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Solvent-Dependent Ester Elimination and Ligand Exchange Reactions between Trimethylsilyl Acetate and Tin(IV) Tetra-*tert*-butoxide

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The reaction between a prototypical metal alkoxide, $Sn(O\text{-}t\text{-}Bu)_4$, and a metal carboxylate, $Me_3Si(OAc)$, has been studied by NMR spectroscopy in different solvents. These species were chosen as a result of the presence of their NMR-active isotopes. In nonpolar solvents such as toluene, ester elimination was observed with formation of $(t\text{-}BuO)_3Sn(OSiMe_3)$ and $(t\text{-}BuO)_2Sn(OSiMe_3)_2$. Experiments employing ^{17}O-labeled $Sn(^{17}O\text{-}t\text{-}Bu)_4$, show that the alkoxide group is transferred to the carbonyl ligand of the silyl acetate. In a coordinating solvent such as pyridine, the ligand exchange product, $Sn(O\text{-}t\text{-}Bu)_3(OAc)(py)$, is formed. This compound has also been characterized in the solid state by single-crystal X-ray diffraction. Crystal data: empirical formula $C_{19}H_{35}NO_5Sn$, crystal system orthorhombic, space group *Pnma*; unit cell dimensions $a = 12.638(4)$ Å, $b = 11.305(5)$ Å, $c = 16.858(9)$ Å; $Z = 4$. This compound is the first Sn(IV) alkoxide carboxylate that has been isolated and structurally characterized. The implications of this study for the use of ester elimination reactions in strategies to prepare metal oxide materials are discussed.

Introduction

The formation of compositionally homogeneous mixed-metal oxide powders such as SiO_2/TiO_2, ZrO_2/SiO_2, and ZrO_2/CeO_2 is attracting attention because these materials have important applications in ceramics coatings with tailored optical properties, membrane separations, and catalysis.[1,2] These materials are frequently prepared by the cohydrolysis of mixtures of the individual metal alkoxide compounds. However, it is often the case that one of the reagents is a silicon alkoxide compound, where the rate of hydrolysis and condensation is generally substantially slower than that of the other metal alkoxide compound in the mixture.[3] As a result, the silicon alkoxide compound is generally intentionally prehydrolyzed in a first step and the other metal alkoxide compound is added subsequently. This cohydrolysis leads to compositional inhomogeneity as a result of the condensation of the silicon-based network prior to the introduction of the second metal species and has been documented in a number of cases.[4]

We are interested in exploring alternative methods of formation of mixed-metal oxides in which there is potential for the control of homogeneity and stoichiometry at the molecular level and where there is an opportunity for control over the evolution of microstructure. One strategy potentially capable of control over stoichiometry and homogeneity is to use a metal–organic ligand system which requires reaction between two different ligands where each type of ligand is bonded to a different metal center and where an organic fragment is eliminated to produce only the elements required in the final material. By eliminating an organic fragment in an intermolecular reaction between two compounds containing different metal centers, the metals may become connected by covalent bonds (via an oxo bridge for example), fixing their stoichiometry and improving homogeneity in this system. This strategy is being studied extensively for formation of semiconductor nanoclusters of 13/15 compounds where trimethylsilyl chloride elimination results in formation of a bond between the group 13 and 15 elements.[5,6]

One example of an analogous strategy that can be adopted for the formation of metal oxides involves the elimination of an ester between a metal alkoxide compound and a metal carboxylate as shown in eq 1. In principle, this strategy can

$$M(OR)_n + M'(O_2CR')_n \rightarrow MM'O_{n/2} + nRO_2CR' \quad (1)$$

allow for complete elimination of the organic supporting ligands and formation of heterobimetallic μ-oxo bridges, resulting in molecular level control over composition and homogeneity. Bradley et al.[7,8] showed that the reaction between $M(OR)_n$ ($M = Ti, Zr$, $n = 4$; $M = Nb$, $n = 5$) and 4 or 5 equiv of $Me_3Si(OAc)$ resulted in elimination of the corresponding amount of ester to give $M(OSiMe_3)_n$. The metal–organic complex was isolated by azeotropic removal of the ester in boiling cyclohexane according to eq 2 for the case of M = Ti. In this system they also noticed that with higher alkylsilyl acetates the rate of

