*Journal of Organometallic Chemistry*, 291 (1985) 179–183
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# TIN-ELEMENT EXCHANGE: FORMATION AND MULTINUCLEAR NMR CHARACTERISATION OF MIXTURES OF THE TYPE $C(SnMe_3)_n(MMe_3)_{4-n}$ (M = Si, Pb; $n$ = 0–3)

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(Received February 20th, 1985)

## Summary

Treatment of tetrakis(trimethylstannyl)methane with one equivalent of methyllithium followed by one equivalent of $Me_3MCl$ gives mixtures of the type $C(SnMe_3)_n(MMe_3)_{4-n}$ (M = Si, Pb; $n$ = 0–3), which have been characterised by multinuclear ($^{13}C$, $^{29}Si$, $^{119}Sn$, $^{207}Pb$) NMR. The main component (ca. 40%) is in each case $(Me_3Sn)_3$ $CMMe_3$, but considerable amounts of the other tetrametallamethanes are also present.

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## Introduction

The chemistry of tri- and tetrametallamethanes has been the subject of considerable interest in recent years. In Group IV chemistry, introduction of the "trisyl" group $(Me_3Si)_3C$– [1] has been shown to have a considerable influence on the chemistry of compounds containing it, due to its steric bulk: trisyltin compounds have been prepared and studied [2]. Very recently, Wells [3] has reported on bromodemethylation of $C(SnMe_3)_4$, a reaction which proceeds cleanly without bromodestannylation. Tetrametallamethanes containing other elements, such as mercury [4], have been prepared and studied. In connection with synthetic work on the formation of tetrastannacyclohexanes, we thought it of interest to determine whether tetrakis(trimethylstannyl)methane could be used as a starting material for the preparation of pure mixed tetrametallamethanes of the type $C(SnMe_3)_n$-$(MMe_3)_{4-n}$ (M = Si, Pb).

## Results and discussion

Treatment of a solution of tetrakis(trimethylstannyl)methane (**5**) in THF with one equivalent of methyllithium in n-hexane at 0°C, followed by the addition of one equivalent of trimethylchlorosilane or trimethyllead chloride, gave in each case a

TABLE 1

$^{13}C$ NMR DATA FOR COMPOUNDS $C(SnMe_3)_n(MMe_3)_{4-n}$ (M = Si, Pb; $n$ = 0–4)

| Compound | $\delta(C_{quat})$ | $^1J(C-Sn)$ | $^1J(C-M)$ | $\delta(MeSn)$ | $^1J(C-Sn)$ | $^3J(C-Sn-C-M)$ | $\delta(MeM)$ | $^1J(C-M)$ |
|---|---|---|---|---|---|---|---|---|
| $C(SiMe_3)_4$ **(1)** [a] | −1.9 | | 30.0 | | | | 5.4 | 51.6 |
| $C(SiMe_3)_3SnMe_3$ **(2)** [a] | −2.2 | 93.6 | 31.8 | −2.3 | 327.5 | 16.1 | 5.1 | 50.9 |
| $C(SiMe_3)_2(SnMe_3)_2$ **(3)** | −6.5 | 104.4 | 35.6 | −3.2 | 324.9 | 17.0 | 5.0 | 50.3 |
| $C(SiMe_3)(SnMe_3)_3$ **(4)** | −14.4 | 110.8 | 37.2 | −5.9 | 318.2 | 18.2 [b] | 3.3 | 50.1 |
| $C(SnMe_3)_4$ **(5)** | −25.7 | 108.2 | | −3.4 | 316.3 [c] | | | |
| $C(SnMe_3)_3(PbMe_3)$ **(6)** | −19.5 | 113.4 | 142.2 | −3.4 | 314.0 | 22.2 [c] | 3.5 | 186.8 [e] |
| $C(SnMe_3)_2(PbMe_3)_2$ **(7)** | −13.4 | 114.6 | 147.4 | −3.1 | 312.0 | 22.8 [d] | 3.9 | 182.2 [f] |
| $C(SnMe_3)(PbMe_3)_3$ **(8)** | −8.1 | 110.2 | 157.5 | −2.9 | 309.9 | 22.8 | 4.2 | 176.6 [g] |
| $C(PbMe_3)_4$ **(9)** | −3.4 | | 175.1 | | | | 4.6 | 170.5 [h] |

