APPLIED ORGANOMETALLIC CHEMISTRY
*Appl. Organometal. Chem.* 2003; **17**: 298–304
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.443

# Transients from a mixture of $[(R(O)Sn)_2C(CH_3)_2]_2$ and $(RCl_2Sn)_2C(CH_3)_2$ [R = $(SiMe_3)_2CH$]: an identification *in situ* by 1D $^{119}$Sn and 2D $^{1}$H–$^{119}$Sn HMQC NMR spectroscopy and electrospray mass spectrometry

**Monique Biesemans[1], Andrew Duthie[2], Klaus Jurkschat[3]*, Ingrid Verbruggen[1], Rudolph Willem[1] and Bernhard Zobel[3]**

[1]High Resolution NMR Centre (HNMR), Free University Brussels (VUB), Pleinlaan 2, B-1050 Brussels, Belgium
[2]School of Biological and Chemical Sciences, Deakin University, Geelong 3217, Australia
[3]Lehrstuhl für Anorganische Chemie II, Universität Dortmund, D-44221 Dortmund, Germany

Received 2 December 2002; Revised 17 December 2002; Accepted 21 January 2003

**The reaction of the 2,2-bis(organodichlorostannyl)propane $[(Me_3Si)_2CH(Cl_2)Sn]_2CMe_2$ (A) with the corresponding organotin oxide $\{[(Me_3Si)_2CH(O)Sn]_2CMe_2\}_2$ (B) does not provide the corresponding normally expected tetraorganodistannoxane $\{[(Me_3Si)_2CH(Cl)SnCMe_2Sn(Cl)CH(SiMe_3)_2]O\}_n$ but a complex reaction mixture. One major product, namely the 2,4,6,8-tetraorgano-2,6-dichloro-1,5,9-trioxa-2,4,6,8-tetrastannabicyclo[3.3.1]nonane derivative $[(Me_3Si)_2CHSnCMe_2Sn(Cl)CH(SiMe_3)_2]_2O_3$ (C) was identified *in situ* by 2D $^{1}$H–$^{119}$Sn and $^{1}$H–$^{13}$C heteronuclear multiple quantum coherence and heteronuclear multiple bond correlation NMR spectroscopy as well as electrospray mass spectrometry. Compound C is proposed to be in equilibrium with an ionic species C′, the cation of which has an adamantane-type structure. Copyright © 2003 John Wiley & Sons, Ltd.**

**KEYWORDS:** organotin compounds; tetraorganodistannoxanes; NMR spectroscopy; electrospray mass spectrometry

## INTRODUCTION

Tetraorganodistannoxanes of the general formula $[R_2(X)SnOSn(Y)R_2]_2$ (R = alkyl, aryl; X, Y = halogen, OH, OR, $OSiMe_3$, OOCR, $OSP(OR)_2$, $NO_3$, $N_3$, NCS, SH, $OReO_3$) are among the most extensively studied class of organotin compounds.[1–59] The reason for the continuing interest in these compounds is their unique dimeric structure with ladder- or staircase-type structural motifs found in both the solid state and in solution,[4,18–20] and the catalytic activity in a variety of organic reactions.[60–80] The latter is thought to be either the result of the kinetic lability of tetraorganodistannoxanes in solution[45] or of the template effects of the dimeric tetraorganodistannoxane[65] and is still a subject of ongoing discussion. Consequently, any information on the identity of species being present in solutions of tetraorganodistannoxanes or related compounds is welcome. One convenient method for the synthesis of tetraorganodistannoxanes $[R_2(X)SnOSn(Y)R_2]_2$ (R = alkyl, aryl; X = halogen, carboxylate) is the reaction of equimolar amounts of the corresponding diorganotin oxide and diorganotin dihalide or dicarboxylate.[12,50] This method, among others, has also been applied to the synthesis of spacer-bridged tetraorganodistannoxanes of the general type $\{[R(Cl)Sn(CH_2)_nSn(Cl)R]O\}_m$ (R = alkyl, $n = 3$–$12$).[81–83] For less bulky substituents R, such as the $Me_3SiCH_2$ group, these compounds in the solid state exhibit the so-called double ladder structure ($m = 4$), whereas in solution equilibria involving dimers ($m = 2$) and tetramers ($m = 4$) are observed. For $\{[R(Cl)Sn(CH_2)_3Sn(Cl)R]O\}_m$ containing the bulky substituent R = $(Me_3Si)_2CH$, monomers ($m = 1$) were found in solution.[84]

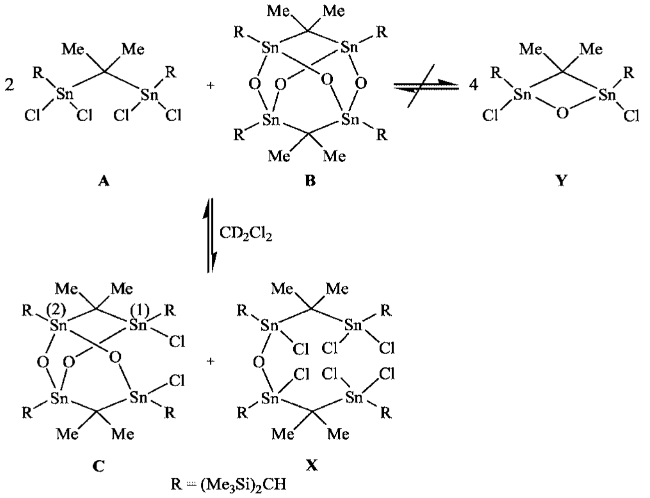
Recently, we have shown that, under appropriate reaction conditions, even methylene-bridged ditin compounds can give rise to the formation of tetraorganodistannoxanes of the type $\{[Ph(X)SnCH_2Sn(OH)Ph]O\}_4$ (X = Cl, Br, I) with a double ladder-type structure.[85]

By contrast, here we report that no product $\{[(Me_3Si)_2CH(Cl)SnCMe_2Sn(Cl)CH(SiMe_3)_2]O\}_n$ (**Y**) (Scheme 1) with $n = 1$, 2, 3, or 4 could be isolated from the reaction of the diorganotin

---

*Correspondence to: Klaus Jurkschat, Lehrstuhl für Anorganische Chemie II, Universität Dortmund, D-44221 Dortmund, Germany.
E-mail: kjur@platon.chemie.uni-dortmund.de

Copyright © 2003 John Wiley & Sons, Ltd.



