

## Chloromethylstannylenes

R. HANI and R. A. GEANANGEL\*

Department Of Chemistry, University of Houston, University Park, Houston, Tex. 77004, U.S.A.

Received April 17, 1984

### Abstract

Bis(dichloromethyl)stannylene was obtained as a solvate,  $(\text{CHCl}_2)_2\text{Sn}\cdot x\text{THF}$ , from the low-temperature reaction of  $\text{LiCHCl}_2$  with  $\text{SnCl}_2$ . The stannylene was characterized by its NMR, mass, and  $^{119}\text{Sn}$  Mossbauer spectra. The low velocity of its MB resonance demonstrated that the stannylene associates forming Sn-Sn-bonded oligomers upon removal of solvent. An attempt to synthesize  $(\text{CCl}_3)_2\text{Sn}$  was unsuccessful apparently owing to its instability at ambient temperature.

### Introduction

The chemical characteristics of organostannylenes,  $\text{R}_2\text{Sn}$ , differ markedly from those of inorganic tin(II) compounds. In order to study the influence of the substituents on such behavior, we have attempted to prepare chloromethylstannylenes. It was of interest to ascertain whether the inductive effect of halomethyl groups would modify the characteristics of stannylenes towards those of  $\text{SnX}_2$  (X = halogen) compounds.

### Experimental

Inert atmosphere ( $\text{N}_2$ ) and vacuum line techniques were used throughout.

#### Attempted Synthesis of $(\text{CCl}_3)_2\text{Sn}$

Preparation of  $(\text{CCl}_3)_2\text{Sn}$  was attempted through the reaction of  $(\text{CCl}_3)_2\text{Hg}$  [1] with  $\text{SnI}_2$  at  $25^\circ\text{C}$  in THF solution with reactant ratios from 1:1 to 2:1. In every case,  $\text{HgI}_2$ , identified by its X-ray powder diffraction pattern and mp, was a major product of the reaction. After removal of  $\text{HgI}_2$  (and any unreacted  $(\text{CCl}_3)_2\text{Hg}$ ) by extraction with ether, the solid residue from a 1:1 reaction exhibited an asymmetric doublet resonance in its  $^{119}\text{Sn}$  Mössbauer (MB) spectrum (IS = 3.87) and was

found to contain 42.1% Sn. This identifies the tin product as  $\text{SnICl}$ , (theory: 42.2% Sn; Lit. [2] IS = 3.76, QS =  $0.55\text{ mm s}^{-1}$ ).

#### Synthesis of $(\text{CHCl}_2)_2\text{Sn}$

Several reactions were carried out with 1:1 mixtures of  $(\text{CHCl}_2)_2\text{Hg}$  [3] and  $\text{SnX}_2$  (X = Cl, I) in tetrahydrofuran, acetone or benzene at room temperature and up to reflux. Examination of the residues after solvent removal revealed unchanged tin(II) halides by MB and the absence of mercury halides by X-ray powder diffraction.

In a modification of a literature method for the preparation of  $\text{LiCHCl}_2$  [4], about 50 ml of dry tetrahydrofuran was transferred into a reaction flask along with 1.4 ml (2.18 mmol) of dichloromethane. The solution was cooled with a Dry Ice-isopropanol bath and 9.9 ml of 1.6 M n-BuLi (15.8 mmol) in n-hexane were added *via* syringe over 25 minutes. The solution was then stirred for 30 minutes and a solution of 1.50 g (7.9 mmol)  $\text{SnCl}_2$  in 25 ml dry tetrahydrofuran was added over 30 minutes also using a syringe. The reaction mixture was stirred at  $-78^\circ\text{C}$  for 1.5 h then during warming to room temperature over 4 h.