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$$\mathrm{Ti(OR)_4 + 4Me_3Si(OAc) \rightarrow Ti(OSiMe_3)_4 + 4ROAc} \quad (2)$$

the reaction and the extent of acylation decreased with increasing size of the organosilyl groups. This reaction has also been used by Teyssie and co-workers for the formation of mixed-metal species (eq 3), generally in decalin, although few data are available on the properties of the mixed-metal intermediates.[9,10]

$$\mathrm{2Al(OR)_3 + Fe(OAc)_2 \rightarrow Fe[OAl(OR)_2]_2 + 2ROAc} \quad (3)$$

Ester elimination has been observed in a few specific reactions between metal carboxylates and metal alkoxides and has been invoked in the formation of a wide variety of mixed-metal oxides,[11-14] but the details of the mechanism and generality of this reaction have not been studied in detail and the involvement of ester elimination in many processes is controversial.[12,15-22]

In this paper we report an investigation of a model ester elimination between trimethylsilyl acetate and tin(IV) *tert*-butoxide to derive more detailed information concerning the nature of ester elimination reactions in general. We chose Si and Sn specifically because each element possesses at least one NMR-active nucleus (^{29}Si, ^{119,117}Sn) so that the presence of an M−O−M′ bridge could be established unambiguously. Tin(IV) tetra-*tert*-butoxide was chosen because it is known to be monomeric in benzene solution, and trimethylsilyl acetate was chosen because it is an example of a simple, metal acetate that is soluble in a number of different solvents so the effects of different solvents could be studied.

Experimental Section

General Procedures. All manipulations were carried out under a dinitrogen atmosphere. All hydrocarbon, ethereal, and pyridine solvents were distilled over sodium benzophenone ketyl and stored over predried 4 Å molecular sieves. The NMR data were recorded on a Bruker AC-250 spectrometer. External standards for ^{29}Si, ^{119}Sn, and ^{17}O were tetramethylsilane, tetraethyltin, and $H_2{}^{17}O$ (10 atom %), respectively. The ^{29}Si, ^{119}Sn, and ^{17}O spectra were recorded at 49.7, 93.3, and 33.9 MHz, respectively, utilizing a composite pulse 90° sequence[23] with a 16 step phase cycle. GC−MS data were recorded on a Finnigan MAT Series 450 comparing samples against an authentic *tert*-butyl acetate standard. The reagent $Me_3Si(OAc)$ was purchased from Aldrich and distilled before use. Labeled water (20 atom % $H_2{}^{17}O$) was purchased from Isotec.

Syntheses. $Sn(O\text{-}t\text{-}Bu)_4$ was prepared by the literature method.[24,25]

Synthesis of $H^{17}O$-*t*-Bu. Oxygen-17 labeled *tert*-butyl alcohol was prepared by a modified procedure of Read and Priestly.[26] Into a 500 mL three-necked flask cooled in a dry ice/acetone bath fitted with a reflux condenser, dropping funnel, and gas inlet tube was condensed 20 mL (212 mmol) of isobutylene. A solution consisting of 5 mL (94 mmol) of 96% H_2SO_4 and 5 mL (277 mmol) of $H_2{}^{17}O$ was cooled below room temperature, placed in the dropping funnel, and added slowly to the isobutylene. After the addition was complete (several hours), the reaction mixture and flask were placed in an ice/2-propanol bath and allowed to warm slowly to room temperature over several hours with constant, rapid stirring. The flask was cooled again by a dry ice/acetone bath, another 20 mL of isobutylene was condensed into the mixture, and the warming procedure was repeated. The flask was reimmersed in a dry ice/acetone bath, and the solution was neutralized slowly with concentrated aqueous KOH until it remained at basic pH. The alcohol was extracted with diethyl ether (3 x 50 mL); the extract was distilled over magnesium metal and redistilled from CaH. The yield after initial distillation was 50% (10.2 g). ^{1}H NMR (C_6D_6): δ = 1.18 (s). ^{17}O NMR (C_6D_6): δ = 66 (s, $\Delta\nu_{1/2}$ = 220 Hz).

Preparation of $Sn(^{17}O$-*t*-Bu$)_4$. To a 5 mm NMR tube were added 0.110 g (0.27 mmol) of $Sn(O\text{-}t\text{-}Bu)_4$, 0.100 mL (1.06 mmol) of $H^{17}O$-*t*-Bu, and 0.5 mL of a dry 4:1 (v/v) THF/C_6D_6 solution. The reaction mixture was allowed to stand at room temperature for 24 h; the solvent and alcohol were then removed under vacuum. The yield was quantitative (20 atom % $Sn(^{17}O\text{-}t\text{-}Bu)_4$ ^{1}H NMR (C_6D_6): δ = 1.42 (s). ^{17}O NMR (C_6D_6): δ = 90 ppm (s, $\Delta\nu_{1/2}$ = 600 Hz).