Scheme 1.

dichloride derivative $\{[(Me_3Si)_2CH(Cl_2)Sn]_2CMe\}_2$ (**A**) with the corresponding molecular diorganotin oxide $\{[(Me_3Si)_2CH\text{-}(O)Sn]_2CMe_2\}_2$ (**B**).[84] This somewhat unexpected result was obtained regardless of the molar ratio of the reactants **A** and **B**, which ranged from 1:2 to 5:1. The $^{119}$Sn NMR spectrum of the crude reaction mixture (Fig. 1) also indicated (i) that a reaction indeed took place and (ii) that this reaction gave a complex product distribution. By application of gradient-enhanced (ge) $^{1}$H–$^{119}$Sn correlation NMR spectroscopy[86–89] and by electrospray mass spectrometry we present here a complete characterization *in situ* of the major product **C** in dichloromethane-$d_2$ solution, as obtained at room temperature from simply mixing compounds **A** and **B** in the molar ratio 2:1 (Scheme 1).

## RESULTS AND DISCUSSION

### Room-temperature NMR data

The $^{119}$Sn spectrum (Fig. 1a) at 303 K displays four major resonances **A**, **B**, **C1**, and **C2**, together with two minor resonances **E1** and **E2**. The resonances **A**, **B**, and **C1** clearly show $^{2}J(^{119}\text{Sn–X–}^{117/119}\text{Sn})$ coupling satellites, the intensity and magnitude of which provide information about the environment and configuration of the tin atoms.

The resonance at $\delta$ 78.6 (integral 40%), with $^{2}J(^{119}\text{Sn–CMe}_2\text{–}^{117}\text{Sn})$ coupling satellites having a relative intensity of about 8% (corresponding to the natural abundance of $^{117}$Sn) and a splitting of 572 Hz is assigned to the tin atoms of the diorganotin dichloride **A**.[84] The latter shows in $CD_2Cl_2$ a $\delta^{119}$Sn of 78.1 ($^{2}J(^{119}\text{Sn–CMe}_2\text{–}^{117}\text{Sn}) =$ 573 Hz). The resonance at $\delta$ 24.1 (integral 26%), with a $^{2}J(^{119}\text{Sn–CMe}_2\text{–}^{117}\text{Sn})$ of 741 Hz, a $^{2}J(^{119}\text{Sn–O–}^{117}\text{Sn})$ of 392 Hz, and relative intensities of *ca* 8% and 14% respectively, are assigned to the diorganotin oxide **B**[84] having an adamantane-type structure. The resonances **C1** and **C2** at $\delta$ 44.4 and at *ca* $\delta$ 5 respectively (each integral 16%), are assigned to the two tin atoms of compound **C** (Scheme 1), and arguments to support this assignment are given in the subsequent discussion.

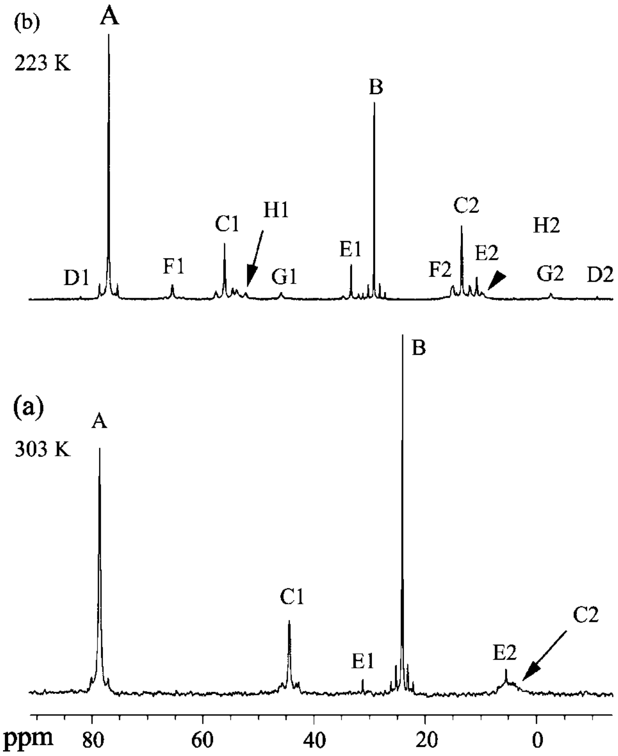


**Figure 1.** Proton decoupled $^{119}$Sn NMR spectra of a mixture of compounds **A** and **B** in the molar ratio 2:1 in $CD_2Cl_2$ at (a) 303 K and (b) at 223 K. The resonances arising from the major species **C** generated in the equilibrium mixture are labeled **C1** and **C2**. The other labels correspond to resonances of minor species from which the $^{119}$Sn resonances decoalesce upon temperature decrease, except for the pair **E1** and **E2**, which are observed at both 223 and 303 K and do not participate to the coalescence. The $^{119}$Sn resonances of the minor species **D**, **F**, **G** and **H** appear in pairs, as determined from detailed analysis of the $^{1}$H–$^{119}$Sn HMQC spectra, and have identical letters but different numbers.

