

NMR Study on Ligand Exchange Reaction between a Chiral Allylsilane and SnCl₄[†]

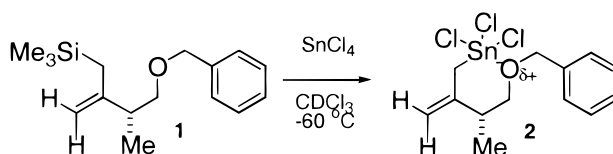
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ABSTRACT



A spectroscopic (¹H, ¹³C, and ¹¹⁹Sn NMR) study of the reaction of chiral allylsilane **1** with SnCl₄ is described. We have found that the ligand exchange between SnCl₄ and this allylsilane is instantaneous and quantitative at 25 °C as well as at –60 °C, affording the corresponding allyltrichlorostannane.

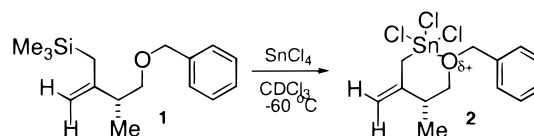
The Lewis acid-mediated reaction of allylsilanes with aldehydes is a well-known procedure for the preparation of homoallylic alcohols and is of current interest in the context of acyclic stereoselection. In all of these reactions the Lewis acid is employed presumably to activate the aldehyde toward nucleophilic attack by the allylsilane. However, the possibility that the Lewis acid first reacts with allylsilane generating a new species prior to addition cannot be ruled out.¹

There are a few studies in the literature about transmetalation reactions between allyltrialkyltins and Lewis acids, and the possibility of transmetalation process between trialkyltin compounds and Lewis acids has been discussed by Tagliavini,² Keck,³ Yamamoto,⁴ Denmark,⁵ and Naruta.⁶

To the best of our knowledge, the only spectroscopic information available on exchange reactions involving allylsilanes and SnCl₄ has been reported by Denmark and Wilson in 1988.⁷

We wish to report here the first direct evidence for interaction between SnCl₄ and chiral allylic silane **1** bearing an ether functionality generating a new species by means of NMR spectroscopy (Scheme 1). This allylsilane offers an

Scheme 1



attractive site for metal ligation with a benzyloxy substituent, and this coordination to the Lewis acid was found to play a very important role.¹

(5) (a) Denmark, S. E.; Wilson, T.; Willson, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 984. (b) Denmark, S. E.; Weber, E. J.; Wilson, T.; Willson, T. M. *Tetrahedron* **1989**, *45*, 1053. (c) Denmark, S. E.; Almstead, N. G. *Tetrahedron* **1992**, *48*, 5565. (d) Denmark, S. E.; Almstead, N. G. *J. Am. Chem. Soc.* **1993**, *115*, 3133.

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(1) (a) Dias, L. C.; Giacomini, R. *J. Braz. Chem. Soc.* **1998**, *9*, 357. (b) Dias, L. C.; Giacomini, R. *Tetrahedron Lett.* **1998**, *39*, 5343. (c) Dias, L. C.; Meira, P. R. R. *Synlett*, in press. (d) See also: Evans, D. A.; Coleman, P. J.; Dias, L. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2737.

(2) (a) Boaretto, A.; Marton, D.; Tagliavini, G.; Ganis, P. *J. Organomet. Chem.* **1987**, *321*, 199. (b) Tagliavini, G. *Rev. Silicon, Germanium, Tin Lead Compd.* **1985**, *8*, 237.

(3) Keck, G. E.; Abbot, D. E. *Tetrahedron Lett.* **1984**, *25*, 1883. (b) Keck, G. E. and Castellino, S. *J. Am. Chem. Soc.* **1986**, *108*, 3847. (c) See also: Keck, G. E.; Castellino, S.; Andrus, M. B. In *Selectivities in Lewis Acid Promoted Reactions*; Schinzer, D., Ed.; NATO ASI Series C; Kluwer Academic: Dordrecht, 1989; Vol. 289, Chapter 5, pp 73–105.

(4) Yamamoto, Y.; Maeda, N.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1983**, 742.