Reaction of $Sn(O$-*t*-Bu$)_4$ with $Me_3Si(OAc)$ in Cyclohexane. To a 100 mL Schlenk flask fitted with a Dean-Stark apparatus and reflux condenser were added 0.486 g (1.18 mmol) of $Sn(O\text{-}t\text{-}Bu)_4$, 0.117 mL (1.18 mmol) of Me_3SiOAc, and 60 mL of dry cyclohexane. The solution was refluxed for 4 h, followed by removal of the azeotrope until no further ester was detected. The remaining volatile components were removed under vacuum to leave a pale yellow oil. ^{119}Sn NMR (C_6D_6): δ = −374 (s), −387 (s), −398 (s). ^{29}Si NMR (C_6D_6): δ = 15.3 (s), 16.5 (s) ($^2J_{^{119}Sn-O-^{29}Si}$ = 41.7 Hz), integrated area of satellites with respect to main peaks ≈ 10%.

Reaction of $Sn(^{17}O$-*t*-Bu$)_4$ with $Me_3Si(OAc)$ in Benzene. To a 5 mm NMR tube were added 0.110 g (0.27 mmol) of $Sn(^{17}O\text{-}t\text{-}Bu)_4$, 40 μL (0.27 mmol) of $Me_3Si(OAc)$, and 0.5 mL of C_6D_6. The reaction was immediately monitored by ^{1}H and ^{17}O NMR spectroscopy. ^{119}Sn NMR (C_6D_6): δ = −374 (s), −387 (s), −398 (s). ^{29}Si NMR (C_6D_6): δ = 15.3 (s), 16.5 (s) ($^2J_{^{119}Sn-O-^{29}}$ = 41.7 Hz), integrated area of satellites with respect to main peaks ≈ 10%.

Reaction of $Sn(O$-*t*-Bu$)_4$ with $Me_3Si(OAc)$ in Pyridine. To a 250 mL Schlenk flask were added 3.0 g (7.3 mmol) of $Sn(O\text{-}t\text{-}Bu)_4$, 1.1 mL (7.3 mmol) of $Me_3Si(OAc)$, and 50 mL of pyridine. The solution was stirred for 24 h at room temperature, followed by removal of the solvent under reduced pressure at 40 °C to leave a pale yellow solid. The crude product was then purified by heating to 70 °C under vacuum for several hours, leaving 1.93 g (67% yield). The crude product could be recrystallized from a cold (−20 °C) concentrated pyridine solution. ^{1}H NMR (C_5D_5N): δ = 1.55 (s, 9H), 1.90 (s, 1H). ^{119}Sn NMR (C_5D_5N): δ = −664 (s). ^{13}C NMR (C_5D_5N), δ: 19 (s), $OC(\mathit{C}H_3)_3$; 34 (s), $OC(\mathit{C}H_3)$; 73 (s), $O\mathit{C}(CH_3)_3$; 183 (s), $O(O)\mathit{C}(CH_3)$. Anal. Calcd for $C_{19}H_{35}O_5NSn$: C, 47.9; H, 7.3; N, 2.9. Found: C, 45.8; H, 7.6; N, 2.9. We believe that the low carbon content observed may be due to the low thermal stability of this compound.

Crystallographic Studies. Crystal data collection, and refinement parameters for $Sn(O\text{-}t\text{-}Bu)_3(OAc)(py)$ are given in Table 1. A suitable crystal was selected and mounted in a thin-walled nitrogen-flushed capillary tube. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections (20° ≤ 2θ ≤ 25°).

The systematic absences in the diffraction data for **1** are uniquely consistent for space groups *Pn*2$_1$*a* and *Pnma*. *E* statistics suggested the centrosymmetric alternative. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. A *tert*-butoxy ligand was found disordered about the mirror plane on which the compound molecule is situated. The tin and oxygen atoms were refined with

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Table 1. Crystallographic Data for $C_{19}H_{35}NO_5Sn$

chemical formula	$C_{19}H_{35}NO_5Sn$
formula weight	476.14
lattice type	orthorhombic
space group	*Pnma*
Z	4
a, Å	12.638(4)
b, Å	11.305(5)
c, Å	16.858(9)
V, Å^3	2409(2)
ϱ_{calc}, g/cm^3	1.313
T, K	296(2)
μ, cm^{-1}	1.085
λ(Mo Kα, graphite monochromated), Å	0.710 73
$R(F_o)^a$	5.51
$R_w(F_o)^a$	12.18

