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A ^{119}Sn NMR STUDY OF TIN DERIVATIVES OF CYCLOPENTADIENE

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Summary

A number of organotin derivatives of cyclopentadiene have been studied using the heteronuclear double resonance ^{1}H—{^{119}Sn}. The shielding minimum was found for the series $(C_5H_5)_nSn(CH_3)_{4-n}$ at $n = 1$, attributable to competing electronic effects. The prospects of metallotropic equilibrium studies on the basis of the temperature-dependence of ^{119}Sn chemical shifts are discussed.

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^{119}Sn NMR spectroscopy is one of the most powerful methods for the study of molecular structure and bonding in organotin compounds. This is due to the wide range of tin chemical shifts and to the strong dependence of tin chemical shifts upon the substituent groups and intermolecular effects [1-6].

Earlier, we studied the tin chemical shifts for a number of organotin compounds and worked out an approach to some essential details of the chemical application [7-11]. In this paper we report the results of our ^{119}Sn study of tin derivatives of cyclopentadiene.

Results and discussion

Tin chemical shifts of the cyclopentadienyl compounds

In searching for some regularities of tin chemical shifts in cyclopentadienyl compounds we considered the data on tin chemical shifts in the following series: $R_nSn(CH_3)_{4-n}$ and $R_nCH_{3-n}Sn(CH_3)_3$. The values of tin chemical shifts for these compounds are plotted in Fig. 1.

The following trends are clear:

(i) The successive substitution of the methyl groups at the tin nucleus by vinyl, phenyl or allyl radicals leads to a highfield displacement of tin chemical shifts with the number of substituting radicals. Allylic substitution gives a significantly smaller effect than vinyl or phenyl substitution.

(ii) The substitution of hydrogen in one of the methyl groups by chlorine or a methyl group leads to a regular displacement of tin chemical shifts to lower fields, most markedly in the case of chlorine substitution.

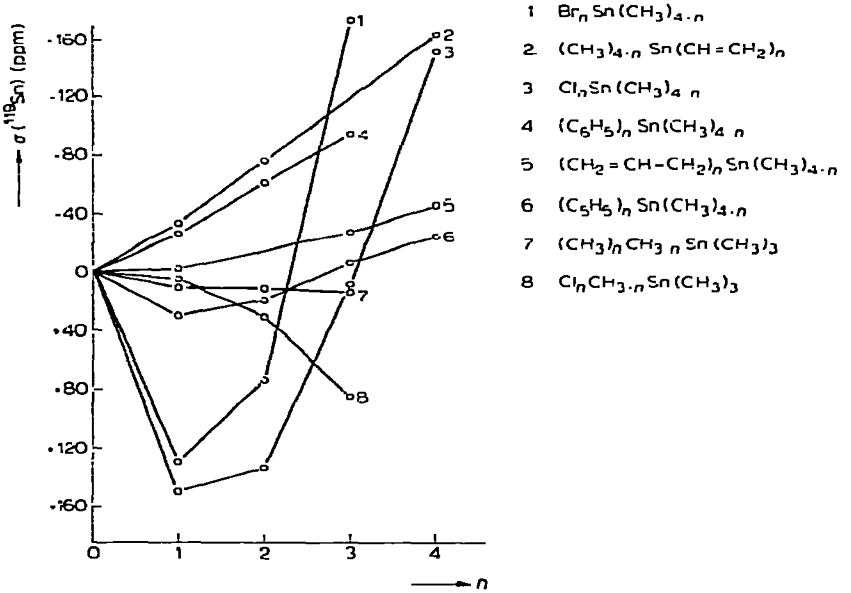


Fig. 1. Variation of tin chemical shifts for the series $R_nSn(CH_3)_{4-n}$ and $R_nCH_{3-n}Sn(CH_3)_3$, as a function of *n*. Chemical shifts are reported in ppm relative to tetramethyltin. Chemical shifts in low fields relative to $(CH_3)_4Sn$ were assumed positive.

(iii) When chlorine replaces CH_3 groups in $(CH_3)_4Sn$ a shielding minimum is observed if one methyl group is replaced, and further substitution displaces tin resonance to higher fields.

These facts are usually interpreted in the following manner. The lowfield displacement of tin chemical shifts is caused by the influence of electronegativity of the substituent at the tin atom. This effect was found to operate also in carbon ^{13}C shielding. However, if the substituent has lone-pair electrons or π-electrons of its multiple bonds, then an increase in ^{119}Sn shielding will be observed due to the partial filling of the vacant 5*d* orbitals of the tin atom (*d*—*p* or d_π—p_π interaction). The combination of these competitive effects leads to the tin shielding minimum for the series $Cl_nSn(CH_3)_{4-n}$ at $n = 1$ and to the ^{29}Si shielding minimum in the series $Cl_nSi(CH_3)_{4-n}$ at $n = 2$ [12].