All reactions were run at 0.15 M in CDCl_3 solution with 1.1 equiv of SnCl_4 under an argon atmosphere, and all of the studies involved direct ^{13}C (75.5 MHz), ^1H (300 MHz), and ^{119}Sn NMR (111.92 MHz) observations. Upon addition of SnCl_4 to chiral allylsilane **1** at -60°C and at 25°C , it was immediately observed that the colorless solution became a slightly yellow homogeneous solution (Scheme 1). At no time did any precipitation of the new species occur at this concentration. The resulting ^1H NMR spectra at room temperature and also at -60°C showed formation of $\text{Me}_3\text{-SiCl}$ and complete consumption of the allylsilane **1** within 2 min (Figures 1–3).^{8,12}

Significantly, the resonances for the methylenic hydrogens α to silicon (H1, 1.46 ppm and H2, 1.52 ppm, Figure 1)

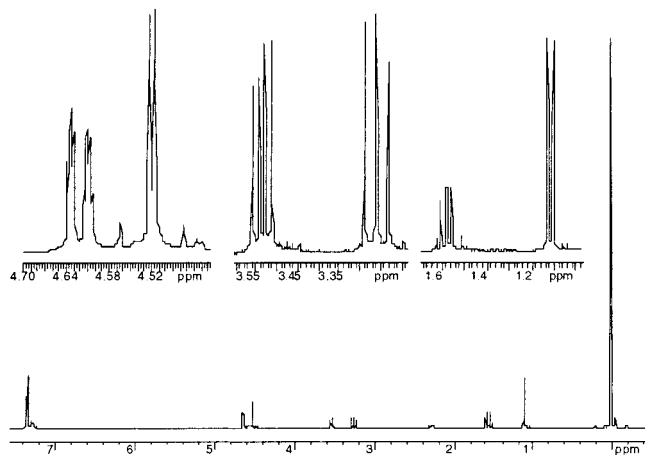


Figure 1. ^1H NMR spectrum of allylsilane **1**.

disappeared and two different signals appeared at 3.20 and 3.36 ppm (Figures 2 and 3).^{8,12}

Most diagnostics also are the deshielding of the hydrogens H3, H4, H5, H6, H7, H8, and H9 (Table 1). The methylenic

(6) Naruta, Y.; Nishigaishi, Y.; Maruyama, K. *Tetrahedron* **1989**, *45*, 1067.

(7) Denmark and Wilson have observed a ligand exchange reaction between allyltrimethylsilane and SnCl_4 (1.0 equiv of SnCl_4 at 0.5 M in 1:1 $\text{CD}_2\text{Cl}_2/\text{CDCl}_3$). They observed that the metathesis is 22% complete at -80°C after 2 min and nearly complete at -20°C . Wilson, T. M. Master's Thesis, University of Illinois, Urbana–Champaign (UIUC), 1988. They found also that (*E*)- and (*Z*)-crotylsilanes are essentially unreactive toward SnCl_4 even at room temperature. See also ref 5c.

(8) The only detectable products in these reactions are the allyltrichlorostannane and chlorotrimethylsilane. However, we have observed the formation of small amounts of product **3** (Scheme 2), formed probably due to the presence of HCl in SnCl_4 .

(9) (a) Almendras, P.; Gruttadauria, M.; Helliwell, M.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2549. (b) Almendras, P.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2561. (c) Thomas, E. J. *Chem. Commun.* **1997**, 411.

(10) For papers dealing with coordination of heteroelements to electron-deficient tin, see: (a) Vedejs, E.; Duncan, S. M.; Haight, A. R. *J. Org. Chem.* **1993**, *58*, 3046. (b) Ochiai, M.; Iwaki, S.; Nagao, Y.; Kitagawa, S.; Munakat, M. *Tetrahedron Lett.* **1991**, *32*, 4945. (c) Brown, J. M.; Pearson, M.; Jastrzebski, J. T. B. H.; Koten, G. V. *J. Chem. Soc., Chem. Commun.* **1992**, 1440.

(11) The order of mixing of allylsilane **1** and SnCl_4 makes no difference in the observed results. The use of 0.5 equiv of SnCl_4 compared to allylsilane **1** (1.0 equiv, 0.15 M solution) under the same conditions led to about 50% conversion, and the resulting NMR spectrum did not change with time.

