CARBON-13 NMR STUDIES OF SOME ORGANOTIN(IV) COMPOUNDS

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Summary

The ^{13}C chemical shifts and $^{13}C-^{119}Sn,^{117}Sn$ coupling constants for several organotin(IV) compounds R_xSnCl_{4-x} (R = Me, Bu^n, Ph; $x = 1-4$) have been measured in both inert ($CDCl_3$) and donor (DMSO-d_6) solvents, as have ^{13}C data for the compounds $R_xSnR'_{4-x}$ (R = Me, Ph; R' = Bu^n and R = Me; R' = Ph; $x = 1-3$) and the compounds Me_3SnX (X = pseudo halide). The δ and ^1J(C–Sn) values appear to depend mainly on the type and number of substituents on tin and the donor ability of the solvent. There are linear relationships between the number of substituents (x), and both δ and ^1J(C–^{119}Sn) for almost all the R_xSnX_{4-x} series (R = Me, Bu^n, Ph; X = Cl and R = Me, Bu^n; X = Ph; x = 1–4), when measured in a single solvent, e.g. $CDCl_3$. There is an excellent linear relationship between ^1J(C–^{119}Sn) and ^2J($^1HC-^{119}Sn$) for the compounds Me_xSnCl_{4-x}. Determination of ^{13}C data for Me_3SnCl and Ph_3SnCl in a range of solvents reveals that the value of ^1J(C–Sn) increases with the donor ability of the solvent.
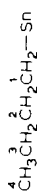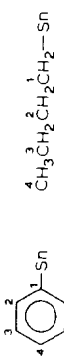
The marked increase in the values of ^1J(C–^{119}Sn) in DMSO-d_6 for the compounds R_xSnCl_{4-x} (R = Me, Bu^n, Ph) on going progressively from $x = 4$ to $x = 1$ suggest tin coordination numbers of 4, 5, 6 and 6, respectively. Some additional physical data are presented for the isolated complexes formed from DMSO and the compounds Ph_xSnCl_{4-x} ($x = 1-3$) and Me_3SnX with X = N_3 or OCOMe.

Introduction

A large body of NMR data for organotin(IV) compounds reported in the period from 1960–1975 have been reviewed by Petrosyan [1]. Additional ^{13}C NMR data were reported subsequently [2–7]. A previous investigation of the ^1H NMR spectra of ethylhalostannanes in $CDCl_3$ and DMSO-d_6 has shown that the spectral parameters depend strongly on the solvent used [8]. Similar observations were made by Mitchell [9], who also found that the ^1J($^{13}C-^{119}Sn$) coupling constants for some organotin compounds provide a good guide to the tin coordination number. Recently some Ph_3SnX [4,5] and Bu^n_3SnX [6] compounds with X = Cl, Br, OCOMe,

TABLE 1

^{13}C NMR DATA: δ (ppm) AND $^nJ(C-^{119}Sn)$ (Hz) FOR THE COMPOUNDS R_xSnCl_{4-x} (R = Me, Bu^n, Ph; $x = 1-4$) IN CDCl$_3$ AND in DMSO-d_6

