Journal of Organometallic Chemistry, 47 (1973) C1–C4

Preliminary communication

NMR $J(\mathrm{Sn}{-}^{13}\mathrm{C})$ coupling constants in substituted aryltrimethyltins

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(Received September 18th, 1972)

SUMMARY

NMR one-bond $J(\mathrm{Sn}{-}^{13}\mathrm{C})$ values have been measured for both the methyltin and C_1 phenyltin bonds in thirteen *meta-* and *para*-substituted aryltrimethyltin compounds.

Conventional interpretation of $J(\mathrm{Sn{-}C{-}H})$ values in methyltin compounds in terms of *s*-electron density distribution and structure is based upon implicit assumptions concerning the situation in the tin–carbon and carbon–hydrogen bonds which could be put on a firm foundation if the relevant one-bond coupling constants were known. $J(^{13}\mathrm{C}{-}^{1}\mathrm{H})$ values are now becoming available for organometallic derivatives of the Group IV[1–4], but as yet $J(\mathrm{Sn}{-}^{13}\mathrm{C})$ values have been measured in only five methyltin compounds: $(CH_3)_4Sn$ [340 ± 2 (ref. 5), 336 ± 3 (ref. 6), 330 ± 5 (ref. 7)], $(CH_3)_3SnBr$ [380 ± 2 (ref. 5)], $(CH_3)_2SnCl_2$ [556 ± 2 (ref. 5)], CH_3SnBr_3 [640 ± 15 (ref. 5)] and $[(CH_3)_3Sn]_2C_5H_4$ [340 ± 8 (ref. 8)] and in tetraethyltin [321.5 (ref. 9)] and tetraallyltin [250 ± 3 (ref. 8) Hz]. An approach to understanding can come through the study of homologous series of compounds, and we report in this Preliminary Communication $J(\mathrm{Sn}{-}^{13}\mathrm{C})$ data for thirteen *meta-* and *para*-substituted aryltrimethyltins.

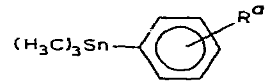
The compounds were obtained from organolithium or Grignard preparations using trimethyltin chloride. Physical properties agree with literature data[10–21]. *p*-Ethoxyphenyltrimethyltin (b.p. 133.5–134.0°/10 mm) was synthesized by Grignard synthesis from *p*-bromophenetole. (Anal. Found: C, 46.51; H, 6.28; Sn, 40.24. $C_{11}H_{18}Sn$ calcd.: C, 46.36; H, 6.32; Sn, 41.69%.)

NMR parameters were measured on a modified Varian HA-100D spectrometer equipped with a Digilab fast Fourier transform FTS-3/NMR pulse and data system. Noise-modulated proton decoupling was effected with a Digilab 50–80 decoupler. Samples were studied in 8 mm O.D. tubes which held 2 mm O.D. coaxial inner cells containing C_6F_6, the ^{19}F lock material. The number of pulses ranged from 2000–10000. In all cases 16384 (16K) data points were collected with a sampling frequency of 4000 s^{-1} to give a resolution of ca. ± 0.25 Hz.

The methyltin–carbon $J(Sn-^{13}C)$ values for the thirteen compounds studied are listed in Table 1 in order of increasing Hammett σ-constant of the substituent group[22]. Substituent groups with negative σ-constants are in general associated with lower J values than those with positive σ-constants, and there is a gradual, but not monotonic increase in J value with increasing σ-constant.

TABLE 1

$J(Sn-^{13}C)$ VALUES ± 0.25 Hz IN



R	$J(^{119}Sn-^{13}CH_3)$ [b]	$J(^{119}Sn-^{13}C_1)$ [b]
p-$N(CH_3)_2$ [c]	343.6	520.2
p-OCH_3	348.0	493.2
p-OC_2H_5	347.2	496.7
p-CH_3	347.0	486.8
m-CH_3	346.2	480.4
H	347.5	474.4
p-F	353.3	467.0 [d] 458.8
m-OCH_3	347.5	471.0
p-Cl	352.8	454.1
p-Br	352.0	452.0
m-F	354.1	449.9 [e] 445.0
m-Cl	353.0	439.0
p-$Sn(CH_3)_3$ [f,g]	347.5	477.0

[a] Neat liquids.

[b] Regression analysis parameters employing the arithmetic mean of methyltin-117 and -119 coupling components: correlation coefficient, $r = 0.866$; slope, $\rho = 10.4$; intercept, $C = 341.6$ Hz; number of compounds 12. The corresponding parameters for the tin–C_1 couplings are $r = 0.991$; $\rho = -80.6$; $C = 462.4$ Hz; number of compounds 12.

[c] Measured in liquid phase (*ca.* 50°).

[d] The α-carbon resonance in this compound is split by a four-bond $^4J(^{19}F-C-C-C-^{13}C)$ coupling of 4.2 Hz.