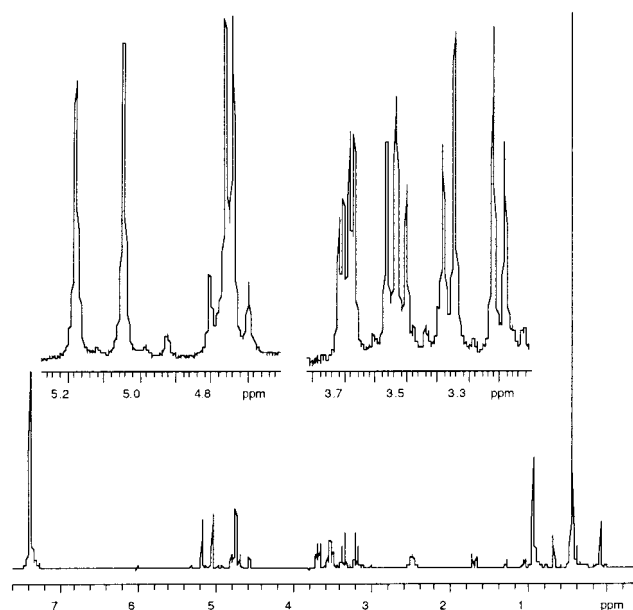


Figure 2. ^1H NMR spectrum of allyltrichlorostannane **2** at 25°C .

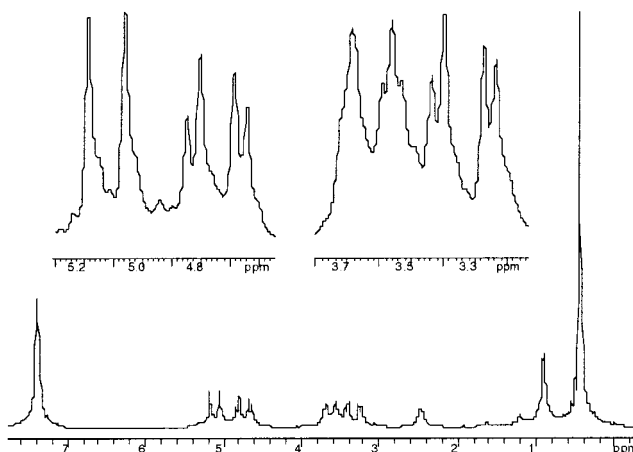
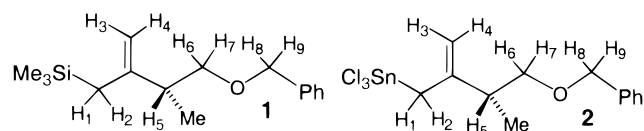


Figure 3. ^1H NMR spectrum of allyltrichlorostannane **2** at -60°C .

hydrogens H6 and H7 as well as the benzylic hydrogens H8 and H9 are too far away from trichlorotin group to suffer from inductive effects (Table 1).

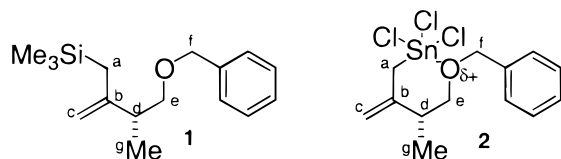
We believe that the deshielding observed for these hydrogens is due to the internal coordination of this oxygen to tin, as proposed in Scheme 1. This intermediate **2** is analogous to a series of allyltrichlorostannanes internally coordinated to the oxygen of a benzyloxy group as proposed by Thomas.^{9,10}

The ^1H NMR spectrum revealed the same behavior at -60°C ^{11–13} (Figure 3). Analysis of the ^{13}C NMR spectrum showed a deshielding for most carbons of **2** when compared to that of allylsilane **1**. Most diagnostic is the chemical shift

Table 1. ^1H NMR Data for Allylsilane **1** and Complex **2**

compd	^1H chemical shift (δ /ppm)								
	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆	H ₇	H ₈	H ₉
1	1.46	1.52	4.54	4.57	2.20	3.18	3.46	4.43	4.48
2	3.20	3.36	5.05	5.18	2.48	3.56	3.69	4.72	4.77

of 39.95 ppm for carbon a in the new species, compared to 26.63 ppm for the same carbon in the allylsilane (Table 2).^{11,12}

Table 2. ^{13}C NMR Data for Allylsilane **1** and Complex **2**

compd	^{13}C chemical shift (δ /ppm)						
	a	b	c	d	e	f	g
1	26.63	149.72	106.49	40.98	75.02	72.95	17.12
2	39.95	144.03	114.67	42.68	73.02	74.48	15.66

