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Synthesis, Structure, and Properties of $\{(Me_3Si)_2CH\}_2SnH(OH)$

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The Lappert stannylene SnR_2, R = $CH(SiMe_3)_2$, adds water and methanol to yield the low-melting-point, crystalline hydroxy- and methoxydiorganostannanes $R_2SnH(OH)$ (**1**) and $R_2SnH(OMe)$ (**2**). The corresponding deuterated derivatives $R_2SnD(OD)$ (**1**-d_2) and $R_2SnD(OCD_3)$ (**2**-d_4) have also been prepared. Compounds **1** and **2** react with D_2O with retention of the Sn−H bond to give $R_2SnH(OD)$ (**1**-d(SnOD)). The reaction is thought to proceed by an S_N2 type mechanism via a $[R_2SnH(OR')_2]^-$ (R′ = H, D, or Me) intermediate or transition state. Consistent with this, **2**-d_4 is hydrolyzed to $R_2SnD(OH)$ (**1**-d(SnD)). A single-crystal X-ray structure analysis of **1** reveals that individual molecules form C_i-symmetrical dimers in the solid with short O−H···O* hydrogen bridges (O···O* = 2.854(2) Å). Reaction of **1** with $(^iPr_2PC_2H_4P^iPr_2)Pd(C_2H_4)$ results in oxidative addition of the Sn−H bond to Pd^0 to give the known $(^iPr_2PC_2H_4P^iPr_2)Pd(H)-SnR_2(OH)$ (**3**).

Introduction

There have only been a few reports of well-characterized hydroxy- and alkoxy stannane compounds. Among these is Mes_3SnOH[1] (Mes = mesityl), which presumably because of the bulky mesityl substituents contains tetrahedrally (*T*-4) coordinated Sn centers (Sn−O = 2.00 Å) and is monomeric in the solid state. In contrast, solid Ph_3SnOH[2] is polymeric and exhibits trigonal-bipyramidal (*TB*-5) Sn centers with the phenyl substituents in the trigonal plane and two hydroxy ligands at the axial positions. The hydroxy ligands form unsymmetrical bridges between the Sn centers (Sn−O = 2.20 Å, Sn−O′ = 2.26 Å), and the resulting chain has a zigzag structure. For $Me_3Sn(OH)$, on the other hand, a linear chain structure with almost equivalent Sn−O bonds has been proposed on the basis of X-ray diffraction experiments, but complete structural data have not been given.[3] While the compounds $^nBu_2SnH(OR')$ (R′ = Me, Et)[4] represent the first thermally stable alkoxydiorganostannanes, there are apparently no hydroxydiorganostannanes $R_2SnH(OH)$ known thus far. Oxidative addition of water or alcohol to a stannylene such as $Sn\{CH(SiMe_3)_2\}_2$[5a,b] immediately suggests itself as a possible synthetic route to both compounds, but it has been indicated that $Sn\{CH(SiMe_3)_2\}_2$ is decomposed by water and ethanol.[5b,c]

Our interest in the reactivity of uncoordinated $Sn\{CH(SiMe_3)_2\}_2$ toward water and alcohol was stimulated by the observation that stannylene complexes of the type $(R''_2PC_2H_4PR''_2)M{=}SnR_2$ (R″ = ^iPr, ^tBu; M = Ni, Pd; R = $CH(SiMe_3)_2$) react with water and methanol to afford the *bimetallic* hydrido, hydroxy, or methoxy complexes $(R''_2PC_2H_4PR''_2)M(H)\text{-}SnR_2(OR')$ (R′ = H, CH_3).[6] As solids these complexes reversibly eliminate water or methanol at elevated temperature under vacuum. In solution, with an excess of water and methanol present, rapid nucleophilic exchange reactions proceed at the Sn^{IV} center by an S_N2-type mechanism. These findings raised the question as to whether uncoordinated SnR_2 also undergoes water and methanol activation reactions and, if so, what the properties of the products would be. We therefore set out to reinvestigate the hydrolysis and methanolysis of $Sn\{CH(SiMe_3)_2\}_2$, and the results of these studies[7] are described here.

Results and Discussion

Reaction of $Sn\{CH(SiMe_3)_2\}_2$ with Water and Methanol (Scheme 1). When (air-free) H_2O is added to a red THF solution of SnR_2 (R = $CH(SiMe_3)_2$) at 0 °C, the solution decolorizes instantly. After evaporation to dryness and crystallization from pentane (−30 °C) colorless plates of the hydroxydiorganostannane **1** are obtained in about 90% yield.[8] By using D_2O in a corresponding reaction the isotopomer **1**-d_2 is formed. Similarly, a THF solution of $Sn\{CH(SiMe_3)_2\}_2$ reacts

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[1] Reuter, H.; Puff, H. *J. Organomet. Chem.* **1989**, *379*, 223.

[2] Glidewell, C.; Liles, D. C. *Acta Crystallogr., Sect. B* **1978**, *34*, 129.

[3] Kasai, N.; Yasuda, K.; Okawara, R. *J. Organomet. Chem.* **1965**, *3*, 172.

[4] (a) Hayashi, K.; Iyoda, J.; Shiihara, I. *J. Organomet. Chem.* **1967**, *10*, 81. (b) Ito, Y.; Murata, K.; Kondo, T.; Takahashi, H. *Chem. Abstr.* **1977**, *86*, 90029u. (c) Schumann, H.; Schumann, I. *Gmelin Handbook of Inorganic Chemistry,* 8th ed.; Springer: Berlin, 1989; Part 17 (Sn; Organotin Compounds), p 78.

