^{-3}$  mmHg) was applied to remove any volatiles and then the material was transferred to a glovebox where 9.7 g of **2** was collected (99% yield). Analytically pure material was obtained by recrystallization from a toluene/acetonitrile solvent mixture (*ca* 1:1) at  $-40$  °C. For **2**: mp  $216\text{--}217$  °C dec.  $^1\text{H}$  NMR (25 °C, toluene- $d_8$ )  $\delta$  0.23;  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  4.5;  $^{119}\text{Sn}\{^1\text{H}\}$  NMR  $\delta$   $-137.8$ . IR (KBr), 2947 (vs), 1255 (vs), 850 (vs), 570 (vs)  $\text{cm}^{-1}$ . UV (pentane)  $\lambda_{\text{max}}$  230 nm ( $\epsilon_{\text{max}}$  51 664). Anal. Calcd for  $\text{C}_{12}\text{H}_{36}\text{O}_8\text{Si}_4\text{Sn}_6$ : C, 12.72; H, 3.20. Found: C, 12.85; H, 3.21. Mass spectrum (EI), see Figure 1.

**Preparation of the  $\text{Fe}(\text{CO})_4$  Adducts, **5** and **6**.** To a suspension of 84 mg (0.23 mmol) of **3** in 5 mL of toluene was added 0.26 g (0.23 mmol) of **2** and the mixture was stirred at room temperature for 24 h whereupon it was filtered through a small pad of Celite and the solvent removed *in vacuo*. A  $^1\text{H}$  NMR spectrum revealed the product to consist cleanly of the desired compound **5** (90% yield via integration) together with small amounts of the starting material **2** and the bis adduct **6**. Fractional crystallization of this material from a benzene/acetonitrile solvent mixture (*ca* 1:1) at  $-40$  °C provided analytically pure **5** in the form of orange-yellow rods (50% isolated yield). For **5**:  $^1\text{H}$  NMR  $\delta$  0.10 (s, 18 H), 0.38 (s, 18 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  2.7, 3.4, 218.0;  $^{119}\text{Sn}\{^1\text{H}\}$  NMR (see figures for lettering scheme)  $\delta$   $-38.5$  (1  $\text{Sn}_a$ ),  $-141.0$  (1  $\text{Sn}_b$ ),  $-179.8$  (4  $\text{Sn}_c$ ); IR (KBr)  $\nu_{\text{C-O}}$  2043, 1950  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{16}\text{H}_{36}\text{FeO}_{12}\text{Si}_4\text{Sn}_6$ : C, 14.77; H, 2.79. Found: C, 14.94; H, 2.62.

Using 2 equiv of **3**, the same procedure from above provided, after 48 h, a product consisting of a 2.5:1 ratio of **6** to **5** for a combined yield of 66%.  $^1\text{H}$  NMR spectroscopy also revealed the presence of another major  $\text{Fe}(\text{CO})_4$  adduct, tentatively assigned as the "para" isomer of **6** (23% yield). Fractional crystallization of this material from a benzene/acetonitrile solvent mixture (*ca* 1:1) at  $-40$  °C provided analytically pure **6** in the form of orange-red cubes (35% isolated yield). For **6**:  $^1\text{H}$  NMR  $\delta$   $-0.03$  (s, 9 H), 0.30 (s, 18 H), 0.51 (s, 9 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  3.0, 3.7, 4.5, 217.7;  $^{119}\text{Sn}\{^1\text{H}\}$  NMR  $\delta$   $-41.9$  (2  $\text{Sn}_a$ ),  $-187.2$  (2  $\text{Sn}_b$ ),  $-216.2$  [1  $\text{Sn}_c$  (or  $\text{Sn}_d$ )],  $-222.5$  [1  $\text{Sn}_c$  (or  $\text{Sn}_d$ )]; IR (KBr)

**Table 2.** Summary of Crystallographic Data for **5** and **6**

	<b>5</b>	<b>6</b> ·(0.70) $^{1/2}$ C <sub>6</sub> H <sub>6</sub>
formula	C <sub>16</sub> H <sub>36</sub> FeO <sub>12</sub> Si <sub>4</sub> Sn <sub>6</sub>	C <sub>22.1</sub> H <sub>38.1</sub> Fe <sub>2</sub> O <sub>16</sub> Si <sub>4</sub> Sn <sub>6</sub>
formula weight	1300.80	1496.03
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å	13.404(2)	11.804(2)
<i>b</i> , Å	16.964(3)	17.489(2)
<i>c</i> , Å	17.766(2)	23.222(3)
$\beta$ , deg	90.38(1)	97.146(9)
<i>V</i> , Å <sup>3</sup>	4040(1)	4756(1)
<i>Z</i>	4	4
cryst color	orange-yellow	orange-red
<i>D</i> (calc), g cm <sup>-3</sup>	2.139	2.089
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	41.57	38.41
temp, K	298	251
radiation	MoK $\alpha$ ( $\lambda$ = 0.71073 Å)	
<i>R</i> ( <i>F</i> ), <sup>a</sup> %	4.43	4.19
<i>R</i> ( <i>wF</i> <sup>2</sup> ), <sup>a</sup> %	8.14	7.87

<sup>a</sup> Quantity minimized =  $R = \Sigma\Delta/\Sigma(F_o)$ ,  $\Delta = |(F_o - F_c)|$ ;  $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$ .

$\nu_{\text{C-O}}$  2043, 1950  $\text{cm}^{-1}$ . Anal. Calcd for single crystals of C<sub>20</sub>H<sub>36</sub>Fe<sub>2</sub>O<sub>16</sub>Si<sub>4</sub>Sn<sub>6</sub>·0.5 C<sub>6</sub>H<sub>6</sub> (see below): C, 18.32; H, 2.61. Found: C, 18.20; H, 2.44.

**Crystallographic Analyses of Compounds **5** and **6**.** Crystallographic data are summarized in Table 2.

The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least squares procedures.<sup>16</sup> Semiempirical absorption corrections were applied. Half of a benzene molecule was located in the asymmetric unit of the structure for **6**, centered on an inversion point, with a partial, refined occupancy of 70%. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions.

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**Supporting Information Available:** Full tables of the data collection parameters, isotropic and anisotropic temperature factors, and bond distances and bond angles (14 pages). See any current masthead page for ordering and Internet access information.

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(16) SHELXTL-PLUS, A program for Crystal Structure Determination, Version 5.3, Siemens Analytical X-Ray Instruments: Madison, Wisconsin.