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# Brief Communications

## NMR study of mono- and dilithium derivatives of alkyl and arylstannanes

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Element-centered mono- and dianions of alkyl- and arylstannanes were studied by NMR spectroscopy. The $^{13}$C and $^{119}$Sn NMR chemical shifts for the dianions $R_2SnLi_2$ (R = Ph, Et) were measured for the first time.

**Key words:** anions, dianions, stannanes, $^{13}$C and $^{119}$Sn NMR.

High-resolution NMR spectroscopy is an important tool to study the structure of element-centered anions in solutions. A number of recent publications[1–4] are devoted to $^{13}$C and $^{119}$Sn NMR studies of tin-centered monoanions; a communication[5] reports measurement of the $^{119}$Sn chemical shift of the stannol dianion. Nevertheless, alkyl and aryl-substituted tin-centered geminal dianions have not been studied by NMR as yet. The purpose of our work was to study these anions by NMR spectroscopy.

Mono- and dilithium derivatives of organylstannanes were generated by reducing the corresponding halostannanes with metallic lithium under sonication directly in an NMR tube.

$$R_nSnX_{4-n} + 2(4-n)\ Li \longrightarrow R_nSnLi_{4-n} + (4-n)\ LiX$$

$n = 1, 2$

This procedure has long been known and used in classical works to generate $Me_2SnNa_2$,[6] $Ph_2SnNa_2$,[7] and $Ph_2SnLi_2$.[8]

The chemical shifts observed in the $^{119}$Sn and $^{13}$C NMR spectra of the compounds $R_3SnLi$, $R_2SnLi_2$ and the starting halides are listed in Table 1. The assignment of the $^{13}$C NMR spectra of lithium- and halogen-substituted arylstannanes is based on the relative intensity of the signals and on the spin-spin coupling constant $^{n}J$(SnC) for the signal satellites, because the vicinal spin-spin coupling constant is greater than the geminal constant.

On passing from $Et_3SnCl$ to $Et_3SnLi$ and from $Et_2SnCl_2$ to $Et_2SnLi_2$, the $^{119}$Sn signals shift upfield ($\Delta\delta$($^{119}$Sn) are −195 and −189, respectively). In both cases, this attests to an increase in the negative charge on the tin atom. In turn, on passing from $Ph_2SnCl_2$

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**Table 1.** $^{119}$Sn and $^{13}$C NMR chemical shifts of $R_3SnLi$, $R_2SnLi_2$, and the starting halides

| Compound | δ | | | | | | | $J$/Hz |
|---|---|---|---|---|---|---|---|---|
| | $^{119}$Sn | $^{13}$C | | | | | | |
| | | $C^{\alpha}$ | $C^{\beta}$ | $C_{ipso}$ | $C_{ortho}$ | $C_{meta}$ | $C_{para}$ | |
| $Et_3SnCl$ | +103 | 10.38 | 10.37 | | | | | $^1J(^{119}Sn, ^{13}C_{\alpha}) = 300$, |
| | | | | | | | | $^1J(^{117}Sn, ^{13}C_{\alpha}) = 286$, |
| | | | | | | | | $^2J(^{119}Sn, ^{13}C_{\beta}) = 32$ |
| $Et_2SnCl_2$ | +9 | 22.58 | 10.02 | | | | | $^1J(^{119}Sn, ^{13}C_{\alpha}) = 586$, |
| | | | | | | | | $^1J(^{117}Sn, ^{13}C_{\alpha}) = 560$, |
| | | | | | | | | $^2J(^{119}Sn, ^{13}C_{\beta}) = 50$, |
| | | | | | | | | $^1J(^{119}Sn, ^{13}C_{ipso}) = 650$ |
| $Ph_3SnCl$ | −105 | | | 140.56 | 136.97 | 129.45 | 130.59 | $^1J(^{117}Sn, ^{13}C_{ipso}) = 682$, |
| | | | | | | | | $^2J(^{119}Sn, ^{13}C_{ortho}) = 47.6$, |
| | | | | | | | | $^2J(^{119}Sn, ^{13}C_{meta}) = 65.5$, |
| | | | | | | | | $^4J(^{119}Sn, ^{13}C_{para}) = 13.5$, |
| | | | | | | | | $^2J(^{119}Sn, ^{13}C_{ortho}) = 61$ |
| $Ph_2SnI_2$ | −290 | | | 138.44 | 135.26 | 129.73 | 131.57 | $^3J(^{119}Sn, ^{13}C_{meta}) = 81$, |
| | | | | | | | | $^4J(^{119}Sn, ^{13}C_{para}) = 17$, |
| | | | | | | | | $^1J(^{119}Sn, ^{13}C_{\alpha}) = 124$ |
| $Et_3SnLi$ | −92 | 18.62 | 22.08 | | | | | $^2J(^{119}Sn, ^{13}C_{\beta}) = 32$ |
| $Et_2SnLi_2$ | −180 | 15.91 | 3.12 | | | | | $^2J(^{119}Sn, ^{13}C_{ortho}) = 50.3$ |
| $Ph_3SnLi$ | −105 | | | 166.87 | 137.94 | 125.83 | 122.93 | $^1J(^{119}Sn, ^{6}Li) = 282$ |
| $Ph_2SnLi_2$ | −103 | | | 140.74 | 139.11 | 126.45 | 123.79 | $^1J(^{119}Sn, ^{13}C_{ortho}) = 52.9$ |