The sharp resonance **C1** displays two pairs of coupling satellites of equal intensity (both 16%) with magnitudes of 621 and 444 Hz. The equal intensity of the coupling satellites suggests that resonance **C1** is to be assigned to tin atom Sn(1) of **C** having four possible coupling pathways: $^{2}J(^{119}\text{Sn(1)–C–}^{119\,\text{and}\,117}\text{Sn(2)})$ and $^{2}J(^{119}\text{Sn(1)–O–}^{119\,\text{and}\,117}\text{Sn(2)})$. The tin atom Sn(2) should have one extra coupling pathway, i.e. $^{2}J(^{119}\text{Sn(2)–O–}^{117}\text{Sn(2)})$, the coupling between the two symmetry equivalent Sn(2) tin atoms.

No attempt is made at this stage to obtain more information about the origin of the two minor $^{119}$Sn resonances at $\delta$ 31.5 (**E1**) and $\delta$ 5.5 (**E2**) (total integral 2%).

Copyright © 2003 John Wiley & Sons, Ltd.

The $^1$H resonances of the major species **A** and **B** were assigned with the aid of 2D ge-$^1$H–$^{119}$Sn heteronuclear multiple quantum coherence (HMQC) spectra[86–89] and are summarized in Table 1. For compound **C**, only $^1$H resonances associated with the sharp $^{119}$Sn resonance **C1** at 44.4 ppm could be assigned from the correlation spectrum, as possible correlations with the broad $^{119}$Sn resonance **C2** had already faded within the applied evolution delays (60 and 100 ms). The $^1$H resonances correlated with the broad $^{119}$Sn resonance **C2** were assigned to the remaining resonances in the 1D $^1$H spectrum.

The $^{2,3}J(^1\mathrm{H}-^{119/117}\mathrm{Sn})$ coupling constants were determined from the 1D $^1$H spectrum and cross-checked using the 2D $^1$H–$^{119}$Sn HMQC spectrum. The methyl groups bound to the carbon atom bridging the two tin atoms are diastereotopic with slightly different chemical shifts, but with significantly different $^3J(^1\mathrm{H}-^{119/117}\mathrm{Sn})$ coupling constants. Their characteristics are also dependent on the nature of the tin atom, since those associated with the sharp $^{119}$Sn resonance **C1** are larger for both methyl groups than those associated with the broad $^{119}$Sn resonance **C2**.

When comparing the values of the $^{2,3}J(^1\mathrm{H}-^{119/117}\mathrm{Sn})$ coupling constants of compound **C** with those of the diorganotin dichloride **A** and the diorganotin oxide **B**, it is noticed that the sharp $^{119}$Sn resonance **C1** has coupling constants close to those of compound **A**. Also, its chemical shift is intermediate between those of compounds **A** and **B**, whereas the broad $^{119}$Sn resonance **C2** appears in the $^{119}$Sn chemical shift area of compound **B**. Both observations are in line with the above proposal that the $^{119}$Sn resonance **C1** has to be assigned to the tin atom Sn(1), and that the $^{119}$Sn resonance **C2** then necessarily corresponds to the tin atom Sn(2) of **C**.

In order to assign all $^{13}$C resonances unequivocally 2D $^1$H–$^{13}$C HMQC[90] and heteronuclear multiple bond correlation (HMBC)[91] spectra were recorded. Starting from the $^1$H chemical shifts determined above for each compound, the corresponding $^{13}$C resonances were straightforwardly assigned. The $^{13}$C chemical shifts and $^nJ(^{13}\mathrm{C}-^{119/117}\mathrm{Sn})$ coupling constants are summarized in Table 2.

## Low-temperature NMR data

Upon lowering the temperature to 223 K, the broad $^{119}$Sn resonance **C2** observed at 303 K sharpens and, simultaneously, several minor $^{119}$Sn resonances appear (Fig. 1b). Apart from the $^{119}$Sn resonances of the diorganotin dichloride **A** (integral 33%) and the diorganotin oxide **B** (integral 11%), two major equally intense and relatively sharp resonances are observed at 55.8 (signal **C1**) and 13.1 ppm (signal **C2**), and are tentatively assigned to product **C** (total integral 22%).

**Table 1.** $^1$H NMR data of the reaction mixture at 303 K[a]

| | | | **C** | |
|---|---|---|---|---|
| | **A** | **B** | Sn(1) | Sn(2) |
| Si(C$H_3$)$_3$ | 0.28 | 0.20 | 0.25 | 0.26 |
| | | | 0.22 | 0.23 |
| SiC$H$ | 1.05 [95/91] | 0.09 [93/89] | 0.38 [91/88] | 0.45 [112/107] |
| (C$H_3$)$_2$C | 2.00 [134/129] | 1.70 [112/107] | 1.80 [141/134] | 1.80 [98/94] |
| | | | 1.78 [125/120] | 1.78 [118/112] |

[a] $^{2,3}J(^1\mathrm{H}-^{119/117}\mathrm{Sn})$ coupling constants, as determined from the 1D $^1$H spectrum, in brackets. The assignments were achieved from 2D ge-$^1$H–$^{119}$Sn HMQC spectra recorded at two evolution delays, 60 and 100 ms.