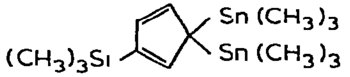
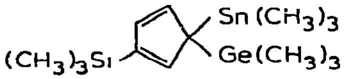
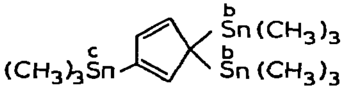
For the compounds Cl_nCH_{4-n} the ^{13}C shielding decreases constantly for $n = 0 \rightarrow 4$, since the ^{13}C nucleus has no vacant low-lying orbitals.

Tin chemical shifts are extremely sensitive to the d_π—p_π interaction. With vinyl and phenyl substituents this effect evidently exceeds the inductive influence.

The introduction of alkyl groups in the β-position with respect to the tin atom results in a decrease of ^{119}Sn shielding for the series $(CH_3)_nH_{3-n}CH_2Sn(CH_3)_3$ but at the same time the alkyl groups in the γ-position somewhat increase tin shielding. Allylic substitution results in gradual increase of tin shielding and this fact has been interpreted [13] as obvious evidence of considerable d_π—p_π interaction in these compounds. However, this effect (less than 5 ppm per allyl group) is too small to fit with an unequivocal interpretation, because opposite effects are caused by β and γ substitution in carbon chain, as described above.

TABLE 1

^{119}Sn CHEMICAL SHIFTS OF TIN DERIVATIVES OF CYCLOPENTADIENE (in ppm from $(CH_3)_4Sn)^a$

	Compound	Conditions	$\sigma^{119}Sn$
I	$(C_5H_5)_4Sn$	CCl_4, 20°	−24.4
II	$(C_5H_5)_3SnCH_3$	CCl_4, 20°	− 7.0
III	$(C_5H_5)_2Sn(CH_3)_2$	CCl_4, 20°	23.2
IV	$(C_5H_5)_2Sn(C_2H_5)_2$	C_6H_{12}, 20°	14.6
V	$C_5H_5Sn(CH_3)_3$	CCl_4, 20°	26.0
VI	$C_5H_5Sn(CH_3)_2Cl$	CCl_4, 20°	101.6
VII	$(CH_3)_3SiC_5H_4Sn(CH_3)_3$	CCl_4, 20°	11.5
VIII	$(CH_3)_3GeC_5H_4Sn(CH_3)_3$	CCl_4, 20°	11.5
IX	$C_5H_4[Sn(CH_3)_3]_2$	CCl_4, 20°	10.6
X		CCl_4, 20°	7.0
XI		CCl_4, 20°	8.8
XII		CCl_4, 20°	9.0
XIII		CCl_4, 20° Toluene, -80°	−11.7 b 11.2 c −49.8
XIV	$C_5H_2[Sn(CH_3)_3]_4$	Toluene, 20°	−20.2
XV	$C_9H_7Sn(CH_3)_3$	Neat, 20°	31.3

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[a] Chemical shifts in low fields relative to $(CH_3)_4Sn$ were assumed positive.

In our opinion, the presence of d_π—p_π interaction may be established only in that case when the shielding curve with a minimum is observed for the compounds $R_n(CH_3)_{4-n}$ (substituent R must exert a negative inductive effect), or if the shielding effect exceeds 10 ppm per substituent.

Tin chemical shifts of the cyclopentadienyl compounds are listed in Table 1. The data for the series $(C_5H_5)_nSn(CH_3)_{4-n}$ give a typical curve with a minimum at $n = 1$.

Tin chemical shifts of the cyclopentadienyl compounds are not affected by the degenerate metallotropic rearrangement that occurs in these compounds, singe the organometallic group migrates between equivalent positions in the cyclopentadienyl ring. The observed dependence of tin chemical shifts in the cyclopentadienyl series reflects the presence of two effects. The first of these is the considerable electronegative influence of the cyclopentadienyl ring, which is greater than that for an allyl group, but lower than that for indenyl group. The negative inductive influence of the cyclopentadienyl moiety may be explained by delocalization of the C—Sn bonding electrons over the ring (σ—π conjugation). The second effect, that of increasing shielding for $n = 2 \rightarrow 4$, is also present. As in the case of stannyl halides this effect is attributed to tin $5d$-orbitals filling with π-electrons of the cyclopentadiene double bonds (d_π—p_π interaction).