Sn $\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2-Sn$

Compound	Solvent	C(1) δ^a	C(1) $^1J(C-Sn)$	C(2) δ^a	C(2) $^2J(C-Sn)$	C(3) δ^a	C(3) $^3J(C-Sn)$	C(4) δ^a	C(4) $^4J(C-Sn)$
Me$_4$Sn	CHCl$_3$	−9.4	337						
	DMSO^c	−9.1	333						
Me$_3$SnCl	CHCl$_3$	−0.7	381.7						
	DMSO	3.3	510.6						
Me$_2$SnCl$_2$	CHCl$_3$	6.7	481.4						
	DMSO	22.7	1014.4						
MeSnCl$_3$	CHCl$_3$	11.0	701.5						
	DMSO	22.6	1017.6						
Bu$_4^n$Sn^b	CCl$_4$	9.1	310	29.6	25.0	27.6	52.0	13.7	
Bu$_3^n$SnCl	CHCl$_3$	17.6	338.7	28.0	20.6	27.0	65.4	13.7	
	DMSO	21.0	459.0	28.0	29.2	26.5	72.2	13.7	
Bu$_2^n$SnCl$_2$	CHCl$_3$	26.9	421.2	26.9	43.0	26.2	84.2	13.4	
	DMSO	37.5	854.5	27.7	46.4	25.6	153.1	13.8	
Bu^{n}SnCl$_3$	CHCl$_3$	33.4	651.6	26.8	42.7	26.2	85.2	13.3	
	DMSO	37.8	826.0	27.6	44.1	25.5	147.0	13.6	
Ph$_4$Sn	CHCl$_3$	138.4	515.7	137.6	36.8	128.8	53.4	129.3	5.2
Ph$_3$SnCl	CHCl$_3$	137.3	614.7	136.2	50.0	129.2	64.7	130.5	11.8
	DMSO	143.7	811.8	136.0	50.0	128.3	70.6	128.9	17.0
Ph$_2$SnCl$_2$	CHCl$_3$	136.8	786.8	134.9	63.3	129.7	86.8	131.8	17.7
	DMSO	155.0	1548.7	134.7	70.6	127.3	125.0	127.7	23.5
PhSnCl$_3$	CHCl$_3$	135.9	1123.6	133.9	77.5	130.3	126.4	133.1	25.4
	DMSO	155.2	1629.6	132.9	79.4	127.5	138.3	128.2	50.0
	DMF	156.0	1645.8	133.9	76.4	128.2	141.2	128.9	49.2

^{a} Downfield from internal TMS. ^{b} Data from ref. 1. ^{c} DMSO = dimethyl sulphoxide.

TABLE 2

CARBON-13 NMR DATA; δ^a (ppm) AND $^nJ(C-^{119}Sn)$ (Hz) FOR THE COMPOUNDS $R_xSnR'_{4-x}$ ($R = Me$, $R' = Ph$ or Bu^n and $R = Ph$, $R' = Bu^n$; $x = 1-3$) IN $CDCl_3$

Compound[b]	Me	Bu^n				Ph			
	(δ) $J(C-Sn)$	($\delta C(1)$) $^1J(C-Sn)$	($\delta C(2)$) $^2J(C-Sn)$	($\delta C(3)$) $^3J(C-Sn)$	($\delta C(4)$) —	($\delta C(1)$) $^1J(C-Sn)$	($\delta C(2)$) $^2J(C-Sn)$	($\delta C(3)$) $^3J(C-Sn)$	($\delta C(4)$) $^4J(C-Sn)$
Me$_3$SnPh	(−9.7) 350.7					(142.1) 395.4	(135.8) 36.1	(128.4) 49.2	(128.7) 10.5
Me$_2$SnPh$_2$	(−10.2) 364.8					(140.5) 488.4	(136.2) 36.1	(128.3) 50.0	(128.6) 10.5
MeSnPh$_3$	(−10.6) 376.6					(139.1) 509.0	(136.7) 36.1	(128.5) 48.1	(128.9) 10.3
Me$_3$SnBu^n	(−11.5) 300.9	(10.2) 350.7	(29.1) 25.8	(27.2) 51.6	(13.8)				
Me$_2$SnBu$^n_2$	(−11.4) 301.0	(10.2) 357.6	(29.1) 25.6	(27.3) 50.2	(13.8)				
MeSnBu$^n_3$	(−12.7) 288.7	(9.6) 330.1	(29.3) 20.7	(27.4) 44.7	(13.8)				
Bu$^n_3$SnPh		(9.6) 339.7	(29.2) 20.6	(27.4) 47.0	(13.7)	(141.9) 391.2	(136.5) 30.9	(128.0) 39.7	(128.0) 10.3
Bu$^n_2$SnPh$_2$		(10.7) 357.4	(29.4) 20.6	(27.8) 59.0	(14.1)	(140.8) 435.3	(137.3) 32.4	(126.7) 44.2	(128.9) 14.7
Bu^{n}SnPh$_3$		(10.3) 366.2	(29.2) 20.6	(27.4) 61.8	(13.7)	(139.1) 480.0	(136.8) 35.3	(128.3) 47.0	(128.4) 17.6

^{a} Downfield from internal TMS. ^{b} For the data of Me_4Sn, Bu_4Sn and Ph_4Sn, see Table 1.