The product was isolated as a pale yellow oil by chloroform extraction of the residue after removal of the tetrahydrofuran by vapor transfer. The solid residue was identified as a mixture of lithium chloride and a small amount of  $\text{SnCl}_2$  by its X-ray powder diffraction pattern and MB spectrum. Yields based on  $\text{LiCl}$  formed were in excess of 90%. The  $^1\text{H}$  NMR spectrum of the oil in acetone- $d_6$  contains a broad singlet,  $\delta$  6.0, and two multiplets centered at  $\delta$  1.85 and  $\delta$  3.75, characteristic of tetrahydrofuran. The singlet is assigned to  $\text{CHCl}_2\text{Sn}$  by comparison with the shift of  $\delta$  6.08 observed for  $(\text{CHCl}_2)_2\text{Hg}$  [5]. The area ratio between the singlet and multiplets varied from reaction to reaction. The  $^{13}\text{C}$  NMR spectrum of the product in  $\text{CDCl}_3$  (Fig. 1) shows singlets at  $\delta$  25.4 and 68.5 (ref. TMS), representing the carbons of THF, and a singlet at  $\delta$  69.3 assigned as  $\text{CHCl}_2\text{Sn}$ . In the proton coupled  $^{13}\text{C}$  spectrum the latter resonance appears as the expected doublet (J = 178 Hz) confirming the presence of a

\*Author to whom correspondence should be addressed.

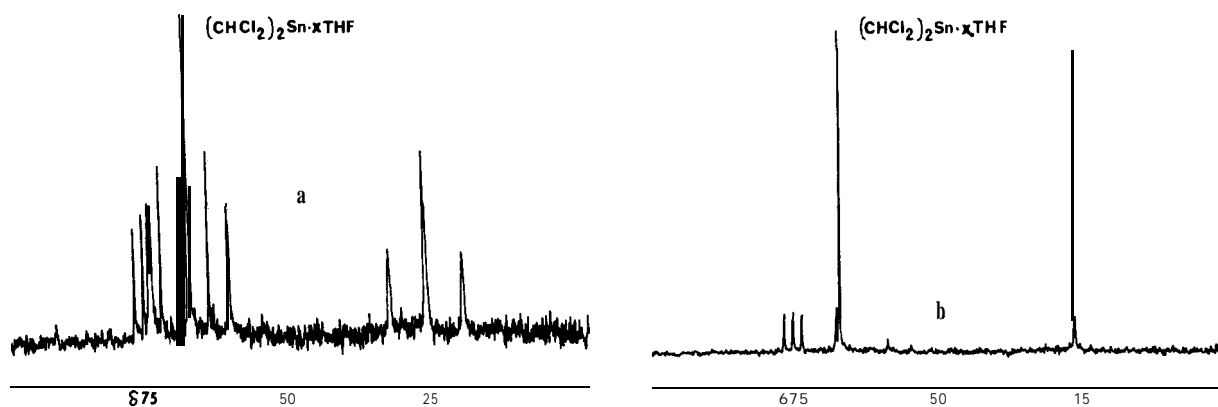


Fig. 1.  $^{13}\text{C}$  NMR Spectrum of  $(\text{CHCl}_2)_2\text{Sn}\cdot x\text{THF}$  in  $\text{CDCl}_3$ . a) Proton coupled. b) Proton decoupled.

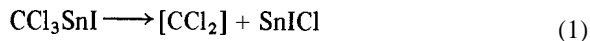
single proton on carbon. The  $^{119}\text{Sn}$  MB spectrum of the product as a frozen film at 77 K consists of a single broad resonance at 1.89 mm/sec (source  $\text{Ba-SnO}_3$ ).

#### Bromine Addition to $(\text{CHCl}_2)_2\text{Sn}\cdot x\text{THF}$

A sample of 5 mmol of freshly prepared  $(\text{CHCl}_2)_2\text{Sn}$  in the original THF reaction solution was cooled in an ice bath and treated dropwise with 5 mmol  $\text{Br}_2$ . The bromine decolorized immediately and the reaction mixture was stirred for 3 h at room temperature. The THF was removed by vacuum transfer overnight and the product was isolated as a yellow oil by extraction of the residue with benzene. The  $^1\text{H}$  NMR spectrum of the oil in  $\text{CDCl}_3$  consists of a singlet at  $\delta$  6.20. The assignment of the bromination product as  $(\text{CHCl}_2)_2\text{SnBr}_2$  was supported by its EI mass spectrum. As expected for a metal halide, no parent ion was detected but isotopic envelopes appeared in mass ranges indicative of the ions  $(\text{CHCl}_2)_2\text{SnBr}^+$ ,  $\text{CHCl}_2(\text{CHCl})\text{SnBr}^+$ ,  $\text{CHClSnBr}^+$ ,  $\text{CHCl}_2\text{Sn}^+$ ,  $\text{SnBr}^+$  and  $\text{CHCl}_2^+$  (100%). The distribution of fragments was consistent with that expected for the product as formulated.