For tris(trimethylstannyl)cyclopentadiene (XIII), in which a non-degenerate metallotropic rearrangement takes place [14], two distinct resonances of $(CH_3)_3Sn$ groups in the 2 and 5 positions of the cyclopentadiene have been observed at low temperatures. The difference between these signals is ca. 60 ppm. The tin atom at the double bond is shielded even more strongly (—49.8 ppm) than in $CH_2{=}CHSn(CH_3)_3$ (—35.4 ppm). The introduction of the second $(CH_3)_3$-Sn group in the 5 position somewhat increases the shielding [+11.1 ppm against +26.0 ppm for $C_5H_5Sn(CH_3)_3$].

The disagreement between the observed averaged tin chemical shift (—11.7 ppm) and the value estimated on the basis of the chemical shifts in the rigid structure (—9.2 ppm) should be attributed to solvent effects, since the measurements were performed under the different conditions.

Investigation of metallotropic rearrangement in stannylcyclopentadienes on the basis of the temperature-dependence of ^{119}Sn chemical shifts

As mentioned above, with degenerate rearrangements the values of tin chemical shifts did not depend upon the dynamic process rate. However, if this process is not degenerate, the chemical shifts must exhibit strong dependence upon temperature, reflecting a displacement of the fast metallotropic equilibrium.

The shielding difference between the allyl and vinyl tin atoms is approximately 60 ppm, which corresponds to 2240 Hz at the ^{119}Sn frequency of 37.313 MHz in a field of 2.35 T. This difference is significantly larger than that for the shielding of allyl and vinyl carbons in the same magnetic field. The measurements of tin chemical shifts at different temperatures may provide more correct data on the equilibrium constants.

We studied temperature-dependence of tin chemical shifts in the compounds $C_5H_4[Sn(CH_3)_3]_2$ (IX) and in $(CH_3)_3SiC_5H_3[Sn(CH_3)_3]_2$ (X). The results of this study are plotted in Fig. 2.

Experimental

JEOL C-60HL and Varian XL-100-15 spectrometers operating at 60 and 100.1 MHz respectively were used in the experiments on heteronuclear double resonance. The frequency sweep mode was employed in both cases and the signal from the standard compound added to the sample was used for internal proton lock. The ^{119}Sn frequency was 22.37 MHz for a JEOL C-60HL spectrometer and 37.313 MHz for the Varian XL-100-15. Heteronuclear INDOR technique was applied to obtain ^{119}Sn chemical shifts on a Varian XL-100-15 spectrometer. More detailed information on these experiments is available [7,9,15].

Compounds I-IV and VI were synthesized by N.A. Kocheshkov, N.N. Zemlyansky and N.D. Kolosova.

The synthesis of VII-XIV is described elsewhere [16]. Compound V was synthesized according to Jones and Lappert [17]. The synthesis of XV was proposed by Rakita and Davison [18].

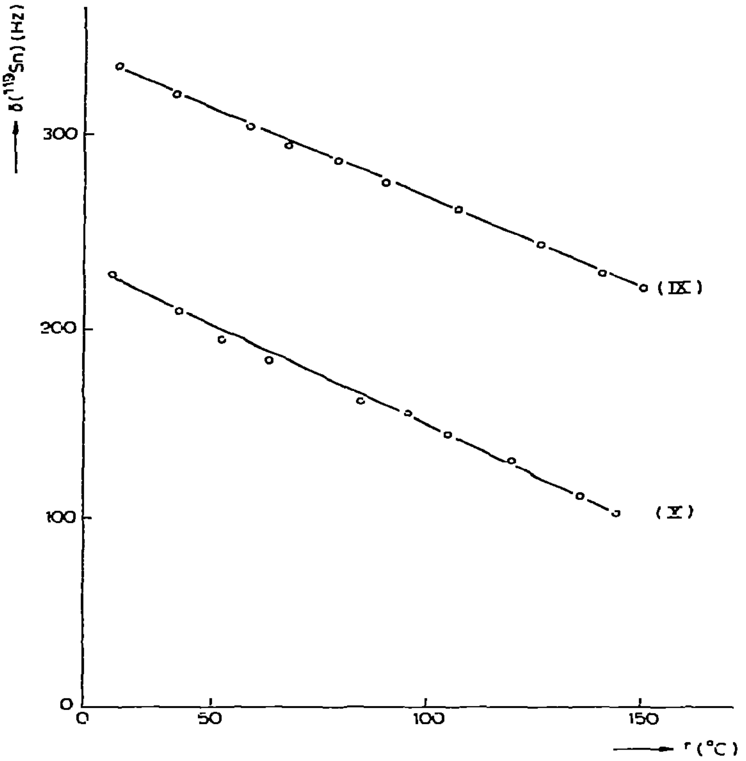

Fig. 2. Temperature dependence of ^{119}Sn chemical shifts for neat IX and X. Chemical shifts are quoted in Hz relative to $(CH_3)_4Sn$.

Acknowledgements

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