etc., have been studied in one inert, and several donor solvents. Some complexes of organotin compounds of the type Me_xSnCl_{4-x}, $x = 0, 1, 2, 3$ with donor solvents have been isolated but they were characterized only by elemental analysis [10], the complex $Ph_2SnCl_2 \cdot 2DMSO$ has been characterized by X-ray diffraction [11a,b]. There has been no detailed study of solvent and substituent effects of ^{13}C NMR parameters of organotin compounds, and because of this, and in order to obtain additional information about the nature of the $^{13}C-^{119}Sn$ interaction for some organotin compounds not previously studied I have examined the ^{13}C spectra of the compounds. R_xSnCl_{4-x} (R = Me, Bu^n, Ph; $x = 4, 3, 2, 1$) in both inert and donor solvents, those of the compounds $R_xSnR'_{4-x}$ (R = Me, Bu^n; R' = Ph and R = Me; R' = Bu^n) in $CDCl_3$ only, and those of the compounds Me_3SnX, (X = pseudohalide) in DMSO-d_6 only.

Results and discussion

The carbon-13 chemical shifts (δ(ppm)) and $^{13}C-^{119}Sn,^{117}Sn$ coupling constants (^nJ (Hz)) for the compounds R_xSnCl_{4-x} (R = Me, Bu^n, Ph; $x = 4, 3, 2, 1$) are listed in Table 1. The ^{13}C data for the compounds $R_xSnR'_{4-x}$, (R = Me, Bu^n; R' = Ph and R = Me; R' = Bu^n; $x = 3, 2, 1$) in $CDCl_3$ are listed in Table 2, and those for the compounds Me_3SnX (X = pseudohalide) in DMSO-d_6 are listed in Table 3. The $^nJ(^{13}C-^{117}Sn)$ values are not given since they can be derived from the relationship, $^nJ(C-^{117}Sn) =^n J(C-^{119}Sn)/1.046$.

The ^{13}C data previously reported [1-7] for some of the compounds R_xSnCl_{4-x} (R = Me, Bu^n, Ph) and Me_3SnPh are similar to those reported here, but a detailed study of these compounds as series has not been previously carried out. In the present study I have concentrated mainly on two factors which influence the ^{13}C data viz. (i) the type and number of substituents on tin, and (ii) the donor ability of the solvent.

(i) Substituent effects

For the methyl series Me_xSnCl_{4-x}, with $x = 4, 3, 2, 1$, the values of both δ and $^1J(C-^{119}Sn)$ measured in the non-complexing solvent $CDCl_3$ are significantly increased on going progressively from Me_4Sn to $MeSnCl_3$, i.e. on replacing the methyl groups by the more electronegative chlorine atoms. This is due to the electron-withdrawing inductive effect of chlorine which causes an increase in the p-character of the tin orbital bonded to chlorine and thus in the s-character of the tin orbital used in the bonding with a methyl group. A similar trend has been observed for lead compounds [12]. Thus satisfactory linear relationships are observed between the number of chlorine atoms in the tin compounds and their δ or $^1J(C-^{119}Sn)$ values ($r = 0.970$ and 0.900, respectively). There is also a linear relationship between $^1J(^{13}C-^{119}Sn)$ and $^2J(^1HC-^{119}Sn)$ for the compounds Me_xSnCl_{4-x} with $x = 4, 3, 2, 1$, the r value being typically (Fig. 1); extrapolation of the correlation line gives large intercept for $^2J(^1HC-^{119}Sn)$. McFarlane [13] and, more recently, Singh [14] observed a similarly large intercept for $^2J(^1HC-Sn)$ in series of methyltin compounds, and suggested that one of the coupling constants receives a significant contribution from J(dipole) and/or J(orbital); probably it is J(dipole) which mainly contributes to $^1J(C-Sn)$, since the dipole term is usually stronger when heavy nuclei are involved.

TABLE 3

CARBON-13 NMR DATA; δ (ppm) AND $J(C-^{119}Sn)$ (Hz) FOR THE COMPOUNDS Me_3SnX IN DMSO-d_6

X	δ^a	$J(C-Sn)$
OH	-1.4	441.2
Cl	3.3	510.6
NO_3	0.0	519.2
CN	3.6	521.0
$OCOCH_3$	0.0	524.4
N_3	0.6	529.5
NCS	0.3	536.4
NCO	0.6	541.6

^{a} Downfield from internal TMS.