[a] Data in good agreement with Ref. 7. [b] $^3J(C-Sn-C-Sn)$ 10.6 Hz. [c] $^3J(C-Sn-C-Sn)$ 11.7 Hz. [d] $^3J(C-Sn-C-Sn)$ 12.2 Hz. [e] $^3J(C-Pb-C-Sn)$ 8.9 Hz. [f] $^3J(C-Pb-C-Sn)$ 9.4, $^3J(C-Pb-C-Pb)$ 18.9 Hz. [g] $^3J(C-Pb-C-Sn)$ 10.0, $^3J(C-Pb-C-Pb)$ 19.4 Hz. [h] $^3J(C-Pb-C-Pb)$ 19.5 Hz.

high-melting solid which was indicated by proton NMR spectroscopy to be a complex mixture of products, and not the required monosubstitution product expected from the sequence shown in eqs. 1 and 2

$$\underset{(\mathbf{5})}{(Me_3Sn)_4C} + MeLi \rightleftharpoons (Me_3Sn)_3CLi + Me_4Sn \qquad (1)$$

$$(Me_3Sn)_3CLi + Me_3MCl \rightarrow \underset{(\mathbf{4}\text{ or }\mathbf{6})}{(Me_3Sn)_3CMMe_3} + LiCl \qquad (2)$$

Metal and $^{13}C$ NMR spectra (see below) show the presence of a large amount of **5**. Since the reaction represented by eq. 1 is reversible and the reactions of the metal chlorides with the organolithium reagent formed relatively slow, compounds **4** or **6** can undergo lithiodestannylation by reaction with methyllithium still present in the solution, and further reactions lead to the formation of $(Me_3Sn)_2C(MMe_3)_2$, $Me_3SnC(MMe_3)_3$ and $C(MMe_3)_4$. The formation of $(Me_3Sn)_2C(MMe_3)Li$ will be favoured by the better carbanion stabilisation by silicon [5] or lead [6] than by tin.

### *NMR characterisation of the product mixtures*

$^{13}C$, $^{29}Si$, $^{119}Sn$ and $^{207}Pb$ spectra of the product mixtures were recorded.

Identification of the products was based on peak heights in conjunction with data for known compounds **1**, **2** [7], **3** (which we had prepared independently) and **5** and the presence or absence of particular coupling constants.

The spectra showed that the product distributions were approximately as follows:
$M = Si$: $CSn_4$ 30%, $CSn_3Si$ 40%, $CSn_2Si_2$ 23%, $CSnSi_3$ 6%, $CSi_4$ 1%.
$M = Pb$: $CSn_4$ 20%, $CSn_3Pb$ 44%, $CSn_2Pb_2$ 26%, $CSnPb_3$ 8%, $CPb_4$ 1%.

While in the former case the agreement between the ratios obtained from the carbon, silicon and tin spectra was extremely good, this was not true in the latter case. The quaternary carbons in $C(PbMe_3)_4$ and $C(SnMe_3)(PbMe_3)_3$ could only be observed when a small pulse angle (ca. 10°) and a long delay (60 s) between pulses was used. Furthermore, the line widths in the $^{207}Pb$ spectra increased by 30% on going from compound **6** to compound **8**.

### *$^{13}C$ spectra (Table 1)*

The quaternary carbon atom shows a progressive high-field shift on replacing silicon by tin (a parallel shift is observed for compounds $CH_n(SnMe_3)_{4-n}$ [8]), which could be interpreted as a heavy-atom effect if it were not for the steady low-field shift which occurs when tin is replaced by lead. It seems likely that the electronegativities of the metals or metalloids attached to carbon play the main role in determining the shift. The chemical shifts of the methyl groups vary little within a series of compounds, but are in each case shifted considerably to low-field of those in the element tetraalkyls ($Me_4Sn$ −9.6, $Me_4Pb$ −2.6 ppm). The one-bond tin–carbon coupling constants involving a quaternary carbon atom are very small (as has been observed by Wells [3] for a number of compounds studied by him): taking $C(SnMe_3)_4$ as the reference point, this coupling appears (with one exception) to decrease slightly on replacing $SnMe_3$ by $SiMe_3$, which apparently has a slightly larger effective steric bulk, and to increase slightly on replacing it by $PbMe_3$, which is thus effectively slightly smaller (due to the longer Pb–C bond). $^1J$(C–Sn) in the methyl groups is of a normal magnitude. The same applies to $^1J$(C–Si): for the