[e] The α-carbon resonance in this compound is split by a three-bond $^3J(^{19}F-C-C-^{13}C)$ coupling of 2.7 Hz.

[f] Saturated solution in CCl_4.

[g] No satisfactory Hammett σ-constant is available for the trimethyltin group, and so it is placed at the bottom of the list.

The Table also lists the phenyltin C_1 $J(Sn-^{13}C)$ values. Data of this kind have not been reported before for tin and are intrinsically more difficult to collect because of the absence of the signal-enhancing nuclear Overhauser effect with carbon atoms lacking a directly-bonded proton[23]. The C_1 region of p-methoxyphenyltrimethyltin is shown in Fig. 1

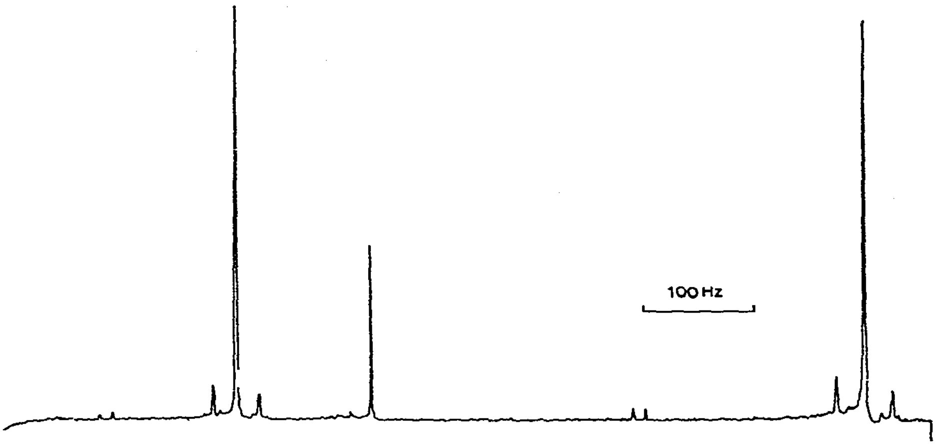
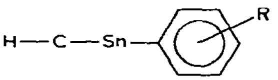


Fig. 1. The C_1 region of *p*-methoxyphenyltrimethyltin. The C_1 resonance [131.68 ppm downfield from internal TMS] is flanked by the downfield 2,6-carbon resonance (*ortho* to the tin atom) [136.70 ppm] and by the upfield 3,5-carbon resonance [114.29 ppm]. Satellites (resolvable on expansion of scale) are observed on all phenyl carbons.

Here there is good correlation with σ-constant, the J values decreasing with increasing σ-constant. Regression analysis parameters for both J-σ plots are listed.

According to Bent's isovalent hybridization model[24], increasing the electron demand at R in the system



will bring about a redistribution of electron density at the tin atom in which 5*s*-character will tend to concentrate in those hybrid orbitals directed toward the methyl group carbon atoms. Given a fixed amount of 5*s*-character to distribute, this should reduce the 5*s*-character in the hybrid orbital tin directs toward the C_1 of the phenyl group*. In a Fermi contact dominated mechanism for the spin–spin interaction, these electron density redistributions will be reflected in an increase in J value for the methyltin–carbon coupling with Hammett σ-constant, and decreased J values in the phenyltin-C_1 series. Our observations bear this out. Indeed, this model also predicts a corresponding redistribution, although smaller in magnitude, at the methyl group carbon atom in which an increased electron demand registered at the tin atom would tend to bring about a parallel concentration of 2*s*-character in the methyl carbon hybrid orbitals directed toward hydrogen. A slight general trend in this direction has been noted in the fourth group derivatives for t-butylbenzenes[25], phenyltrimethylsilanes[1–3], germanes[1] and stannanes[4].

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*The total isotropic $|\psi_{ns}(0)|^2$ at the tin nucleus as measured by ^{119m}Sn Mössbauer isomer shift values remains constant within experimental error in our series[4] despite the anisotropic redistribution in 5*s*-density along the bonding axes.

The somewhat more scattered nature of the correlation of $J(\mathrm{Sn}-{}^{13}\mathrm{C})$ with σ-constant for the methyltin Sn–C bond may be due in part to the combination of the increased 5*s*-contribution made by the tin atom, and the decreased 2*s*-contribution by carbon to the hybrid orbitals each atom provides for overlap. The general trend of the data is predominantly controlled by the changes registered at tin, as expected, since this atom lies closer to the substituent group.

Direct comparison of $J(\mathrm{Sn}-{}^{13}\mathrm{C})$ values for the methyltin and phenyltin bonds in the thirteen compounds studied shows that the relative increase in J for the sp^3 *vs.* sp^2 situation at carbon corresponds closely to the 0.25/0.33 ratio of coefficients in the simple valence bond LCAO approach.

ACKNOWLEDGEMENT

Our work is supported by the National Science Foundation under Grant GP-16544. We thank Dr. Richard J. Mynott for helpful discussions.

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