Sign and Magnitude of ${}^1K$(Sn–C) in Trimethylstannyl-lithium: the First Example of a Negative Reduced Nuclear Spin–Spin Coupling Constant Between Two Directly Bound Group IV Elements

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Summary The electron-mediated reduced nuclear spin–spin coupling constants ${}^1K$(Sn–C) and ${}^2K$(Sn–H) are negative and positive respectively in trimethylstannyl-lithium; this is attributed to the presence of a lone pair of electrons on the tin atom.

Hitherto all studies, both experimental and theoretical, have shown that the reduced nuclear spin coupling constants between directly bound pairs of Group IV elements (C to Pb) are positive.[1–4] This supports the view that for coupling among these elements the use of the mean electronic excitation energy approximation is valid and that it is reasonable to use these coupling constants to assess changes in atomic hybridisation and/or effective nuclear charge in a relatively simple way.[5,6] We now report the first observation of a negative reduced coupling constant between any pair of directly bound Group IV elements, namely ^1K(Sn–C) in Me_3SnLi,3 THF.

A sample of Me_3SnLi enriched to 7 mol % in ^{13}C was prepared from Me_3SnI and metallic lithium and examined as a *ca.* 25% solution in tetrahydrofuran (THF) on a modified JEOL spectrometer operating at a proton frequency of 60 MHz. $^1H-\{^{13}C\}$ and $^1H-\{^{119}Sn\}$ double resonance experiments gave the parameters:

$$^1J(^{13}C–^1H) = +122 \pm 1, \; ^1J(^{119}Sn–^{13}C) = +155 \pm 5,$$
$$^2J(^{119}Sn \cdots ^1H) = -6{\cdot}2 \pm 0{\cdot}2, \; |^3J(^{13}C \cdots ^1H)| = 3{\cdot}2 \pm 0{\cdot}2 \text{ Hz};$$
$$\delta(^{119}Sn) = -180{\cdot}7 \pm 0{\cdot}5, \; \delta(^{13}C) = -1{\cdot}5 \pm 0{\cdot}2,$$
$$\delta(^1H) = -0{\cdot}35 \pm 0{\cdot}05 \text{ p.p.m.}$$

The signs of the coupling constants are based on the assumption that $^1J(^{13}C–H)$ is positive. Since ^{119}Sn has a negative magnetic moment it follows that the reduced coupling constants ^1K(Sn–C) and ^2K(Sn–H) are negative and positive respectively in this species, in contrast to all other results obtained for the Me_3Sn units, and indeed for other Group IV elements.[2] The Figure shows that there is a monotonic relation between $^1J(^{119}Sn–^{13}C)$ and $^2J(^{119}Sn–H)$ as suggested previously[7] on the basis of a much narrower range of values for these two couplings, and confirms the view that $^2J(^{119}Sn–H)$ may be used to deduce $^1J(^{119}Sn–^{13}C)$ in the Me_3Sn group. However, when small values of the former coupling constant are encountered it will be essential to know the sign; for larger values this can be assumed to be positive. The failure of this plot to pass through the origin shows that it is unwise to use either of these coupling constants to estimate the tin atom hybridisation as is common practice.[5,8]

In terms of Pople and Santry's molecular orbital theory of spin coupling[1] our result shows that the *s*-overlap integral between tin and carbon in Me_3SnLi is very small, leading to a negative value for the mutual polarizability of these two atoms. That is, the tin hybrid orbitals used to form the Sn–C bonds have high *p*-character, and the tin 5*s* energy level is well below the tin 5*p* and the carbon 2*s* and 2*p* energy levels. On the basis of the core electron polarization approach of Jameson and Gutowsky[4] a change of sign of ^1K(Sn–C) from positive to negative would arise if either atom ceased to have an (accessible) open *s*-shell configuration. If Me_3SnLi is regarded as having a large contribution from the extreme structure $Me_3Sn^-Li^+$ then the tin atom will have a lone pair of electrons and no accessible open *s*-shell configuration. The sign reversals of both ^1K(Sn–C) and ^2K(Sn–H) can then be seen as analogous to the corresponding reversals of ^1K(P–C) and ^2K(P–H) which accompany[2] the transformation $P^{III} \rightarrow P^{V}$, and also to the change in sign of certain coupling constants involving selenium.[9]

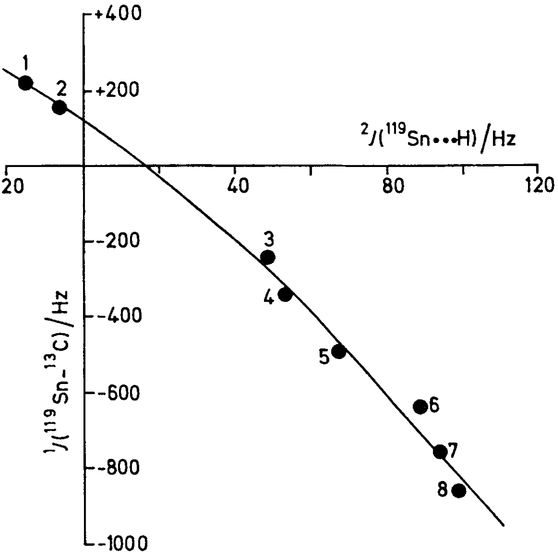

FIGURE. $^1J(^{119}Sn–^{13}C)$ *vs.* $^2J(^{119}Sn \cdots H)$ in representative organotin compounds. (1) Me_3SnLi in $(Me_2N)_3PO$. (2) Me_3SnLi in THF. (3) Me_6Sn_2. (4) Me_4Sn. (5) Me_3SnBr in H_2O. (6) $MeSnBr_3$ in C_6H_6. (7) Me_2SnCl_2 in wet Me_2CO. (8) Me_2SnCl_2 in H_2O.

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