**Table 2.** $^{13}$C NMR data of the reaction mixture at 303 K

| | | | **C** | |
|---|---|---|---|---|
| | **A** | **B** | Sn(1) | Sn(2) |
| Si(CH$_3$)$_3$ | 3.3 | 3.8 | 3.5–3.7 | |
| SiCH | 21.9 [160/152,[a] 34[b]] | 9.8 [208/198,[a] 38[b]] | 12.2 [176,[a,c] 36[b]] | 12.8 (broad) |
| (CH$_3$)$_2$C | 25.3[21[d]] | 25.3[21[d]] | 25.3[21[d]] | |
| | | | 28.8[25[d]] | |
| (CH$_3$)$_2$C | 60.6[430/411[a]] | 47.8[436/414[a]] | 48.4 | |

$^nJ(^{13}\mathrm{C}-^{119/117}\mathrm{Sn})$ coupling constants as derived from the 1D $^{13}$C spectrum in brackets.

[a] $^1J(^{13}\mathrm{C}-^{119/117}\mathrm{Sn})$.

[b] $^1J(^{13}\mathrm{C}-^{29}\mathrm{Si})$.

[c] Approximate value (noise and overlap).

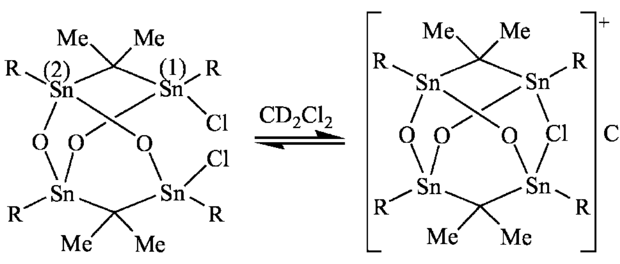
[d] $^2J(^{13}\mathrm{C}-^{119/117}\mathrm{Sn})$, unresolved.

Evidence for the proposed structure of **C** arises from the relative areas of the $^{2}J(^{119}\text{Sn–X–}^{117/119}\text{Sn})$ (X = CH$_2$, O) coupling satellites of its $^{119}$Sn resonances, as determined by line shape analysis of the spectra using the PERCH software.[92] The $^{119}$Sn resonance **C1**, assigned to Sn(1), has one broad pair of such satellites with a total area of about 30% and coupling constant of 548 Hz, a value that lies between the 621 and 444 Hz observed at 303 K. The $^{119}$Sn resonance **C2**, assigned to Sn(2), has two overlapping pairs of coupling satellites (570 and 524 Hz) with a total area of 28% and an additional one (344 Hz) with an area of 5%. The latter coupling is assigned to the $^{2}J(^{119}\text{Sn(2)–O–}^{117}\text{Sn(2}'))$ coupling pathway.

From $^{1}$H–$^{119}$Sn correlation experiments at 223 K (evolution delays of 3.6, 25, 62 and 100 ms), it was demonstrated that the $^{119}$Sn resonances **C1** at 55.8 ppm and **C2** at 13.1 ppm indeed belong to the same product, since they show both $^{1}$H–$^{119}$Sn HMQC correlation peaks with the same (C$H_3$)$_2$C proton resonances. Table 3 presents the assignments of the $^{1}$H and $^{119}$Sn resonance pairs of the major species **A**, **B** and **C** as obtained from the $^{1}$H–$^{119}$Sn HMQC correlation data at 223 K. The $^{2,3}J(^{1}\text{H–}^{119}\text{Sn})$ coupling constants mentioned here are obtained from 1D $^{1}$H slices at the resonance frequencies of the corresponding $^{119}$Sn resonances in the 2D $^{1}$H–$^{119}$Sn HMQC spectrum. Some slight variations in the coupling constants, especially for Sn(2), are observed when compared with the values at 303 K. These, and the NMR data of Tables 1–3, unambiguously identify the species **C** as one product of the reaction of **A** and **B**, and its structure as given in Scheme 1 can be considered as formally established.

The NMR-based identity of species **C** is further supported by electrospray mass spectrometry. Thus, the positive-ion electrospray mass spectrum of a solution of two mole equivalents of **A** and one mole equivalent of **B** exhibits, in addition to isotopic cluster patterns centered at $m/z$ 685, $m/z$ 705, and $m/z$ 1261 and assigned to $[\mathbf{A} - 2\text{Cl} + \text{OH}]^+$, $[\mathbf{A} - \text{Cl}]^+$, and $[\mathbf{B} + \text{H}]^+$ respectively, an isotopic cluster pattern at $m/z$ 1315 that corresponds to $[\mathbf{C} + \text{H}]^+$. Furthermore, the electrospray mass spectrum shows an isotopic cluster pattern centered at $m/z$ 1279, which, according to a characteristic Sn$_4$Cl isotopic profile, is assigned to the cation of species **C**′ being in equilibrium with **C** (Scheme 2).

In fact, the existence of such an equilibrium is in agreement with the observation of the $^{119}$Sn **C1** resonance shifting to higher frequency at low temperature (Fig. 1) because of the lower shielding at the $^{119}$Sn(1) nuclei associated with chlorine-bridge formation, as well as with the change of the corresponding satellites. Furthermore, the easy formation of **C**′ with the adamantane-type structured cation expected to be rather stable might be one reason why the reaction according to Scheme 1 does not go to completion under formation of compound **Y** or its oligomers. The abstraction of an oxygen