#### Results and Discussion

The mercury reagent  $(\text{CCl}_3)_2\text{Hg}$  [1] exchanges  $\text{CCl}_3$  with  $\text{SnI}_2$  in THF eventually forming  $\text{HgI}_2$  and  $\text{SnICl}$ . These products suggest that  $\text{CCl}_3\text{SnI}$  is an intermediate in the reaction which decomposes through dichlorocarbene elimination (eqn. 1).

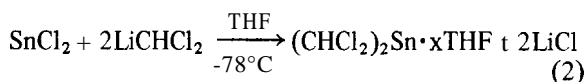


Metal- $\text{CCl}_3$  derivatives have not been widely studied; dichlorocarbene elimination occurs at low temperature in  $\text{LiCCl}_3$  [4] and even in a more stable derivative such as  $\text{C}_6\text{H}_5\text{HgCCl}_3$  upon gentle heating [6]. Thus, similar behavior by the desired tin compound is not entirely surprising.

TABLE I. Major Ions in the Negative-Ion LC-MS Spectrum of  $(\text{CHCl}_2)_2\text{Sn}\cdot x\text{THF}$ .

Relative %	Ion
100	$(\text{CHCl}_2)_2\text{SnCl}^-$
25	$\text{CHCl}_2\text{SnCl}_2^-$
25	$(\text{CHCl}_2)_3\text{Sn}\cdot\text{THF}^-$
15	$\text{SnCl}_3^-$

Assuming that  $\text{CHCl}_2$  substituents would be less susceptible to  $\text{CCl}_2$  elimination, attempts were made to prepare dichloromethylstannylene compounds. The mercurial,  $(\text{CHCl}_2)_2\text{Hg}$ , [3] proved unreactive towards  $\text{SnI}_2$  and  $\text{SnCl}_2$  so a more reactive  $\text{CHCl}_2$  reagent was found in  $\text{LiCHCl}_2$  [4] which combined readily with the latter even at low temperature (eqn. (2)). Attempts to remove the solvating THF by

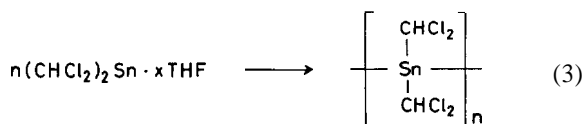


extraction with benzene, ether and pentane were unsuccessful and warming the oil under a dynamic vacuum only partially removed the THF up to about 57 °C where decomposition commenced. No effective method was found to either isolate a stoichiometric solvate or remove all the THF precluding characterization of the product by elemental analysis.

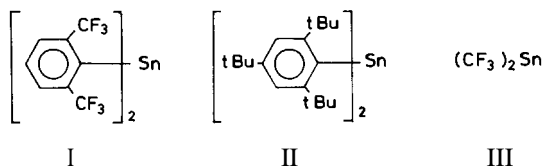
Nevertheless, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the oil are consistent with our formulation of the product. Additional support was obtained using a liquid chromatograph-mass spectrometer instrument employing the thermospray technique [7]. The thermospray method yields spectra similar to those produced by field desorption and related soft ionization techniques. The instrument accepts direct ( $\mu\text{l}$ ) solution injections which are vaporized in a heated nozzle leading to an ion source and conventional quadrupole mass analyzer. Table I lists the major

species seen in the negative ion spectrum of THF and  $\text{CHCl}_3$  solutions of the product. Typically, in the negative ion mode, one sees chemically derived anions (e.g.  $\text{SnCl}_3^-$ ) as opposed to anion radicals produced by simple electron attachment. For example, the most abundant ion produced,  $(\text{CHCl}_2)_2\text{SnCl}^-$ , probably forms when the neutral stannylene combines with chloride ion in the vaporization process where any free ions form coordinate clusters with available solution species [7]. The LCMS results confirm the formation of  $(\text{CHCl}_2)_2\text{Sn}$  while giving no indication of  $\text{Sn(IV)}$  species.