The ^{13}C NMR spectra proved less useful than the ^1H NMR spectra in establishing complexation to the benzyl oxygen, as there was no significant difference between the chemical shifts for carbons e and f in both species. For this purpose ^{119}Sn NMR spectroscopy proved informative. The ^{119}Sn resonance signals appeared at -156 ppm and as a single line at -187 ppm. The former corresponds to free SnCl_4 and the latter corresponds to allyltrichlorostannane.³ Acquir-

(12) Allylsilane **1**: ^1H NMR (CDCl_3 , 300 MHz) δ -0.04 (s, 9H), 1.04 (d, 3H, $^3J = 6.96$ Hz), 1.46 (dd, 1H, $^3J = 13.55$ – 1.10 Hz), 1.56 (dd, 2H, $^3J = 13.55$ – 1.10 Hz), 2.20 (m, 1H), 3.18 (dd, 1H, $^3J = 8.06$ – 9.15 Hz), 3.46 (dd, 1H, $^3J = 5.12$ – 9.15 Hz), 4.45 (d, 2H, $^3J = 2.19$ Hz), 4.50 (dd, 1H, $^3J = 2.19$ – 1.09), 4.55 (t, 1H, $^3J = 1.09$), 7.23 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz) δ -1.33 (CH_3), 17.12 (CH_3), 26.63 (CH_2), 40.98 (CH), 72.95 (CH_2), 75.02 (CH_2), 106.49 (CH_2), 127.41 (CH), 127.50 (CH), 128.28 (CH), 138.70 (C_0), 149.72 (C_0); IR (film) 3068, 3030, 2957, 2851, 1632, 1497, 1453, 1414, 1364, 1247, 1158, 1097, 1031. Mass spectra (CG-MS) 262 (1%), 181 (25%), 91 (62%), 73 (100%). TLC: R_f 0.26, hexanes/ethyl ether 99:1. $[\alpha]_D^{20} = +12.6$ (c 1.3, CHCl_3). Allylstannane **2**: ^1H NMR (CDCl_3 , 300 MHz) δ 0.95 (d, 3H, $^3J = 6.96$ Hz), 2.48 (m, 1H), 3.19 (d, 1H, $^3J = 10.98$ Hz), 3.36 (d, 1H, $^3J = 11.35$ Hz), 3, 53 (dd, 1H, $^3J = 8.42$ – 9.88 Hz), 3.70 (dd, 1H, $^3J = 4.39$ – 9.88 Hz), 4.71 (1H, d, $^3J = 13.18$ Hz), 4.77 (d, 1H, $^3J = 5.86$ Hz), 5.04 (s, 1H), 5.18 (s, 1H), 7.40 (s, 5H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 15.66 (CH_3), 39.95 (CH_2), 42.68 (CH), 73.02 (CH_2), 74.48 (CH_2), 114.64 (CH_2), 144.03 (C_0), 127.50 (CH), 128.28 (CH), 128.67 (CH), 138.70 (C_0). ^{119}Sn (CDCl_3 , 111.92 MHz) δ -186.87 (t, $^2J_{\text{Sn-H}} = 136$ Hz, $^4J_{\text{Sn-H}} = 78$ Hz).

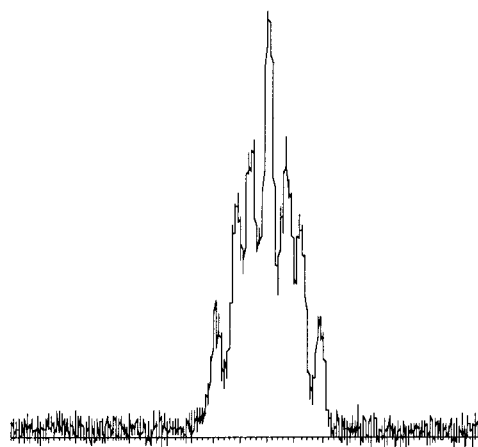
(13) The low-resolution observed for the ^1H NMR spectrum at -60 °C is due to the fact that this experiment has been done in a 10 mm NMR resonance tube.