[5] (a) Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 317. Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268. (b) Cotton, J. D.; Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2275. (c) The actual statements in ref 5b are that $Sn\{CH(SiMe_3)_2\}_2$ is "virtually insoluble in EtOH, but slowly decomposed thereby" and "crystals of R_2Sn were ... only slowly decomposed by degassed water or ethanol, probably on account of insolubility".

[6] Schager, F.; Seevogel, K.; Pörschke, K.-R.; Kessler, M.; Krüger, C. *J. Am. Chem. Soc.* **1996**, *118*, 13075.

[7] Schager, F. Dissertation, Universität Düsseldorf, 1997.

[8] The water and methanol addition and nucleophilic exchange reactions in Scheme 1 also proceed at −78 °C within a few minutes. The reactions are markedly faster than the addition and exchange reactions of the stannylene complex $(d^ippe)Pd{=}SnR_2$, which occur readily ≥−40 °C (eq 3b). The reaction of $(d^ippe)Pd(C_2H_4)$ with **1** to afford **3** is slowest (≥−10 °C; eq 3a).

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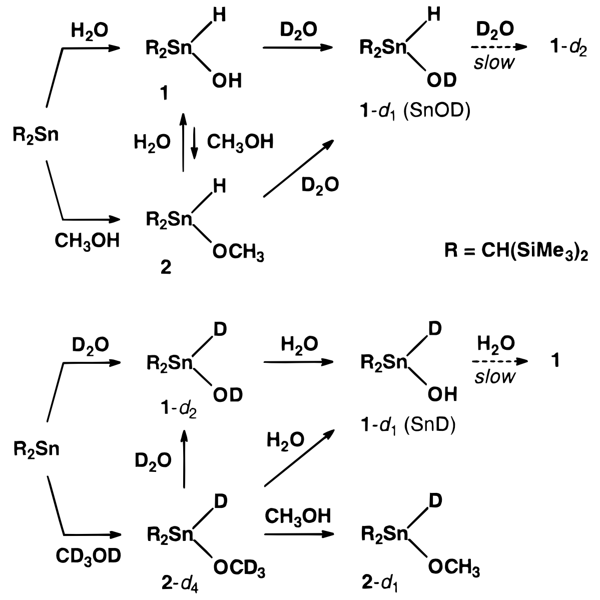
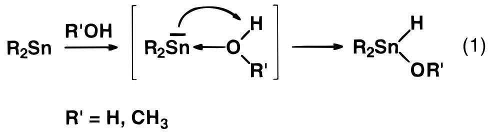
Scheme 1



with methanol (0 °C) to afford the colorless methoxydiorganostannane **2** in 83% yield. The corresponding reaction with CD_3OD yields **2**-d_4. The syntheses of **1** and **2** (and isotopomers) formally represent oxidative additions of water and methanol to the Sn^{II} center. Although such reactions are known for SnR_2 with halogens (Cl_2, Br_2), alkyl iodides (MeI), and acids (HCl, HF), giving $R_2Sn(X)Y$-type compounds,[5b,9] the ready formation of **1** and **2** is nevertheless unexpected because water and methanol are not usually considered to be particularly oxidative. In analogy to addition reactions of SnR_2 with other donors and the results of theoretical calculations on hypothetical water adducts,[10] the formation of **1** and **2** probably involves initial generation of the adduct $R_2Sn(R'OH)$ between the donors R′OH (R′ = H, Me) and the electronically unsaturated SnR_2. Subsequent proton migration from the coordinated oxygen atom to the lone electron pair on Sn^{II} results in formal oxidation of Sn^{II} to Sn^{IV} (eq 1). Thus, oxidative



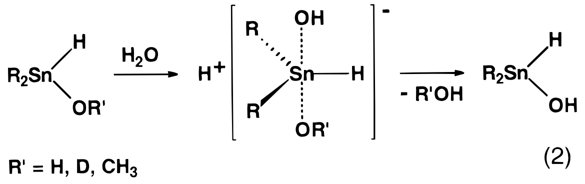
(1)

addition of R′OH to SnR_2 is initiated by a nucleophilic interaction of the addendum with SnR_2. This is in contrast to reactions of SnR_2 with electrophiles, for which a free radical reaction pathway has been proposed.[9]

Deuterium crossover reactions were undertaken in order to study the chemistry of the Sn(H)OH group more closely. When a 10-fold excess of D_2O is added to a THF-d_8 solution of the hydroxystannane **1** at 0 °C, an immediate exchange of the OH function for OD occurs, and partially deuterated **1**-d(SnOD) is formed. Total Sn−H/D exchange is observed after only 2 weeks, giving **1**-d_2, in accompaniment with partial decomposition (ca. 25%) of the system. Similarly, **1**-d_2 reacts rapidly with H_2O to afford **1**-d(SnD), while additional Sn−D/H exchange to give **1** is very slow.