[a] $R = \{\Sigma[|F_o| - |F_c|]\}/\{\Sigma|F_o|\}$; $R_w = \{\Sigma[w^{1/2}][|F_o| - |F_c|]\}/\{\Sigma w^{1/2}|F_o|\}$ where $w = [\sigma^2(F_o) + (pF_o{}^2]^{-1}$. The quantity minimized was $\{\Sigma[wF_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$. Sources of the scattering factors are in the γ-test version of SHELXTL-92 (G. Sheldrick, Siemens XRD, Madison, WI).

anisotropic displacement coefficients. In order to conserve data, C−C distances in the *tert*-butoxy ligands were refined as constrained bond lengths. Hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in either the SHELTXTL (5.1) or the SHELTXTL PLUS (4.2) program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

Tin(IV) *tert*-butoxide, $Sn(O\text{-}t\text{-}Bu)_4$, reacts with 1 equiv of trimethylsilyl acetate, $Me_3Si(OAc)$, in benzene-d_6 at room temperature after several minutes to form *tert*-butyl acetate, $C_4H_9OC(O)CH_3$, as evidenced by the two ^1H NMR resonances of the ester at 1.68 and 1.35 ppm, consistent with the chemical shifts of an authentic sample. The generation of ester was also confirmed by combined gas chromatography−mass spectrometry, GC−MS, which exhibited two molecular ion peaks at *m/z* 59 and 101 corresponding to the fragments $H_3CC(O)O^+$ and $C_4H_9OC(O)^+$, respectively, consistent with an authentic sample of this ester. The ^{119}Sn NMR spectrum of the reaction mixture revealed the presence of two new tin-containing reaction products with chemical shifts of −387 and −398 ppm, consistent with a four-coordinate tin center,[27] together with a resonance at −374 ppm corresponding to unreacted $Sn(O\text{-}t\text{-}Bu)_4$ as shown in Figure 1a. A ^{29}Si NMR spectrum of the same reaction mixture showed the presence of two resonances at 16.5 and 15.3 ppm. Each resonance exhibited ^{119}Sn and ^{117}Sn satellites where $^2J_{^{119,117}Sn-O-^{29}Si} = 39.8$ Hz, indicative of the formation of μ-oxo-bridged species Sn−O−Si as shown in Figure 1b. No resonance for $Me_3Si(OAc)$ was detected, indicating that it had been completely consumed in the reaction. The ^{29}Si and ^{119}Sn NMR spectra are consistent with the formation of the two new species $(Me_3SiO)Sn(O\text{-}t\text{-}Bu)_3$ and $(Me_3SiO)_2Sn(O\text{-}t\text{-}Bu)_2$. While tin satellites are clearly visible in the ^{29}Si NMR spectrum, the tin resonances are too broad (typical $\Delta\nu_{1/2} = 75$ Hz) in the ^{119}Sn NMR spectrum to allow for identification of silicon satellites. Many attempts to separate these species proved unfruitful.

In an attempt to gain further insight into this ester elimination process, we set out to isotopically enrich one oxygen site in the reactant mixture and follow the label throughout the reaction. The metal alkoxide $Sn(O\text{-}t\text{-}Bu)_4$ was chosen as the site of enrichment and was enriched by means of an alcohol interchange reaction between the alkoxide ligands of unlabeled $Sn(O\text{-}t\text{-}Bu)_4$ and ^{17}O-labeled *tert*-butyl alcohol.[28] Alcohol exchange reactions between metal alkoxides and their parent alcohols are well-known where the alcohols have low steric demands. In the case of tin(IV) alkoxide compounds, the alcohol/alkoxide exchange has been studied in $[Sn(O\text{-}i\text{-}Pr)_4{\cdot}HO\text{-}i\text{-}Pr]_2$,[24] $[Sn(O\text{-}i\text{-}Bu)_4{\cdot}HO\text{-}i\text{-}Bu]_2$,[5] and more recently $Sn(O\text{-}t\text{-}Bu)_4$,[28] which despite the substantial steric demands of the O-*t*-Bu ligands was shown to undergo slow O-*t*-Bu/HO-*t*-Bu exchange.