**C** R = (Me$_3$Si)$_2$CH **C′**

**Scheme 2.**

**Table 3.** $^{119}$Sn (303 and 223 K) and $^{1}$H (223 K) NMR data of the major species **A**, **B** and **C** of the reaction mixture

| | | | **C** | |
|---|---|---|---|---|
| | **A** | **B** | Sn(1) | Sn(2) |
| $^{119}$Sn (303 K) | 78.6 (572) | 24.1 (741, 392) | 44.4 (621, 444) | 5$^a$ |
| $^{119}$Sn (223 K) | 76.6 (609) | 28.9 (730, 381) | 55.8 (548) | 13.1 (570, 524, 344) |
| $^{1}$H | | | | |
| Si(C$H_3$)$_3$ | 0.19 | 0.12 | 0.12 | 0.14 |
| SiC$H$ | 1.02 [92] | 0.02 [91] | 0.30 [83] | 0.23 [99] |
| (C$H_3$)$_2$C | 1.93 [136] | 1.60 [113] | 1.67 [143]<br>1.65 [123] | 1.67 [103]<br>1.65 [112] |
| $^{13}$C | | | | |
| Si(CH$_3$)$_3$ | 2.4 | 2.9 | | |
| SiCH | 20.6 | 7.8 | 8.3/10.5 | |
| (CH$_3$)$_2$C$^b$ | 24.7 | 24.7 | 24.7 | |
| (CH$_3$)$_2$C | 61.8 | 46.3 | 45.8$^c$ | |

$^{2}J(^{119}\text{Sn–X–}^{119/117}\text{Sn})$ coupling constants in parentheses; $^{2,3}J(^{1}\text{H–}^{119}\text{Sn})$ coupling constants, as determined from $^{1}$H–$^{119}$Sn HMQC spectra, in brackets.

[a] Broad signal.

[b] Overlapping signals between $\delta$ 24 and $\delta$ 25 with maximum at $\delta$ 24.7.

[c] Broad.

Copyright © 2003 John Wiley & Sons, Ltd.

by the diorganotin dichloride **A** from the positively charged cation in **C**′ is presumably less favored.

The generation of compound **C**/**C**′ in the equilibrium mixture shown in Scheme 1 necessarily requires the presence of a further species in an equal molar amount. Compound **X** (Scheme 1) is likely to be this species, firstly because it completes appropriately the stoichiometry of the reaction by which **C** is generated from **A** and **B**, and secondly it is supported by observation in the electrospray mass spectrum mentioned above of an isotopic cluster pattern at $m/z$ 1445 that fits for $[\mathbf{X} + H_3O]^+$.

The 2D $^1H-^{119}Sn$ HMQC correlation data at low temperature, unfortunately, do not fit directly into this proposal, since no resonances can be assigned unambiguously to species **X**. Instead, the 2D $^1H-^{119}Sn$ HMQC spectrum (evolution delay 3.6 ms) shows numerous minor resonances that can be assigned likewise in pairs, since they also show HMQC correlation peaks with common $(CH_3)_2C$ proton resonances. This indicates that these additional species have two types of symmetry non-equivalent tin atom, as have species **C** and **X**. A partial assignment of the $^{119}Sn$ and $^1H$ resonances of these pairs is given in Table 4.

The pairs of resonances **D1**/**D2** (initially 1% integration area but increasing to 5% after several months) and **E1**/**E2** (*ca* 6%) do not arise from species equilibrating with **A**, **B**, and **C**, since these resonances are sharp at both room and low temperatures (Fig. 1). Accordingly, they were not analyzed further.

The other pairs of $^{119}Sn$ resonances, **F1**/**F2**, **G1**/**G2**, and **H1**/**H2**, with integrals ranging from 2% to no more than 6%, appear only upon lowering the temperature, suggesting that they are involved in some decoalescense processes paralleling the simultaneous **C2** signal sharpening. A partial assignment of the $^{13}C$ resonances of these minor species could be achieved at 223 K (see Table 5).

**Table 4.** $^{119}Sn$ (203 K) and $^1H$ (223 K) NMR data from minor species of the reaction mixture

| | $^{119}Sn$ $[^2J(^{119}Sn-^{117/119}Sn)]$ | $^1H$ $[^{2,3}J(^1H-^{119}Sn)]$ | |
|---|---|---|---|
| | | SiC*H* | (C$H_3$)$_2$C |
| **D1** | 80.6 [572] | 0.97 [87] | 1.82 [151] and 1.88 [132] |
| **D2** | −14.0 [578] | 0.64 [97] | 1.82 [109] and 1.88 [130] |
| **E1** | 33.0 [502] | 0.41 [86] | 1.75 [124] and 1.84 [146] |
| **E2** | 10.8 [456] | 0.30 [94] | 1.75 [120] and 1.84 [127] |
| **F1** | 66.7 [739, 446] | 0.33 [90] | 1.62 [121] |
| **F2** | 14.8 | 0.25 [100] | 1.62 [113] |
| **G1** | 46.4 [554] | 0.30 [85] | 1.72 [137] |
| **G2** | −2.6 [606, 380] | —[a] | 1.72 [104] |
| **H1** | 53.3 [598, 436] | 0.31 [85] | 1.67 [137] |
| **H2** | 8.8 [572] | 0.22 [103] | 1.67 [103] |

[a] Not found.

**Table 5.** $^{13}C$ NMR data of the reaction mixture at 223 K

| | **D** | **E** | **F** | **G** | **H** |
|---|---|---|---|---|---|
| $Si(CH_3)_3$ | | | | | |
| SiCH | 20.2/14.9 | | | | |
| $(CH_3)_2C$ | 24.7 | 24.7 | 24.7 | 24.7 | |
| $(CH_3)_2C$ | 56.8 | —[a] | 44.7 | 48.5 | —[a] |

[a] Not observed.