The methoxystannane **2** reacts with a stoichiometric amount of H_2O or D_2O by instantaneous exchange of the OCH_3 moiety for hydroxide or deuterioxide to yield **1** or **1**-d(SnOD), respectively. The subsequent slow reaction of **1**-d(SnOD) with D_2O to give **1**-d_2 proceeds as described above. In contrast, when **1** is reacted with a ca. 35-fold excess of methanol, only the partial formation of **2** (about 70%) is observed due to an unfavorable equilibrium. Analogous reactions of **2**-d_4 with D_2O and H_2O yield **1**-d_2 and **1**-d(SnD), respectively. When an excess of CH_3OH is added to a THF solution of **2**-d_4, singly deuterated **2**-d is obtained.

The rapid $R_2(H)Sn{-}OH/OMe$ exchange reactions[11] of **1** and **2** (and their isotopomers), which proceed without participation of the hydrido substituent at Sn, presumably occur by an associative, S_N2-type mechanism. Coordination of the incoming group (e.g., OH^-) to the initial *T*-4 Sn^{IV} center results in a formally anionic *TB*-5 Sn^{IV} intermediate, with the R and H substituents lying in the trigonal plane and the oxygen donor atoms at the apical positions, before eventual elimination (eq 2).[12a]



(2)

The much slower Sn−H/D exchange reaction, in contrast, probably proceeds by the reductive elimination of water or methanol, i.e., by the reverse of the synthesis reaction.

Both **1** (42 °C) and **2** (30 °C) have relatively low melting points. When the compounds are heated under vacuum (**1**, 130 °C; **2**, 100 °C), they slowly decompose to a mixture of unidentified products. Interestingly, elimination of water or methanol with recovery of SnR_2 apparently does not take place (NMR).

When a colorless THF-d_8 solution of equimolar amounts of the hydroxydiorganostannane **1** and $(d^ippe)Pd(C_2H_4)$ ($d^ippe = {}^iPr_2PC_2H_4P^iPr_2$) is warmed from −78 to −10 °C, the color changes to tan. No further change is observed when the solution is warmed to 20 °C. According to the ^1H and ^{31}P NMR spectra, the bimetallic hydrido hydroxy complex **3** is formed quantitatively (eq 3a).[8] As mentioned in the Introduction, complex **3** is

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[9] (a) Gynane, M. J. S.; Lappert, M. F.; Miles, S. J.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1976**, 256; **1978**, 192. (b) Gynane, M. J. S.; Lappert, M. F.; Miles, S. J.; Carty, A. J.; Taylor, N. J. *J. Chem. Soc., Dalton Trans.* **1977**, 2009. (c) Lappert, M. F.; Misra, M. C.; Onyszchuk, M.; Rowe, R. S.; Power, P. P.; Slade, M. J. *J. Organomet. Chem.* **1987**, *330*, 31.

[10] With the nitrogen donors pyridine, 4-methylpyridine, and piperidine, the heterocarbenes $E\{CH(SiMe_3)_2\}_2$ (E = Ge, Sn) form labile adducts of the type $(donor)E\{CH(SiMe_3)_2\}_2$.[5b] Moreover, MO calculations for the hypothetical water adducts $(H_2O)EH_2$ (E = Si, Ge, Sn) gave a sufficiently large bonding energy (11.5−13.2 kcal/mol) that their formation as intermediates can be postulated. Schoeller, W. W.; Schneider, R. *Chem. Ber./Rec.* **1997**, *130*, 1013.

[11] For related $R_2(X)Sn{-}OH/OR'$ exchange reactions at Sn^{IV}, see: (a) Okawara, R.; Wada, M. *J. Organomet. Chem.* **1963**, *1*, 81. (b) Alleston, D. L.; Davies, A. G.; Hancock, M. *J. Chem. Soc.* **1964**, 5744. (c) Poller, R. C. *The Chemistry of Organotin Compounds*; Academic Press: New York, 1970.

[12] (a) Pentacoordination of organo Sn^{IV} compounds is frequently observed, both in the solid state (e.g., Me_3SnOH and Ph_3SnOH, see Introduction) and in solution.[9b] (b) For the related nucleophilic attack of Pt^{II} at a Sn^{IV} center, see: Levy, C. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1995**, 2115.

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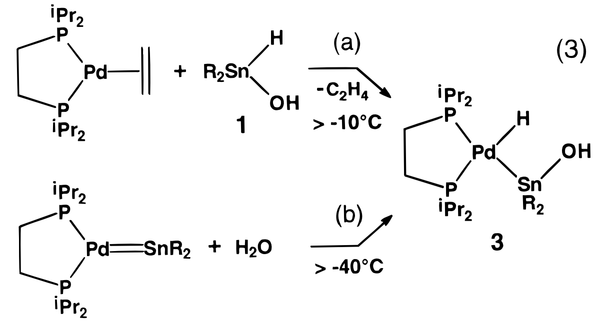
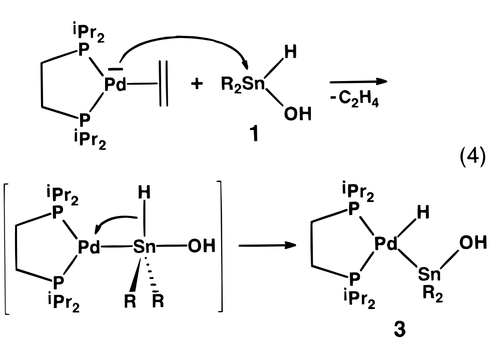


(3)

also obtained by the addition of water to the Pd^0–stannylene complex (d^ippe)Pd=SnR_2 (eq 3b).[6] The formation of **3** according to eq 3a thus formally represents an insertion of the [(d^ippe)Pd^0] moiety into the Sn–H bond of $R_2SnH(OH)$ (oxidative addition of the Sn–H bond to Pd^0). The mechanism most likely involves nucleophilic attack of the electron-rich d^{10} Pd^0 moiety at the Sn^{IV} center of **1**,[12b] formation of a *TB*-5 (or *SPY*-5) Sn^{IV} intermediate,[12a] and subsequent migration of the hydride to the Pd^{II} center to give **3** (eq 4).