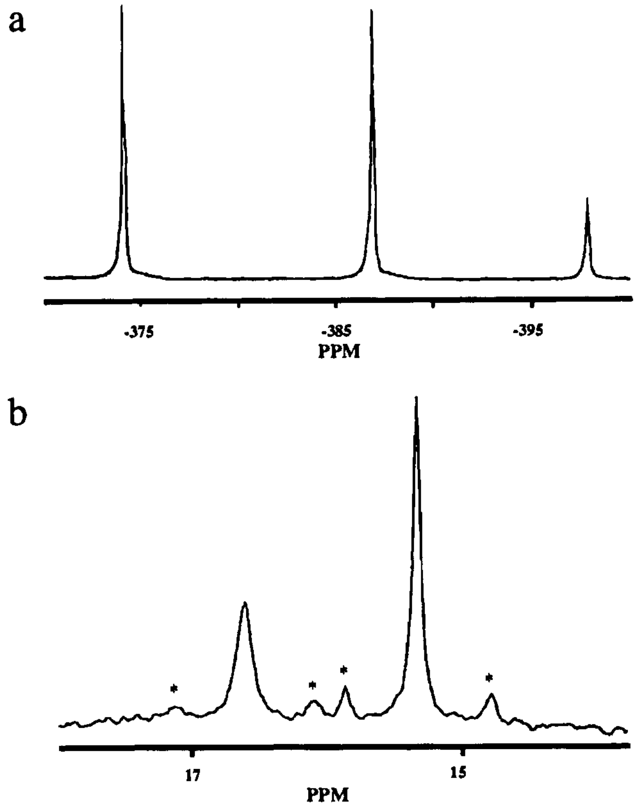

Figure 1. (a) ^{119}Sn NMR and (b) ^{29}Si NMR spectra for the products of the reaction of $Sn(O\text{-}t\text{-}Bu)_4$ and Me_3SiOAc in benzene solution. The $^{119,117}Sn$ satellites in the ^{29}Si NMR spectrum are marked with an asterisk.

The reaction of $Sn(^{17}O\text{-}t\text{-}Bu)_4$ with $Me_3Si(OAc)$ in benzene solution resulted in a new resonance in the ^{17}O NMR spectrum at 205 ppm, after 10 min at room temperature, consistent with the chemical shift of the ether oxygen in *tert*-butyl acetate. The time-dependent ^{17}O NMR spectra are shown in Figure 2. The ester proton resonances also appeared in the ^1H NMR spectrum and grew in area with time. This reaction can be described by eq 4. This labeling experiment confirms that the alkoxide ligand

$$Sn(^{17}O\text{-}t\text{-}Bu)_4 + Me_3SiOC(O)Me \rightarrow (t\text{-}Bu^{17}O)_3SnOSiMe_3 + t\text{-}Bu^{17}OC(O)Me \quad (4)$$

is transferred to the carbonyl carbon on formation of the ester.

When this reaction is repeated in a strongly coordinating solvent such as pyridine, the rate of ester formation is reduced dramatically. The ^{17}O NMR spectra reveal only a trace of ester formation after 36 h at room temperature. The resonance at 90 ppm in the ^{17}O NMR spectrum corresponding to $Sn(^{17}O\text{-}t\text{-}Bu)_4$ diminishes and a peak at 63 ppm appears, consistent with the formation of $Me_3Si^{17}O\text{-}t\text{-}Bu$. The ^{29}Si NMR spectrum showed two resonances, one at 23 ppm assigned to $Me_3Si(OAc)$, whose area was diminished severely during the experiment, and a new resonance at 6.8 ppm, consistent with the formation of a ligand exchange product trimethyl-*tert*-butoxysilane, $Me_3Si(O\text{-}t\text{-}Bu)$, which has a reported ^{29}Si NMR chemical shift of 6.2 ppm.[29]

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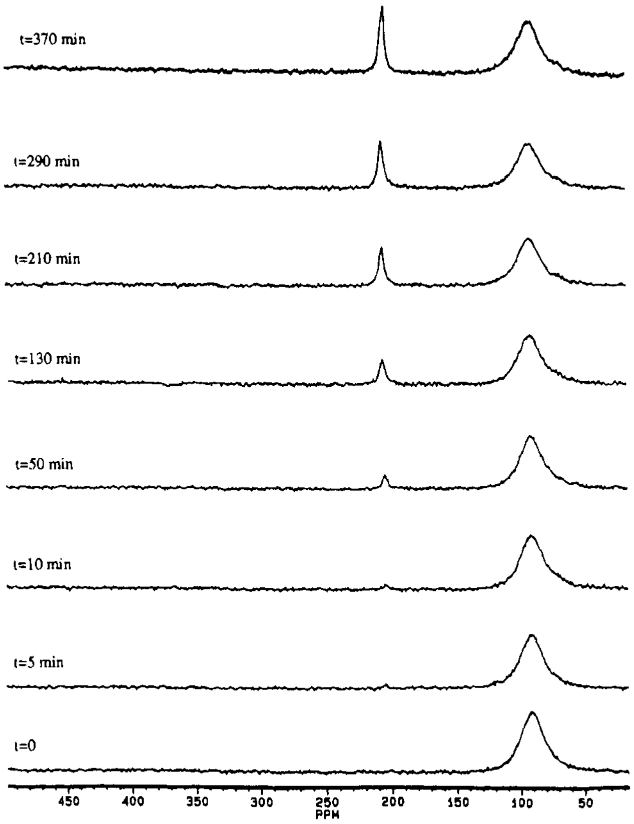