**Table 2.** Changes in the $^{119}$Sn and $^{13}$C NMR chemical shifts upon the formation of $Ph_nSnLi_{4-n}$ from the corresponding halides $Ph_nSnCl_{4-n}$

| $Ph_nSnLi_{4-n}$ | $\Delta\delta$ ($R_nSnCl_{4-n} \rightarrow R_nSnLi_{4-n}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| | $^{119}$Sn | $^{13}$C | | | | | |
| | | $C^{\alpha}$ | $C^{\beta}$ | $C_{ipso}$ | $C_{ortho}$ | $C_{meta}$ | $C_{para}$ |
| $Et_2SnLi_2$ | −189 | 8.24 | 10.37 | | | | |
| $Et_3SnLi$ | −195 | −6.67 | −6.9 | | | | |
| $Ph_3SnLi$ | −0 | | | 2.3 | 3.85 | −3.28 | −7.78 |
| $Ph_2SnLi_2$ | −58[a] | | | 26.31 | 0.97 | −3.62 | −7.66 |

[a] $\delta^{119}Sn(Ph_2SnCl_2) = -45.$[10]

($\delta(^{119}Sn) = -32$ [9]) to the corresponding $Ph_2SnLi_2$ dianion, the upfied shift of the $^{119}$Sn resonance is $\Delta\delta = -58$, whereas upon the formation of the $Ph_3SnLi$ anion from the chloride $Ph_3SnCl$, the tin chemical shift almost does not change. The similarity of the $^{119}$Sn chemical shifts for $Ph_3SnLi$ and $Ph_2SnLi_2$ may be indicative of the fact that only one Sn—Li bond of the latter molecule dissociates in a THF solution to give the $Ph_2SnLi^-$ anion.

It is known from published data[1] that in the series of aryl-substituted organoelement compounds, transition from halo-derivatives to compounds with the E—M bond (M is an alkali metal) is accompanied by a decrease in the shielding of the $C_{ipso}$ and $C_{ortho}$ atoms and an increase in the shielding of the $C_{meta}$ and $C_{para}$ atoms. The change in the $^{13}$C chemical shifts on going from $Ph_2SnI_2$ to $Ph_2SnLi_2$ fully corresponds to these features. The changes in the chemical shifts point to π-polarization of the phenyl substituents and to the lack of resonance stabilization. Thus, there is no significant negative charge delocalization over the aryl substituents in $Ph_2SnLi_2$ or $Ph_3SnLi$.

## Experimental

All experiments were carried out under dry argon. Commercial chemicals purified additionally by distillation or recrystallization were used. Diphenyldiiodostannane $Ph_2SnI_2$ was synthesized by a known procedure.[11] Prior to use, THF-$d_8$ was refluxed over sodium benzophenone ketyl and distilled over argon. $^{13}$C and $^{119}$Sn NMR spectra were recorded on Bruker WM-250 and Bruker DRX-500 spectrometers.

**Preparation of compounds $R_nSnLi_{4-n}$ ($n$ = 2, 3) (general procedures).** $R_nSnX_{4-n}$ ($n$ = 2, 3) (0.00022 mol) and finely cut lithium (0.00053 mol; or 0.0011 mol for dianions) were placed in an NMR tube and 0.5 mL of anhydrous THF-$d_8$ was added. The reaction mixture was sonicated for 10 h and then the NMR spectrum was recorded.

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