(4)

Spectroscopic Characterization.[13] In the EI mass spectra of **1** (20 °C), **1**-d_2 (15 °C), and **2** (2 °C) the molecular ions are observed. The molecular ions of **1** and **1**-d_2 fragment by elimination of water to afford the stannylene ion $[\{(Me_3Si)_2CH\}_2Sn]^+$ (*m/e* 438). In contrast, the molecular ion of **2** (*m/e* 470, 1%) fragments by successive cleavage of the *O*-Me group[14] and the oxygen atom to produce $[\{(Me_3Si)_2CH\}_2SnH]^+$ (*m/e* 439, 57%), which splits off hydrogen to yield $[\{(Me_3Si)_2CH\}_2Sn]^+$ (28%).

The IR spectra (KBr) of **1** and the isotopomers **1**-*d*(SnD), **1**-*d*(SnOD), and **1**-d_2 display the expected bands *in duplicate* in the range of the SnOH, SnOD, SnH, and SnD stretching vibrations (Table 1). Thus, complex **1** (similarly for **1**-*d*(SnD)) exhibits a sharp band at 3652 cm^{-1} and a broad band at 3446 cm^{-1}, attributable to SnO–H stretchings. Correspondingly, complex **1**-d_2 (similarly for **1**-*d*(SnOD)) displays a sharp band at 2691 cm^{-1} and a broad band at 2548 cm^{-1} for SnO–D stretchings, equivalent to a wavenumber ratio ν_D/ν_H of about 0.74. The observed broad bands cannot be explained by water absorptions, since the spectra do not display H_2O (ca. 1600 cm^{-1}) or D_2O (ca. 1180 cm^{-1}) bending vibrations. Instead, it seems likely that they stem from terminal and bridging hydrogens present in the crystal (see below). Furthermore, compound **1** displays Sn–H stretchings at 1856/1826 cm^{-1} (capillary: 1821 cm^{-1}),[15] and for **1**-d_2 the Sn–D stretching vibration is at 1328/1313 cm^{-1}. The line splitting of the Sn–H and Sn–D stretching bands[15] is attributed to through-space coupling in the crystal.

Table 1. Selected IR Data (cm^{-1}; in KBr) for Complexes 1 and 2 and Isotopomers

	ν(SnOH)	ν(SnOD)	ν(SnH)	ν(SnD)
		Compounds in This Paper		
1	3652,[a] 3446[b]		1856/1826[c]	
1-*d*(SnD)	3651,[a] 3442[b]			1332/1310[c]
1-*d*(SnOD)		2692,[a] 2568[b]	1855/1819[c]	
1-d_2		2691,[a] 2548[b]		1328/1313[c]
2			1815	
2-*d*				1305
2-d_4				1304
		Reference Compounds		
Me_3SnH[27]			1837[d]	
Ph_3SnH[27a]			1847[d]	
$R_2Sn(H)Cl$[5b]			1845	
Me_3SnOH[28]	3615[e]			
Ph_3SnOH[29]	3618			
3	3649			

[a] Sharp band; terminal H or D. [b] Broad band; bridging H or D. [c] Line splitting due to coupling effect in the crystal. [d] Capillary. [e] Nujol.

In the IR spectrum of **2** the Sn–H stretching band is at 1815 cm^{-1}, while for **2**-d_4 the Sn–D stretching band is at 1304 cm^{-1}. The $SnOCH_3$ moiety of complex **2** displays an overtone band at 2800 cm^{-1}, the CH_3 bending vibration at 1445 cm^{-1}, and a C–O stretching band at 1065 cm^{-1}. The Sn–H and SnO–H stretching bands of **1** and **2** agree well with those of other Sn compounds (Table 1).

In the ^1H NMR spectra (Table 2), the Sn–H resonance of **1**, **1**-*d*(SnOD), and **2** is at very low field (δ_H ca. 7.3) and the coupling $^1J(^{119}SnH)$ is almost 2000 Hz, which is at the upper limit of the expected range (1750–1940 Hz).[16] In contrast, the SnOH resonances of **1** (δ_H 1.63) and **1**-*d*(SnD) (δ_H 1.81) lie at relatively high field. The $SnOCH_3$ resonance of **2** and **2**-*d* (δ_H 3.69) is as expected. The CH moieties of the two $CH(SiMe_3)_2$ substituents are enantiotopic, but the methyl groups of each $CH(SiMe_3)_2$ substituent are diastereotopic, and this gives rise to one SnCH and two $SiMe_3$ resonances in the ^1H and ^{13}C NMR spectra.[17] For **1** δ_H of SnCH is slightly, and δ_C markedly, at higher field than for **2**.