Figure 2. Time-dependent ^{17}O NMR of the reaction between Sn(^{17}O-*t*-Bu)$_4$ and $Me_3Si(OAc)$ showing formation of *t*-BuOAc through the resonance of the ether oxygen at 205 ppm.

The ^{119}Sn NMR spectrum revealed the presence of a peak at −644 ppm, consistent with a six-coordinate Sn center.[27,30] Furthermore, two upfield peaks (δ < 1.0 ppm) in the ^1H NMR spectrum indicated two Me_3SiX species assigned to unreacted $Me_3Si(OAc)$ and Me_3Si(O-*t*-Bu). In this case, there is essentially no ester elimination, and the data are consistent with ligand exchange leading to the formation of the species (*t*-BuO)$_3$Sn(OAc) and Me_3Si(O-*t*-Bu).

The new mixed tin alkoxide carboxylate, Sn(O-*t*-Bu)$_3$(OAc), has been isolated and characterized by a number of techniques. Single-crystal X-ray diffraction (see later) and elemental analysis data reveal the presence of coordinated pyridine to give an empirical formula, Sn(O-*t*-Bu)$_3$(OAc)(py), although difficulty was experienced in obtaining consistent analytical data. The ^1H NMR spectrum of this compound reveals only two singlets with integrated areas corresponding to *tert*-butoxide and acetate ligands in a 3:1 ratio, respectively. Evidence consistent with the presence of a monomeric species in solution comes from its ^{119}Sn NMR spectrum, where the peak at −644 ppm possesses no ^{117}Sn satellites. Alkoxo-bridged tin centers generally exhibit $^2J_{^{119}Sn-^{117}Sn}$ on the order of 300 Hz.[24]

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**

	x	*y*	*z*	*U*(eq)[a]
Sn	3124.3(7)	2500	5481.5(5)	56(1)
O(1)	3187(10)	1485(11)	6375(8)	70(3)
O(1′)	3093(10)	4174(11)	5872(7)	67(3)
O(2)	1651(7)	2500	5177(6)	99(4)
O(3)	3661(6)	1565(7)	4405(4)	88(2)
C(1)	5449(8)	1502(9)	5718(5)	76(3)
C(2)	6518(9)	1463(12)	5829(7)	101(4)
C(3)	7053(12)	2500	5865(11)	106(6)
C(4)	2542(26)	−408(22)	5922(17)	144(12)
C(5)	3258(25)	−26(26)	7315(15)	104(9)
C(6)	1520(40)	767(48)	6802(26)	85(11)
C(7)	2608(27)	376(43)	6509(19)	50(8)
C(4′)	2991(22)	5958(20)	6568(19)	132(10)
C(5′)	3532(29)	4138(30)	7253(17)	155(15)
C(6′)	1789(44)	4289(64)	6924(35)	172(31)
C(7′)	2902(29)	4624(40)	6739(20)	59(9)
C(8)	1000(14)	1586(21)	4152(10)	507(43)
C(9)	−177(13)	2500	5056(14)	150(8)
C(10)	899(10)	2500	4659(7)	70(4)
C(11)	3836(13)	2500	4049(10)	101(6)
C(12)	4225(13)	2500	3229(9)	152(9)
N	4919(8)	2500	5675(5)	60(3)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Bond Lengths (Å) and Angles (deg) for **1**