Since the intensity of the resonances of these minor species is very low, no other data, apart from their pairwise assignment, could be obtained for them; so, proposing detailed structures is meaningless. Nevertheless, it is important to outline the fact that the minor signals display altogether a total integral that accounts for the mass balance in the formation of species **C** and **X** from the reactants **A** and **B**. Therefore, a general picture of the reaction occurring between **A** and **B** emerges. Thus, it clearly appears that equilibria between Sn–Cl and Sn–O–Sn bonds can occur, on a time scale that varies from moderately fast (decoalescences and broad resonances for species **C** and most of the minor ones) to slow, the $^{119}Sn$ resonances of **A** and **B** remaining sharp over the whole temperature range investigated. Unfortunately, the link between the minor resonance pairs **F1**/**F2**, **G1**/**G2**, and/or **H1**/**H2**, on the one hand, and the structure of the logically expected species **X**, on the other hand, is impossible to establish. Given the two stereogenic centers in compound **X**, where *meso/dl* isomerism is possible, and the fact that the bulky $(Me_3Si)_2CH$ substituents increase the barrier for a possible epimerization, none of the $^1H$, $^{13}C$ and $^{119}Sn$ NMR data at hand for the minor species is actually incompatible with the existence of **X**. Alternatively, the minor resonances could arise simply from the decomposition of the possibly unstable species **X**.

## CONCLUSION

Two main goals have been achieved in this paper. Firstly, despite the reaction of the spacer-bridged ditin compound $(RCl_2Sn)_2C(CH_3)_2$, with its corresponding oxide, $[(R(O)Sn)_2C(CH_3)_2]_2$, not giving rise to isolable reaction products, the main reaction product was identified *in situ* in dichloromethane solution to be a four-tin-containing species with two chlorine atoms and three oxygen bridges. It is a product deviating from the normally occurring pathways, most probably as a consequence of the steric constraints resulting from both the $(Me_3Si)_2CH$ and $CMe_2$ groups. Secondly, it is demonstrated that, even in the absence of isolated substances and crystal structures, the combined use of various gradient-enhanced 2D NMR techniques (focusing mainly on $^1H-^{119}Sn$ HMQC spectroscopy) and of electrospray mass spectrometry enables one to identify reaction transients or unstable compounds in solution in organotin chemistry.

Copyright © 2003 John Wiley & Sons, Ltd.

# EXPERIMENTAL

## NMR experiments

The compounds **A** and **B** were synthesized as described previously.[84] The reaction mixture was prepared by dissolving 58.7 mg (0.0793 mmol) of **A** and 50.0 mg (0.0397 mmol) of **B** directly into the NMR tube in dry $CD_2Cl_2$ from a freshly opened ampoule and subsequently sealed. The spectra were recorded at 303 and 223 K on a Bruker AMX500 instrument, equipped with a BSMS digital lock and a BGU II gradient unit. The spectra were acquired inverse gated with 45° pulses, acquisition time 0.39 s, relaxation delay 0.50 s. Operating frequencies were 500.13 MHz, 125.75 MHz and 186.50 MHz for the $^1H$, $^{13}C$ and $^{119}Sn$ nuclei respectively. Chemical shifts $\delta$ (ppm) are referenced to the residual solvent peak and converted to the tetramethylsilane scale by adding 5.32 ppm and 53.8 ppm for $^1H$ and $^{13}C$ respectively. For $^{119}Sn$, external referencing was used with $\Xi = 37.290\,665$ MHz.[93,94] 2D ge-$^1H-^{119}Sn$ HMQC experiments were performed as previously described.[86–89] Standard 1D and 2D ge-$^1H-^{13}C$ HMQC[90] and HMBC[91] spectra were recorded using standard pulse programs from the Bruker library.

The relative integrated areas of the $^{119}Sn$ resonances and coupling satellites were determined using the deconvolution program PERCH-TLS.[92] The main advantage of this computational strategy is that it can include external information, i.e. doublet patterns for satellites, which greatly improves the statistics of the fitting procedure.

## Electrospray mass spectrometry

Electrospray mass spectra were obtained with a Platform II single quadrupole mass spectrometer (Micromass, Altrincham, UK) using an acetonitrile mobile phase. Acetonitrile solutions (1 mM) of the compounds were injected directly into the spectrometer via a Rheodyne injector equipped with a 50 μl loop. A Harvard 22 syringe pump delivered the solutions to the vaporization nozzle of the electrospray ion source at a flow rate of 10 μl $min^{-1}$. Nitrogen was used as both a drying gas and for nebulization, with flow rates of approximately 200 ml $min^{-1}$ and 20 ml $min^{-1}$ respectively. Pressure in the mass analyzer region was usually about $4 \times 10^{-5}$ Torr. Typically, ten signal-averaged spectra were collected.

## Acknowledgements

MB, IV and RW are indebted to the Fund for Scientific Research Flanders (Belgium, grants no. G0192.98 and G0016.02) and to the Research Council of the 'Vrije Universiteit Brussel' for their financial support. KJ and BZ acknowledge the Deutsche Forschungsgemeinschaft and AD thanks the Australian Research Council for financial support.