Single-Crystal X-ray Structure Analysis of 1. The results of the structure analysis of **1** are summarized in Figure 1 and reveal the molecule to be a monomer, which is hydrogen-bonded to a symmetry-related molecule in the crystal. In accord with the monomeric nature of the molecule, the central Sn atom is tetrahedrally coordinated by two alkyl substituents, a hydroxy group, and a hydrogen atom. The C1–Sn–C2 angle of 115.3(1)° is significantly larger than the equivalent angle in (d^ippe)Pd(H)–Sn(OH)$\{CH(SiMe_3)_2\}_2$ (**3**; 99.6°)[6] or (d^ippe)Pd(CH=CH)Sn$\{CH(SiMe_3)_2\}_2$ (**4**;

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[13] Harrison, P. G. *Chemistry of Tin*; Blackie: Glasgow, U.K., 1989; pp 60–117.

[14] It can be seen in the mass spectrum of **2**-d_4 (see Experimental Section) that some cleavage of *Si*-Me groups also occurs.

[15] The line splitting of the Sn–H and Sn–D stretching bands (KBr samples) does not occur for semisolid, impure products (capillary sample).

[16] Birchall, T.; Pereira, A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1087.

[17] The spectra imply that in THF-d_8 solution the Sn^{IV} center of **1** and **2** is configurationally stable.[9b] See also: Marshall, J. A.; Jablonowski, J. A. *The Chemistry of Organic Germanium, Tin, and Lead Compounds*; (Patai, S., Ed.); Wiley: Chichester, U.K., 1995; p 195.

Table 2. Selected ^{1}H and ^{13}C NMR Data of Complexes 1 and 2 and Isotopomers[a]

	δ_H				
	SnH	SnOH	SnOCH$_3$	SnCH	δ_C SnCH
			Compounds in This Paper		
1	7.27 ($^1J(^{119}SnH)$ 1991, $^3J(HH_{CH})$ 2)	1.63 ($^2J(SnH)$ 28)		−0.22 ($^2J(^{119}SnH)$ 89, $^3J(HH_{SnH})$ 1.5, $^2J(SiH)$ 8.6)	8.20 ($^1J(^{119}SnC)$ 223, $^1J(SiC)$ 40)
1-*d*(SnOD)	7.25 ($^1J(^{119}SnH)$ 1995, $^3J(HH)$ 2)			−0.23 ($^2J(^{119}SnH)$ 89, $^3J(HH_{SnH})$ 1.5, $^2J(SiH)$ 8.6)	8.18 ($^1J(SnC)$ 218, $^1J(SiC)$ 39)
1-*d*(SnD)		1.81[b]		−0.23 ($^2J(^{119}SnH)$ 90, $^2J(SiH)$ 8.6)	8.05 ($^1J(SnC)$ 219, $^2J(CD)$ 2, $^1J(SiC)$ 42)
1-d_2				−0.23 ($^2J(^{119}SnH)$ 89, $^2J(SiH)$ 8.6)	7.99 ($^1J(SnC)$ 219, $^2J(CD)$ 2, $^1J(SiC)$ 39)
2	7.42 ($^1J(^{119}SnH)$ 1968, $^3J(HH)$ 2)		3.69 ($^3J(^{119}SnH)$ 50)	−0.16 ($^2J(SnH)$ 89, $^3J(HH_{SnH})$ 1.6, $^2J(SiH)$ 8.4)	9.59 ($^1J(^{119}SnC)$ 214, $^1J(SiC)$ 39)
2-*d*			3.69 ($^3J(SnH)$ 49)	−0.17 ($^2J(SnH)$ 91, $^2J(SiH)$ 8.6)	9.46 ($^1J(SnC)$ 212, $^2J(CD)$ 2, $^1J(SiC)$ ...)
2-d_4				−0.16 ($^2J(SnH)$ 89, $^2J(SiH)$ 8.6)	9.43 ($^1J(SnC)$ 211, $^2J(CD)$ 2, $^1J(SiC)$ 38)
			Reference Compounds		
Me$_3$SnH[27]	4.14 ($^1J(SnH)$ 1852)				
Ph$_3$SnH[30]	6.83 ($^1J(SnH)$ 1936)				
R$_2$Sn(H)Cl[5b]	7.79[c]				
Me$_3$SnOH[31]		~2.0[c]			
3		−0.55 ($^2J(SnH)$ 22)			

[a] Solvent THF-d_8. Coupling constants in Hertz. [b] Broad signal. [c] $^1J(SnH)$ or $^2J(SnH)$ not reported.

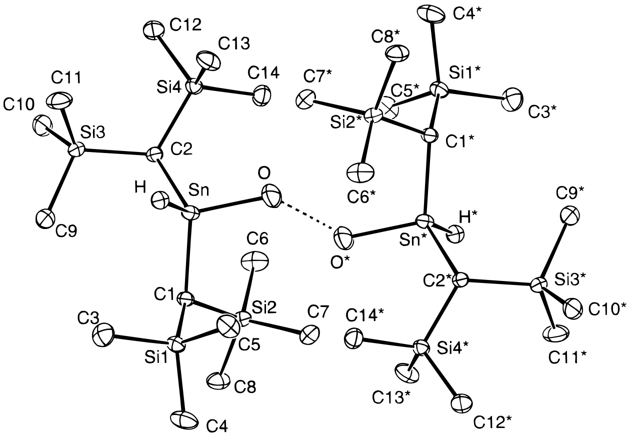

Figure 1. Molecular structure of **1**, showing the O−H···O* hydrogen bond in the crystal (symmetry-related atoms designated by asterisks). Selected bond lengths (Å): Sn−O, 1.984(1); Sn−H, 1.73(2); Sn−C1, 2.149(1); Sn−C2, 2.149(1); O···O*, 2.854(2). Selected bond angles (deg): C1−Sn−C2, 115.3(1); C1−Sn−O, 105.8(1); C2−Sn−O, 107.5(1); O−Sn−H, 108(1); C1−Sn−H, 113(1); C2−Sn−H, 107(1); Sn−O···O*, 124.6(1).