Sn−O(1)	1.895(12)	C(2)−C(3)	1.354(14)
Sn−O(2)	1.931(9)	C(4)−C(7)	1.33(5)
Sn−O(1′)	2.004(12)	C(5)−C(7)	1.65(3)
Sn−O(3)	2.207(7)	C(6)−C(7)	1.53(7)
Sn−N	2.291(10)	C(4′)−C(7′)	1.54(5)
O(1)−C(7)	1.58(2)	C(5′)−C(7′)	1.30(5)
O(1′)−C(7′)	1.47(5)	C(6′)−C(7′)	1.49(7)
O(2)−C(10)	1.292(14)	C(8)−C(10)	1.35(2)
O(3)−C(11)	1.236(11)	C(9)−C(10)	1.52(2)
C(1)−N	1.314(10)	C(11)−C(12)	1.47(2)
C(1)−C(2)	1.364(14)		
O(1)−Sn−O(2)	104.6(4)	O(1′)−Sn−O(3)	136.8(4)
O(1)−Sn−O(1′)	108.1(6)	O(1)−Sn−N	81.1(4)
O(2)−Sn−O(1′)	93.9(4)	O(2)−Sn−N	172.8(4)
O(1)−Sn−O(3)	110.5(5)	O(1′)−Sn−N	88.4(4)
O(2)−Sn−O(3)	94.5(3)	O(3)−Sn−N	79.2(3)

To further identify the nature of this species, it was crystallized from pyridine and characterized by single-crystal X-ray diffraction in the solid state. The crystallographic data are given in Table 1, the fractional coordinates in Table 2, and relevant bond lengths and angles in Table 3. The molecular structure of Sn(O-*t*-Bu)$_3$(OAc)(py) is shown in Figure 3. In the solid state, this compound is monomeric and possesses pseudo-five-coordinate geometry if the acetate ligand is considered to occupy one equatorial coordination site. The remaining coordination sphere is filled with axial pyridine and O-*t*-Bu ligands and two equatorial O-*t*-Bu ligands. This species contains the rather surprising structural feature that the acetate ligand chelates rather than bridges. Examination of the crystal structure reveals no short intermolecular interactions that could be interpreted as resulting from bridging acetate O•••Sn interactions. There are no unusual bond lengths or angles in this compound. The Sn−O bond lengths are similar to those observed in Sn(O-*t*-Bu)$_4$, and there is no statistical difference in the axial vs equatorial Sn−O bond lengths.

The solid-state structural data are inconsistent with the solution NMR data obtained at room temperature in pyridine-d_5 which provided evidence for only one type of O-*t*-Bu resonance. In order to determine whether the room-temperature NMR data are the result of a dynamic exchange process which exchanges the axial and equatorial alkoxide ligands, characteristic of a five-coordinate tin center, a variable-temperature NMR study was carried out. When a pyridine-d_5 solution of Sn(O-*t*-Bu)$_3$(OAc)(py) was cooled, the resonance due to the O-*t*-Bu ligands broadened and decoalesced into two resonances in a 2:1 integration ratio at −35 °C, consistent with the solid-state structural data. The free energy of activation calculated from the coalescence temperature, $\Delta G^{\ddagger}_c$, is 12 kcal/mol.

On the basis of all these data taken together, we speculate that the mechanism of ester elimination is similar to acid-

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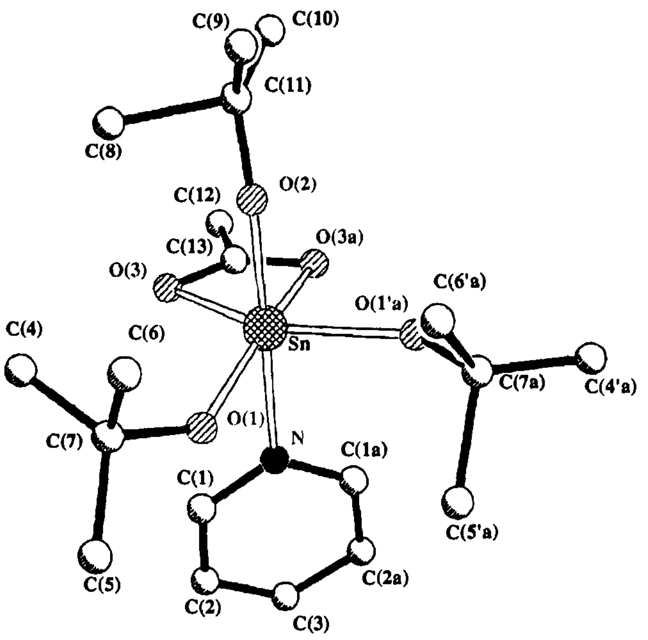

Figure 3. Molecular structure of Sn(O-*t*-Bu)$_3$(OAc)(py).