# REFERENCES

1. Okawara R, White DG, Fujitani K, Sato H. *J. Am. Chem. Soc.* 1961; **83**: 1342.
2. Okawara R. *Angew. Chem.* 1961; **73**: 683.
3. Okawara R. *Proc. Chem. Soc. London* 1961; 383.
4. Okawara R, Wada M. *J. Organometal. Chem.* 1963; **1**: 81.
5. Alleston DL, Davies AG, Hancock M, White RFM. *J. Chem. Soc.* 1963; 5469.
6. Alleston DL, Davies AG, Hancock M. *J. Chem. Soc.* 1964; 5744.
7. Considine WJ, Baum GA, Jones RC. *J. Organometal. Chem.* 1965; **3**: 308.
8. Yasuda K, Matsumoto H, Okawara R. *J. Organometal. Chem.* 1966; **6**: 528.
9. Wada M, Okawara R. *J. Organometal. Chem.* 1967; **8**: 261.
10. Maeda Y, Okawara R. *J. Organometal. Chem.* 1967; **10**: 247.
11. Davies AG, Harrison PG. *J. Chem. Soc. (C)* 1970; 2036.
12. Davies AG, Harrison PG, Palan PR. *J. Chem. Soc. (C)* 1970; 2030.
13. Davies AG, Smith L, Smith PJ, McFarlane W. *J. Organometal. Chem.* 1971; **29**: 245.
14. Chu CK, Murray JD. *J. Chem. Soc. (A)* 1971; 360.
15. Chow YM. *Inorg. Chem.* 1971; **10**: 673.
16. Matsuda H, Mori F, Kashiwa A, Matsuda S, Kasai N, Jitsumori K. *J. Organometal. Chem.* 1972; **34**: 341.
17. Graziani R, Bombieri G, Forsellini E, Furlan P, Peruzzo V, Tagliavini G. *J. Organometal. Chem.* 1977; **125**: 43.
18. Harrison PG, Begley MJ, Molloy KC. *J. Organometal. Chem.* 1980; **186**: 213.
19. Puff H, Friedrichs E, Visel F. *Z. Anorg. Allg. Chem.* 1981; **477**: 50.
20. Puff H, Bung I, Friedrichs E, Jansen A. *J. Organometal. Chem.* 1983; **4**: 23.
21. Graziani R, Casellato U, Plazzogna G. *Acta Crystallogr. Sect. C* 1983; **39**: 1188.
22. Vollano JF, Day RO, Holmes RR. *Organometallics* 1984; **3**: 745.
23. Dakternieks D, Gable RW, Hoskins BF. *Inorg. Chim. Acta* 1984; **85**: L43.
24. Otera J, Yano T, Nakashima K, Okawara R. *Chem. Lett.* 1984; 2109.
25. Yano T, Nakashima K, Otera J, Okawara R. *Organometallics* 1985; **4**: 1591.
26. Lockhart TP, Manders WF, Holt EM. *J. Am. Chem. Soc.* 1986; **108**: 6611.
27. Narula SP, Bharadwaj SK, Sharma HK, Mairesse G, Barbier P, Nowogrocki G. *J. Chem. Soc. Dalton Trans.* 1988; 1719.
28. Gross DC. *Inorg. Chem.* 1989; **28**: 2355.
29. Parulekar CS, Jain VK, Das TK, Gupta AR, Hoskins BF, Tiekink ERT. *J. Organometal. Chem.* 1989; **372**: 193.
30. Tiekink ERT. *Acta Crystallogr. Sect. C* 1991; **47**: 661.
31. Vatsa C, Jain VK, Kesavadas T, Tiekink ERT. *J. Organometal. Chem.* 1991; **408**: 157.
32. Vatsa C, Jain VK, Das TK. *J. Organometal. Chem.* 1991; **418**: 329.
33. Tiekink ERT. *Appl. Organometal. Chem.* 1991; **5**: 1.
34. Jain VK, Mokal VB, Sandor P. *Magn. Reson. Chem.* 1992; **30**: 1158.
35. Flöck OR, Dräger M. *Organometallics* 1993; **12**: 4623.
36. Schoop T, Roesky HW, Noltemeyer M, Schmidt H-G. *Organometallics* 1993; **12**: 571.
37. Kresinski RA, Staples RJ, Fackler JP. *Acta Crystallogr. Sect. C* 1994; **50**: 40.
38. Mokal VB, Jain VK, Tiekink ERT. *J. Organometal. Chem.* 1994; **471**: 53.
39. Cox MJ, Tiekink ERT. *Z. Kristallogr.* 1994; **209**: 622.
40. Bonetti J, Gondard C, Pétiaud R, Llauro M-F, Michel A. *J. Organometal. Chem.* 1994; **481**: 7.
41. Tiekink ERT, Gielen M, Bouhdid A, Biesemans M, Willem R. *J. Organometal. Chem.* 1995; **494**: 247.
42. Gielen M, Bouhdid A, Willem R, Bregadze VI, Ermanson LV, Tiekink ERT. *J. Organometal. Chem.* 1995; **501**: 277.
43. Ng SW, Kumar Das VG. *Acta Crystallogr. Sect. C* 1995; **51**: 1774.
44. Narula SP, Kaur S, Shankar R, Bharadwaj SK, Chadha RK. *J. Organometal. Chem.* 1996; **506**: 181.
45. Houghton RP, Mulvaney AW. *J. Organometal. Chem.* 1996; **517**: 107.

Copyright © 2003 John Wiley & Sons, Ltd.