105°)[18] and presumably reflects the smaller size of H and OH groups. The substituents about the Sn−C bonds are nearly staggered, and the methyne H atom of one of the (Me$_3$Si)$_2$CH substituents lies nearly trans to the H atom bonded to Sn (torsion angle −152°), and the other nearly trans to O (torsion angle −158°), with the result that the two SiMe$_3$ arms of the SnC(SiMe$_3$)$_2$ shells embrace alternately the Sn−OH and Sn−H moieties. Hence, the orientation of the (Me$_3$Si)$_2$CH substituents in **1** corresponds to that observed in **3** and **4**. The Sn−C bonds in **1** of 2.149(2) Å (mean) are nevertheless relatively short (**3**, 2.22 Å; **4**, 2.21 Å). The Sn−OH bond of 1.984(1) Å is slightly shorter than in monomeric Mes$_3$SnOH (2.00 Å).[1] The length of the Sn−H bond is 1.73(2) Å and corresponds to that determined by gas-phase electron diffraction on Me$_3$SnH (1.705(67) Å).[19a] A significantly shorter distance was found crystallographically in *tert*-butyl-8-(dimethylamino)naphthyl-(−)-menthyltin hydride (1.52(5), 1.63(5) Å).[19b] The difference may be due to the fact that the diffraction data of **1** were collected at 100 K.

In the crystal the monomers aggregate in pairs about centers of symmetry and show a short intermolecular O···O* distance of 2.854(2) Å. The distance is typical for an O−H···O hydrogen bond between hydroxides (mean 2.82 Å).[20] Space group symmetry means that the bridging H atom is perforce disordered, since it cannot occur at both sides of the center of symmetry simultaneously. This is indeed observed, and the refined occupancy of the bridging H atom is 0.53(4). Additional kinetic stability of the monomer is presumably conferred by meshing of the SiMe$_3$ groups of both molecules (van der Waals contacts). A possible stabilizing interaction between the tin atom and the oxygen atom of the partner molecule in the dimeric unit is unlikely (Sn···O* = 4.301(1) Å). The structure of **1** in the crystal is therefore different from that of monomeric Mes$_3$SnOH,[1] oligomeric Ph$_3$SnOH,[2] and Me$_3$SnOH[3] (see Introduction).

Conclusions

The reaction of uncoordinated SnR$_2$ (R = CH(SiMe$_3$)$_2$) with R′OH (R′ = H, Me) to give hydroxy- and methoxydiorganostannanes R$_2$SnH(OR′) complements and contrasts our former results on the R′OH addition to (R″$_2$PC$_2$H$_4$PR″$_2$)M^0=SnR$_2$ (R″ = ^{i}Pr, ^{t}Bu; M = Ni, Pd) complexes.[6] The main features of the M^0/SnR$_2$/R′OH system are (a) uncoordinated SnR$_2$ oxidatively and *irreversibly* adds water and methanol at −78 to 20 °C to yield the hydroxy- and alkoxydiorganostannanes **1** and **2**, (b) the stannylene complexes (R″$_2$PC$_2$H$_4$PR″$_2$)-

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$M^0{=}SnR_2$ *reversibly* add water and methanol to give bimetallic hydrido hydroxy and hydrido alkoxy complexes $(R''_2PC_2H_4PR''_2)M^{II}(H){-}SnR_2(OR')$ (**3**: M = Pd, R′ = H, R″ = ^{i}Pr), in which the Sn^{II} oxidation state is maintained,[6] and (c) the Sn−H bond of **1** undergoes an oxidative addition to $[(d^ippe)Pd^0]$ to also give **3**, concomitant with a reduction of Sn^{IV} to Sn^{II}. Thus, the addition of water and methanol is an intrinsic property of uncoordinated SnR_2, leading to the oxidation $Sn^{II} \rightarrow Sn^{IV}$. When SnR_2 is coordinated to $(R''_2PC_2H_4PR''_2)M^0$ to form $(R''_2PC_2H_4PR''_2)M^0{=}SnR_2$, however, this property is shared with and modified by the M^0 center with the result that the $M^0{=}Sn^{II}$ couple is oxidized to $M^{II}{-}Sn^{II}$; i.e., the d^{10} metal is preferentially oxidized and the reaction becomes reversible. Similar reversible oxidations of the $M^0{=}Sn^{II}$ metal pair to $M^{II}{-}Sn^{II}$ and (nonbonded) $M^{II}\cdots Sn^{IV}$ have been observed for reactions of the $M^0{=}Sn^{II}$ system with ethyne[18,21] and butadiene.[22]

Although the reaction of the germylene GeR_2 (R = $CH(SiMe_3)_2$) with alcohols R′OH (R′ = Me, Et) has been reported to yield thermally stable alkoxydiorganogermanes $R_2GeH(OR')$, structurally characterized for R′ = Et,[23] the product of the corresponding reaction with water has not been described. Preliminary results have shown that the Ge homologue $\{(Me_3Si)_2CH\}_2GeH(OH)$ is also formed by a route similar to that found for **1**.[24]