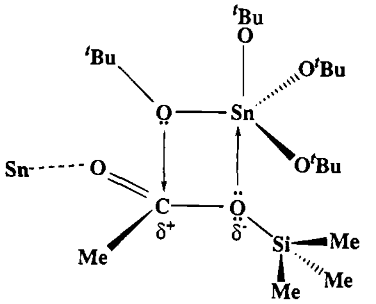

Figure 4. Possible transition state of the ester elimination reaction between Sn(O-*t*-Bu)$_4$ and Me$_3$Si(OAc).

catalyzed transesterification[31] where the electropositive and coordinately unsaturated Sn center probably acts as a Lewis acid center by coordinating to the carbonyl oxygen atom. Coordination of the carbonyl oxygen of the acetate to a tin center decreases the electron density at the carbonyl carbon, allowing for nucleophilic attack of the alkoxide oxygen as depicted in Figure 4. The observation that ester elimination does not occur in the presence of pyridine supports the proposal that a vacant coordination site at tin is necessary to promote ester elimination. Strongly coordinating solvents such as pyridine have been shown to hinder associative processes at tin alkoxide centers such as alcohol/alkoxide exchange.[28] Furthermore, we observe that there is no reaction between Si(OEt)$_4$ and Sn(OAc)$_4$ in toluene, presumably because there are no coordination sites available at Si to activate the carbonyl group toward ester elimination. Although the nature of the transition state cannot be verified at this stage, evidence of the accessibility of the Sn center in Sn(O-*t*-Bu)$_4$ comes from the isolation of KSn(O-*t*-Bu)$_5$,[32] which contains the five-coordinate [Sn(O-*t*-Bu)$_5$]$^-$ unit, and from the proposed transition state [Sn(O-*t*-Bu)$_4$·HO-*t*-Bu] of the degenerate alcohol exchange reaction between Sn(O-*t*-Bu)$_4$ and H^{17}O-*t*-Bu.[28]

Since most reactions between metal alkoxide and metal carboxylate compounds that are carried out with the goal of materials synthesis (i.e. metal oxides) are conducted in alcohol solvents, we also conducted a series of experiments in the presence of the parent alcohol, *tert*-butyl alcohol. In a control experiment, no reaction was observed between Me$_3$Si(OAc) and 1 equiv of HO-*t*-Bu in benzene solution. Only after the reaction mixture was heated to 50 °C overnight with a small amount ($<10\%$) of Sn(O-*t*-Bu)$_4$ was any ester formation observed. When Sn(O-*t*-Bu)$_4$ is reacted with 1 equiv of Me$_3$Si(OAc) using *t*-BuOH as a solvent, ^{29}Si and ^{119}Sn NMR spectroscopies indicate a ligand exchange reaction with no evidence for ester elimination at room temperature.

Conclusions

A model reaction between a tin alkoxide, Sn(O-*t*-Bu)$_4$, and a silicon carboxylate compound, Me$_3$Si(OAc), has been studied to investigate the circumstances under which ester elimination occurs. We find that the nature of the solvent is crucial to the outcome of the reaction. When the noncoordinating solvent benzene or cyclohexane was used, ester elimination was observed at room temperature. In contrast, when the coordinating solvent pyridine was used, no evidence for ester elimination was observed and instead ligand exchange occurred at room temperature. No evidence for ester elimination was observed when the same reaction was carried out in the parent alcohol HO-*t*-Bu as solvent at room temperature, which is the solvent generally used for preparation of metal oxide species from metal alkoxide and carboxylate compounds. By the use of ^{17}O labeling experiments in conjunction with ^{17}O NMR spectroscopy, a plausible transition state for the ester elimination reaction has been described. We believe that, in order for ester elimination to occur between a metal alkoxide and a metal carboxylate compound, the metal alkoxide compound must have vacant coordination sites available, the carboxylate must be capable of bridging two metal centers, and a polar, coordinating solvent should be avoided, presumably because it competes successfully with the carboxylate ligand for the vacant coordination sites at the metal alkoxide center. We are currently exploring reactions between other metal alkoxide and carboxylate compounds to develop criteria which promote or inhibit ester elimination reactions in order to carry out directed synthesis of metal oxo clusters as intermediates in the formation of metal oxide materials with controlled microstructure.

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Supplementary Material Available: For Sn(O-*t*-Bu)$_3$(OAc)(py), tables giving the structure determination summary, atomic coordinates, bond lengths and angles, anisotropic displacement coefficients, and H atom coordinates (9 pages). Ordering information is given on any current masthead page.

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