Table 3. ^{119}Sn NMR Chemical Shift and Coupling Constants

^{119}Sn chemical shift (δ /ppm) ^a	Sn–H coupling constants (Hz)	
	Sn–H ₁ /H ₂	Sn–H ₃ /H ₄
-187	136	78

^a Relative to Me_4Sn (δ 0.00 ppm).

ing the ^{119}Sn spectrum in the absence of broadband ^1H decoupling, we observed the splitting of the signal into a triplet of triplets (broad signal) with $J_{\text{Sn-H}}$ of 136 and 78 Hz (Table 3).⁶ Figure 4 shows the ^{119}Sn NMR chemical shifts and coupling constants between H and Sn.¹²

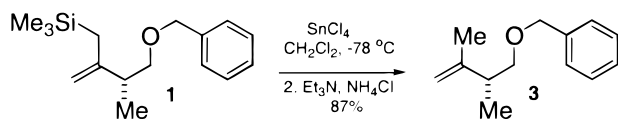
**Figure 4.** ^{119}Sn NMR data for complex **2**.

By comparison of the ^1H , ^{13}C , and ^{119}Sn NMR data with those reported in the literature, it was possible to identify the newly formed species. According to Naruta et al.,⁶ an allyltrichlorotin species characteristically has a chemical shift for H1 of 3.1–3.7 ppm and a coupling constant between H1 and Sn in the range of 104–122 Hz.

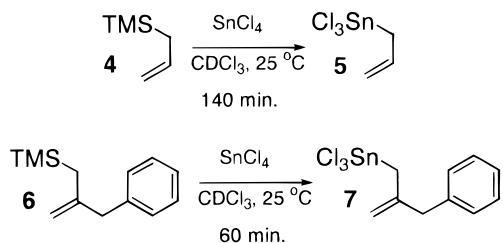
It is also interesting to observe that the chemical shift described for a tin attached to carbon in an allyltrichlorostannane is -28 ppm.⁶ In a very interesting experiment, Keck demonstrated a chemical shift of -571 ppm for a tin complexed with two aldehyde oxygens.³ In our experiment we observed a tin chemical shift of -187 ppm, which lies between that of an allyltrichlorotin intermediate and that complexed with two oxygen atoms. We believe that tin chemical shifts are highly sensitive to oxygen bonding, and this is an observation in favor of the complexed intermediate proposed.

In another very interesting experiment, addition of SnCl_4 to a solution of chiral allylsilane in CH_2Cl_2 at -78 °C, stirring for 5 min, and quenching with Et_3N , followed by saturated NH_4Cl , afforded alkene **3** in 87% yield (Scheme 2).¹ These results are nicely explained by a prior metathesis of allylsilane **1** with SnCl_4 .

Scheme 2



For purposes of comparison we have also carried out a series of NMR experiments using allyltrimethylsilane **4** and 1,1-dissubstituted allylsilane **6** and SnCl_4 (1.1 equiv at 0.15 M in CDCl_3) at room temperature (Scheme 3).¹⁴

Scheme 3. Metathesis of Allylsilanes **4** and **6**

For allyltrimethylsilane **4** the ligand exchange reaction is about 40% complete after 25 min, 75% complete after 80 min, and nearly complete after 140 min. For allylsilane **6**,

(14) Chemical shifts in ppm (multiplicity) for the olefinic hydrogens: allylsilane **4**, 4.73 (sl), 4.79 (d), 5.78 (m); allylstannane **5**, 5.33 (d), 5.40 (d), 5.97 (m); allylsilane **6**, 4.62 (s), 4.67 (s); allylstannane **7**, 5.15, 5.22.

the metathesis is faster, as expected for a 1,1-dissubstituted olefin, being 60% complete after 8 min and nearly complete after 60 min. Our observations were also that the metathesis reaction of allylsilanes **4** and **6** is concentration dependent, being faster at higher concentrations (0.5 M), in agreement with the results described earlier by Denmark and Wilson.⁷

We have observed the resonances for the methylenic hydrogens α to silicon in allylsilanes **4** and **6** as a doublet centered at δ 1.43 and as a singlet at δ 1.53 ppm, respectively. In allyltrichlorostannanes **5** and **7**, these hydrogens appear as a doublet at δ 3.22 and as a singlet at δ 3.08 ppm, respectively.¹⁴ We have also found a tin chemical shift of -27 ppm for allylstannanes **5** and **7**, in accordance with Naruta's observation.⁶

We described here that the transmetalation reaction of allylsilane **1** is nearly instantaneous at -60°C as well as at room temperature. It appears that the oxygen functionality is responsible for the rapid ligand exchange observed even at low temperatures for this particular allylsilane and SnCl_4 . The ligand exchange reaction is probably facilitated by coordination of tin to this oxygen followed by cleavage of the carbon–silicon bond by a free chloride ion. This complex was also found to be stable for more than 24 h at room temperature.

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