Experimental Section

All operations were conducted under an atmosphere of argon by standard Schlenk techniques. $Sn\{CH(SiMe_3)_2\}_2$ was prepared as described.[5a] Microanalyses were performed by the Mikroanalytisches Labor Kolbe, Mülheim, Germany. ^1H NMR spectra (δ relative to internal TMS) were measured at 200, 300, and 400 MHz and ^{13}C NMR spectra (δ relative to internal TMS) at 50.3 and 75.5 MHz on Bruker AC- and AM-200, AMX-300, and AMX-400 instruments. For all NMR spectra solutions of the compounds in THF-d_8 were used. EI mass spectra (the data refer to ^{28}Si and ^{120}Sn) were recorded at 70 eV on a Finnigan MAT 8200, and IR spectra were measured on Nicolet FT 7199 and Magna-IR 750 spectrometers.

$\{(Me_3Si)_2CH\}_2SnH(OH)$ (1). When water (0.5 mL) was added to the red THF solution (20 mL) of $Sn\{CH(SiMe_3)_2\}_2$ (876 mg, 2.00 mmol) at 0 °C, the color changed to pale yellow. After evaporation of the solvent under vacuum (0−20 °C) the residue was dissolved in pentane (5 mL) and the solution was filtered. At −78 °C colorless plates crystallized, and they were separated from the mother liquor, washed twice with cold pentane, and dried under vacuum at 0 °C: yield 810 mg (89%); mp 42 °C. Anal. Calcd for $C_{14}H_{40}OSi_4Sn$ (455.5): C, 36.91; H, 8.85; O, 3.51; Si, 24.66; Sn, 26.06. Found: C, 36.98; H, 8.83; Si, 24.57; Sn, 26.20. IR (KBr): see Table 1. EI-MS (20 °C): *m/e* (%) 456 (M^+, 1), 438 ($[SnR_2]^+$, 36), 279 ($[SnCH(SiMe_3)_2]^+$, 37), 259 (100), 129 ($[Me_3Si_2C_2H_4]^+$, 76). ^1H NMR (300 MHz, 27 °C) (for SnH, SnOH, and SnCH, see Table 2): δ 0.20, 0.15 (each 18H, diastereotopic $SiMe_3$), SnR_2. ^{13}C NMR (75.5 MHz, 27 °C) (for SnCH, see Table 2): δ 3.5 (6C, $^3J(SnC)$ = 17 Hz, $^1J(SiC)$ = 51 Hz, $SiMe_3$), 2.9 (6C, $^3J(SnC)$ = 22 Hz, $^1J(SiC)$ = 51 Hz, $SiMe_3'$), SnR_2.

$\{(Me_3Si)_2CH\}_2SnH(OD)$ (1-*d*(SnOD)). Complex **1** (80 mg) was dissolved in THF (2 mL), and D_2O (0.3 mL) was added at 0 °C. The solution was briefly warmed to 20 °C, and the solvent was evaporated under vacuum. The pure complex has been obtained in the form of a colorless solid in quantitative yield: $C_{14}H_{39}DOSi_4Sn$ (456.5). IR and NMR: see Tables 1 and 2.

$\{(Me_3Si)_2CH\}_2SnD(OH)$ (1-*d*(SnD)). Complex **1**-d_2 was reacted with H_2O as described above to afford the pure complex as a colorless solid: $C_{14}H_{39}DOSi_4Sn$ (456.5). IR and NMR: see Tables 1 and 2.

$\{(Me_3Si)_2CH\}_2SnD(OD)$ (1-d_2). The synthesis was carried out analogously to that of **1** but by using D_2O instead of H_2O; mp 45 °C. Anal. Calcd for $C_{14}H_{38}D_2OSi_4Sn$ (457.5): C, 36.75; H, 8.37; D, 0.88; O, 3.50; Si, 24.55; Sn, 25.95. Found: C, 36.71; H/D, 8.42; Si, 24.58; Sn, 26.13. IR (KBr): see Table 1. EI-MS (15 °C): *m/e* (%) 458 (M^+, 0.3), 438 ($[SnR_2]^+$, 35), 279 ($[SnCH(SiMe_3)_2]^+$, 22), 259 (100), 129 ($[Me_3Si_2C_2H_4]^+$, 63). ^1H NMR (200 MHz, 27 °C) (for SnCH, see Table 2): δ 0.19, 0.15 (each 18H, diastereotopic $SiMe_3$), SnR_2. ^{13}C NMR (75.5 MHz, 27 °C) (for SnCH, see Table 2): δ 3.5 (6C, $^3J(SnC)$ = 17 Hz, $^1J(SiC)$ = 51.5 Hz, $SiMe_3$), 2.9 (6C, $^3J(SnC)$ = 23 Hz, $^1J(SiC)$ = 51 Hz, $SiMe_3'$), SnR_2.