TABLE 2

$^{29}$Si, $^{119}$Sn AND $^{207}$Pb NMR DATA FOR COMPOUNDS $C(SnMe_3)_n(MMe_3)_{4-n}$ (M = Si, Pb; $n$ = 0–4) (in ppm vs. TMS, $Me_4Sn$ or $Me_4Pb$; $J$ in Hz)

| Compound | $\delta(^{119}Sn)$ | $^2J(^{119}Sn-^{119}Sn)$ | $^2J(^{119}Sn-M)$ | $\delta(M)$ |
|---|---|---|---|---|
| **1** | – | – | – | –1.65 |
| **2** | 4.1 | – | 38.0 | 0.69 |
| **3** | 15.3 | 365.8 | 33.6 | 1.17 |
| **4** | 29.9 | 338.2 | 29.6 | 4.35 |
| **5** | 49.8 | 324.4 | – | – |
| **6** | 58.2 | 283.4 | 508.6 | 161.4 |
| **7** | 67.7 | 250.7 | 487.4 | 189.9 |
| **8** | 78.1 | – | 463.3 | 221.5 |
| **9** | – | – | – | 256.5 |

methyl carbons the value is normal, but it is greatly decreased for the quarternary carbon. This effect is not so marked for $^1J$(C–Pb), though similar in nature.

*Metal(loid) NMR Spectra (Table 2)*

There is a steady and for tin and lead considerable downfield shift when $SiMe_3$ is replaced by $SnMe_3$ or $SnMe_3$ by $PbMe_3$: this is in contrast with the behaviour of the carbon shifts noted above. The silicon and tin or tin and lead shifts are linearly correlated.

Although all the compounds studied will have approximately tetrahedral geometry at the quaternary carbon, an exactly tetrahedral arrangement can only exist for **1**, **5** and **9**. The small deviations from ideal geometry in the remaining compounds will have an effect on $\delta$(Sn) [9] and almost certainly on $^2J$(Sn–Sn); Lockhart and Zuckerman [10] have noted a correlation between $^1J$(SnC) in solid methyltin compounds and the bond angle C–Sn–C. It is thus interesting to note that in compounds **2–8** there are linear correlations between $\delta(^{119}Sn)$ and both $^1J(Sn-CH_3)$ ($|r = 0.985|$) and $^2J$(Sn–C–Sn) ($|r = 0.952|$); similar correlations involving silicon and lead appear to exist, but the number of data sets is too small to allow these to be regarded significant.

## Experimental section

Manipulation of organotin compounds was carried out under argon.

Tetrakis(trimethylstannyl)methane [11] and trimethyllead chloride [12] were prepared by literature methods. NMR spectra were recorded using a Bruker AM-300 spectrometer, the resonance frequencies being as follows: $^{13}$C 75.469, $^{29}$Si 59.632, $^{119}$Sn 111.929, $^{207}$Pb 62.790 MHz. Deuterochloroform was used as solvent. $^{29}$Si spectra were obtained by the DEPT technique [13], and $^{119}$Sn spectra by using inversed gated decoupling. The quaternary carbons of **8** and **9** were detected using modified measurement parameters (see text).

*Transmetallation of tetrakis(trimethylstannyl)methane*

A solution of tetrakis(trimethylstannyl)methane (15.0 g, 22.5 mmol) in THF (125 ml) was cooled to 0°C and a solution of methyllithium (24 mmol) in n-hexane added. The yellow solution was stirred for 2 h at 0°C and trimethylchlorosilane (2.45

g, 22.5 mmol) was added. Stirring was continued overnight at room temperature. Water (100 ml) was then added, the organic layer was separated and dried, and the volatiles removed. The colourless crystalline product had a melting-point > 260°C.

The procedure for the reaction with trimethyllead chloride was similar except that the latter was added as a solution in THF: again the crystalline product did not melt below 260°C.

The composition of the mixture was not changed by crystallisation from THF.

## Acknowledgement

We thank the Fonds der Chemischen Industrie for supporting this work.

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