A substantive question concerning the product is whether it is a monomeric stannylene or some type of oligomer,  $(\text{R}_2\text{Sn})_n$ . The isomer shift of the oil after removal of noncoordinated THF was 1.89 mm/sec which is very near the I.S. range usually associated with oligomeric structures [8,9] suggesting that oligomerization (eqn. 3) occurs under these conditions. In this respect the product behaves



'normally' for an  $\text{R}_2\text{Sn}$  compound since the only other sigma-bonded organostannylenes which, according to their isomer shifts, do not form oligomeric structures are I, II and III. Positioning of bulky groups at the 2,6-positions of phenyl substituents,

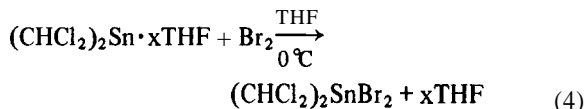


as in the case of I and II, renders stannylenes monomeric because of steric interactions.

It has been suggested that the inductive influence of the  $\text{CF}_3$  groups of III creates a partial positive charge on the tin preventing association through tin-tin bonds [10]. If so, the considerably smaller inductive effect of the  $\text{CHCl}_2$  group is apparently insufficient to prevent oligomerization when the solvent is removed from  $(\text{CHCl}_2)_2\text{Sn} \cdot x\text{THF}$ . Similar

behavior has been seen in this laboratory for  $(\text{CH}_2\text{I})_2\text{Sn} \cdot x\text{THF}$  [11].

Bromination of the stannylene proceeded smoothly, even at  $0^\circ\text{C}$ , as shown in eqn. (4). The brominated tin(IV) product was identified by its  $^1\text{H}$  NMR and mass spectra. The fact that the oxidative



addition of bromine occurs under such mild conditions may indicate that the product is monomeric before the solvent is removed from the original reaction mixture. Oligomeric stannylenes are much less reactive towards oxidative addition than monomeric stannylenes, usually requiring both elevated temperatures and extended reaction times for appreciable reaction to occur [12].

### Acknowledgement

The support of this investigation by the Robert A. Welch Foundation under grant E-439 is gratefully acknowledged. We are indebted to Professor Marvin Vestal for obtaining the reported LC-MS spectra.

### References

- 1 T. J. Logan, *J. Org. Chem.*, 28, 1129 (1963).
- 2 J. D. Donaldson and B. J. Senior, *J. Chem. Soc. A*, 2358 (1969).
- 3 G. Koebrich and H. Merkle, *Chem. Ber.*, 99, 1782 (1969).
- 4 G. Koebrich, K. Flory, H. R. Merkle and H. Trapp, *Angew. Chem. Int. Ed. Engl.*, 4, 28 (1965).
- 5 The  $^1\text{H}$  NMR spectrum of  $(\text{CHCl}_2)_2\text{Hg}$  in  $(\text{CH}_3)_2\text{SO}$  was obtained in this laboratory on a sample prepared according to the procedure given in ref. 3.
- 6 A. N. Nesmeyanov, R. K. H. Freidina and F. K. Velichko, *Doklady Akad. Nauk., SSSR*, 114, 551 (1957).
- 7 C. R. Blakley, J. J. Carmody and M. L. Vestal, *J. Am. Chem. Soc.*, 102, 5931 (1980).
- 8 J. J. Zuckerman, *Adv. Organomet. Chem.*, 9, 21 (1970).
- 9 M. P. Bigwood, P. J. Corvan and J. J. Zuckerman, *J. Am. Chem. Soc.*, 103, 7643 (1981).
- 10 R. Hani and R. A. Geanangel, *Polyhedron*, 1, 826 (1982).
- 11 R. Hani, *Dissertation*, University of Houston, 1983.
- 12 K. Sisido, T. Miyajima, K. Nabika and S. Kozima, *J. Organomet. Chem.*, 11, 28 (1968).