$\{(Me_3Si)_2CH\}_2SnH(OCH_3)$ (2). When methanol (0.2 mL) was added to the red solution of $Sn\{CH(SiMe_3)_2\}_2$ (526 mg, 1.20 mmol) in THF (10 mL) at 0 °C, the color changed to beige. After evaporation of the solvent under vacuum (0−20 °C) the residue was dissolved in pentane (4 mL) and the solution was filtered. At −30/−78 °C colorless crystals separated, and the mother liquor was removed by cannulation. The solid was washed twice with cold pentane and dried under high vacuum at −78 °C: yield 470 mg (83%); mp 30 °C. Anal. Calcd for $C_{15}H_{42}OSi_4Sn$ (469.6): C, 38.37; H, 9.02; O, 3.41; Si, 23.93; Sn, 25.28. Found: C, 39.26; H, 8.89; Si, 23.86; Sn, 25.22. IR (KBr) (for SnH, see Table 1): 2800, 1445, 1065 cm^{-1} (OCH_3). EI-MS (2 °C): *m/e* (%) 470 (M^+, 1), 455 ($[M - CH_3]^+$, 80), 439 ($[M - OCH_3]^+$, 57), 438 ($[SnR_2]^+$, 28), 279 ($[SnCH(SiMe_3)_2]^+$, 36), 259 (66), 129 ($[Me_3Si_2C_2H_4]^+$, 100). ^1H NMR (400 MHz, 27 °C) (for SnH, $SnOCH_3$, and SnCH, see Table 2): δ 0.19, 0.16 (each 18 H, diastereotopic $SiMe_3$), SnR_2. ^{13}C NMR (50.3 MHz, 27 °C) (for SnCH, see Table 2): δ 57.0 (1C, $^2J(SnC)$ = 33 Hz, OCH_3), 3.3 (6C, $^3J(SnC)$ = 17 Hz, $^1J(SiC)$ = 51 Hz, $SiMe_3$), 2.9 (6C, $^3J(SnC)$ = 22 Hz, $^1J(SiC)$ = 51.5 Hz, $SiMe_3'$), SnR_2.

$\{(Me_3Si)_2CH\}_2SnD(OCH_3)$ (2-*d*). **2**-d_4 was reacted with CH_3OH in THF solution as described above (**1**-*d*(SnOD)), and **2**-*d* was isolated as a colorless solid (0 °C). Due to the presence of small amounts of water in the solvent the signals of **1** and/or its isotopomers were also detected in the IR spectrum. IR (KBr) (for SnD, see Table 1): 2800, 1446, 1070 cm^{-1} (OCH_3).

$\{(Me_3Si)_2CH\}_2SnD(OCD_3)$ (2-d_4). The synthesis was carried out analogously to that of **2** but by using CD_3OD instead of methanol; mp 40 °C. Anal. Calcd for $C_{15}H_{38}D_4OSi_4Sn$ (473.6): C, 38.04; H, 8.09; D, 1.70; O, 3.38; Si, 23.72; Sn, 25.07. Found: C, 37.88; H/D, 8.99; Si, 23.85; Sn, 23.22. IR (KBr) (for SnD, see Table 1): 2229, 2180, 2041, 1115 cm^{-1} (OCD_3). EI-MS (8 °C): *m/e* (%) 474 (M^+, <0.1), 459 ($[M - CH_3]^+$, 82), 456 ($[M - CD_3]^+$, 28), 440 ($[M - OCD_3]^+$, 19), 438 ($[SnR_2]^+$, 19), 279 ($[SnCH(SiMe_3)_2]^+$, 29), 259 (41), 129 ($[Me_3Si_2C_2H_4]^+$, 100). ^1H NMR (200 MHz, 27 °C) (for SnCH, see Table 2): δ 0.19, 0.16 (each 18H, diastereotopic $SiMe_3$), SnR_2. ^{13}C NMR (50.3 MHz, 27 °C) (for SnCH, see Table 2): δ ~57 (1C, OCD_3), 3.3 (6C, $^1J(SiC)$ = 51 Hz, $^3J(SnC) \approx 16$ Hz, $SiMe_3$), 2.9 (6C, $^1J(SiC)$ = 51 Hz, $^3J(SnC) \approx 23$ Hz, $SiMe_3'$), SnR_2.

Crystal Data for 1: $C_{14}H_{40}OSi_4Sn$, M_r = 455.5, colorless crystal, size 0.39 × 0.42 × 0.42 mm, a = 9.340(1) Å, b = 11.383(1) Å, c = 11.999(1) Å, α = 94.352(7)°, β = 95.023(7)°, γ = 108.047(8)°, V = 1201.1(2) Å^3, T = 100 K, D_{calcd} = 1.26 g cm^{-3}, μ = 12.6 cm^{-1}, $F(000)$ = 476 e, Z = 2, triclinic, space group $P\bar{1}$ (No. 2), Enraf-Nonius CAD4 diffractometer, λ = 0.710 69 Å, $\omega - 2\theta$ scan, 14637 measured reflections ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda]_{max}$ = 0.70 Å^{-1}, 6975 independent reflections (R_{av} = 0.021),

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6645 observed reflections ($I \geq 2\sigma(I)$). The structure was solved by direct methods (SHELXS-97)[25] and refined by full-matrix least-squares[26] against F_2 for all data with Chebyshev weights: $R = 0.020$ (observed data), $R_w = 0.055$ for 189 refined parameters, non-H atoms anisotropic, H atom bonded to Sn located and refined isotropically ($U_H = 0.020(4)$ Å^2), otherwise H atoms riding, with the OH H atom disordered over three positions (one along the O···O* vector, occupancy refined to 0.53(4)), residual electron density 1.0 e Å^{-3}.

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Supporting Information Available: Tables of X-ray data collection information, atom coordinates and thermal parameters, and bond lengths and angles for **1** (5 pages). Ordering information is given on any current masthead page.

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