46. Teoh S-G, Looi E-S, Teo S-B, Ng SW. *J. Organometal. Chem.* 1996; **509**: 57.
47. Yu ZK, Wang SH, Yan SG. *Heteroatom Chem.* 1996; **7**: 3.
48. Danish M, Ali S, Mazhar M. *Heteroatom Chem.* 1996; **7**: 233.
49. Lacroix C, Bousmina M, Carreau PJ, Llauro MF, Pétiaud R, Michel A. *Polymer* 1996; **37**: 2949.
50. Dakternieks D, Jurkschat K, van Dreumel S, Tiekink ERT. *Inorg. Chem.* 1997; **36**: 2023.
51. Blair JA, Howie A, Wardell JL, Cox PJ. *Polyhedron* 1997; **16**: 881.
52. Ribot F, Sanchez C, Meddour A, Gielen M, Tiekink ERT, Biesemans M, Willem R. *J. Organometal. Chem.* 1998; **552**: 177.
53. Suciu EN, Kuhlmann B, Knudsen GA, Michaelson RC. *J. Organometal. Chem.* 1998; **556**: 41.
54. Primel O, Llauro M-F, Pétiaud R, Michel A. *J. Organometal. Chem.* 1998; **558**: 19.
55. Beckmann J, Biesemans M, Hassler K, Jurkschat K, Martins JC, Schürmann M, Willem R. *Inorg. Chem.* 1998; **37**: 4891.
56. Gimenez J, Michel A, Pétiaud R, Llauro M-F. *J. Organometal. Chem.* 1999; **575**: 286.
57. Jain VK, Mokal VB, Satyanarayana CVV. *Indian J. Chem. A* 1999; **38**: 249.
58. Beckmann J, Jurkschat K, Kaltenbrunner U, Rabe S, Schürmann M, Dakternieks D, Duthie A, Müller D. *Organometallics* 2000; **19**: 4887.
59. Beckmann J, Jurkschat K, Rabe S, Schürmann M, Dakternieks D. *Z. Anorg. Allg. Chem.* 2001; **627**: 458.
60. Van der Weij FW. *J. Polym. Sci.* 1981; **19**: 3063.
61. Otera J, Yano T, Kawabata A, Nozaki H. *Tetrahedron Lett.* 1986; **27**: 2383.
62. Otera J, Yano T, Himeno Y, Nozaki H. *Tetrahedron Lett.* 1986; **27**: 4501.
63. Otera J, Nozaki H. *Tetrahedron Lett.* 1986; **27**: 5743.
64. Otera J, Ioka S, Nozaki H. *J. Org. Chem.* 1989; **54**: 4013.
65. Otera J, Dan-Oh N, Nozaki H. *J. Org. Chem.* 1991; **56**: 5307.
66. Otera J, Dan-Oh N, Nozaki H. *J. Chem. Soc. Chem. Commun.* 1991; 1742.
67. Otera J, Dan-Oh N, Nozaki H. *Tetrahedron* 1992; **48**: 1449.
68. Otera J. *Chem. Rev.* 1993; **93**: 1449.
69. Laas HJ, Halpaap R, Pedain J. *J. Prakt. Chem.* 1994; **336**: 185.
70. Hori Y, Yamaguchi A, Hagiwara T. *Polymer* 1995; **36**: 4703.
71. Espinasse I, Pétiaud R, Llauro MF, Michel A. *Int. J. Polym. Anal. Charact.* 1995; **1**: 137.
72. Roelens S. *J. Org. Chem.* 1996; **61**: 5257.
73. Morcuende A, Ors M, Valverde S, Herradón B. *J. Org. Chem.* 1996; **61**: 5264.
74. Furlán RLE, Mata EG, Mascaretti OA. *Tetrahedron Lett.* 1996; **37**: 5229.
75. Otera J, Kawada K, Yano T. *Chem. Lett.* 1996; 225.
76. Orita A, Mitsutome A, Otera J. *J. Org. Chem.* 1998; **63**: 2420.
77. Sakamoto M, Satoh K, Nagano M, Nagano M, Tamura O. *J. Chem. Soc. Perkin Trans.* 1998; **1**: 3389.
78. Orita A, Sakamoto K, Hamada Y, Mitsutome A, Otera J. *Tetrahedron* 1999; **55**: 2899.
79. Hori Y, Hagiwara T. *Int. J. Biol. Macromol.* 1999; **25**: 237.
80. Mascaretti OA, Furlán RLE. *Aldrichim. Acta* 1997; **30**: 55.
81. Mehring M, Schürmann M, Paulus I, Horn D, Jurkschat K, Orita A, Otera J, Dakternieks D, Duthie A. *J. Organometal. Chem.* 1999; **574**: 176.
82. Schulte M, Schürmann M, Dakternieks D, Jurkschat K. *Chem. Commun.* 1999; 1291.
83. Mehring M, Paulus I, Zobel B, Schürmann M, Jurkschat K, Duthie A, Dakternieks D. *Eur. J. Inorg. Chem.* 2001; 153.
84. Zobel B, Schürmann M, Jurkschat K, Dakternieks D, Duthie A. *Organometallics* 1998; **17**: 4096.
85. Mehring M, Gabriele G, Hadjikakou S, Schürmann M, Dakternieks D, Jurkschat K. *Chem. Commun.* 2002; 834.
86. Willem R, Bouhdid A, Kayser F, Delmotte A, Gielen M, Martins JC, Biesemans M. Mahieu B, Tiekink ERT. *Organometallics* 1996; **15**: 1920.
87. Martins JC, Kayser F, Verheyden P, Gielen M, Willem R, Biesemans M. *J. Magn. Reson.* 1997; **124**: 218.
88. Pieper N, Klaus-Mrestani C, Schürmann M, Jurkschat K, Biesemans M, Verbruggen I, Martins JC, Willem R. *Organometallics* 1997; **16**: 1043.
89. Martins JC, Biesemans M, Willem R. *Prog. Nucl. Magn. Reson. Spectrosc.* 2000; **36**: 271, and references cited therein.
90. Bax A, Griffey R, Hawkins BL. *J. Magn. Reson.* 1983; **55**: 301.
91. Bax A, Summers MF. *J. Am. Chem. Soc.* 1986; **108**: 2093.
92. Laatikainen R, Niemitz M, Malaisse WJ, Biesemans M, Willem R. *Magn. Reson. Med.* 1996; **36**: 359.
93. Davies AG, Harrison PG, Kennedy JD, Puddephatt RJ, Mitchell TN, McFarlane W. *J. Chem. Soc. C* 1969; 1136.
94. Mason J. *Multinuclear NMR.* Plenum Press: New York, 1987; 627.

Copyright © 2003 John Wiley & Sons, Ltd.