In the series R_xSnCl_{4-x} ($R = Bu^n$ or Ph; $x = 4, 3, 2, 1$) the values of $^nJ(^{13}C-^{119}Sn)$ decrease in the order $^1J > ^3J > ^2J > ^4J$ (Table 1). The values of $^4J(C-Sn)$ for C(4) of the butyl group is too small to be satisfactorily defined but it is probably ca. 8 Hz. As in the methyl series (vide ultra), the values of δ and $^1J(^{13}C-^{119}Sn)$ for C(1) (the carbon atom directly attached to tin) show significant changes. The δ and $^1J(C-Sn)$ values rise on replacing butyls in Bu_4^nSn progressively by chlorines, i.e., the values in $CDCl_3$ decrease in the order $BuSnCl_3 > Bu_2SnCl_2 > Bu_3SnCl > Bu_4Sn$. As for the methyl series, there is also a linear relationship ($r = 0.995$) between the number of chlorine atoms in the compounds Bu_xSnCl_{4-x}, $x = 4, 3, 2, 1$ and their $\delta(C(1))$ values in $CDCl_3$. The values of δ and $^nJ(C-Sn)$ for C(2), C(3) and C(4) in the butyl group show no significant change on going from Bu_4Sn to $BuSnCl_3$.

In contrast, the δ values for C(1) and C(2) of the phenyl group (in $CDCl_3$) decrease whereas those for C(3) and C(4) increase on going progressively from Ph_4Sn to $PhSnCl_3$.

There is a linear relationship ($r = 0.982$) between the number of chlorine atoms in the compounds Ph_xSnCl_{4-x} and the $\delta(C(1))$ values in $CDCl_3$ (see Fig. 2a). The
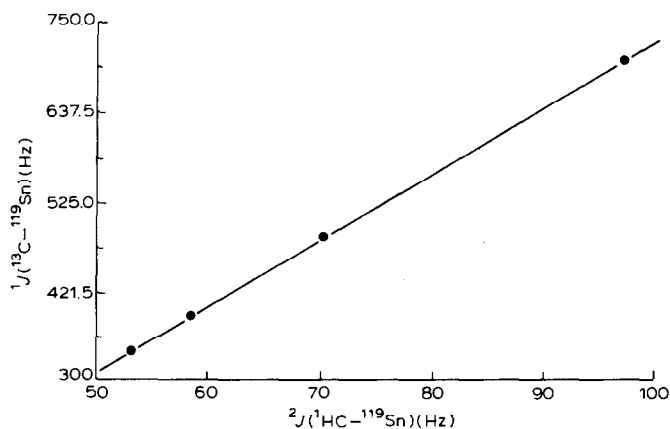

Fig. 1. Linear relationship ($r = 0.999$) between $^2J(HC-^{119}Sn)$ of Me_4Sn (53 Hz), Me_3SnCl (58 Hz), Me_2SnCl_2 (70.2 Hz) and $MeSnCl_3$ (97.2 Hz) and their $^1J(^{13}C-^{119}Sn)$ (Table 1) measured in $CDCl_3$.
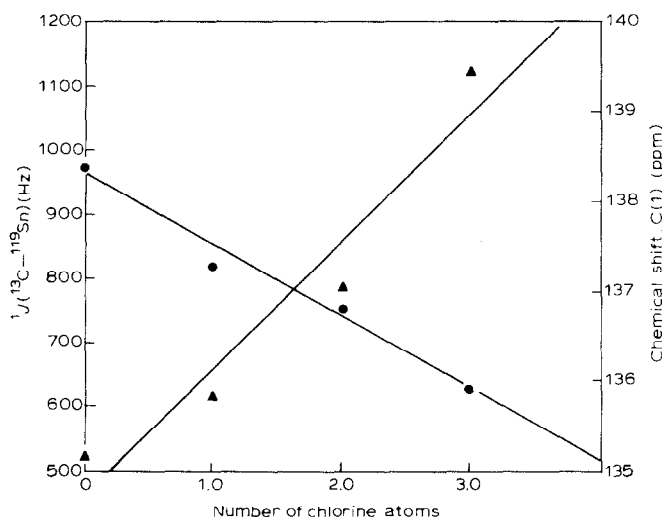
Fig. 2. Linear relationships between number of chlorine atoms and either (a) $^1J(C-^{119}Sn)$ (▲) ($r = 0.932$) or (b) $\delta(C(1))$ (⊙) ($r = 0.982$), in Ph_xSnCl_{4-x} ($x = 1-4$) in $CDCl_3$.

$^1J(C-^{119}Sn)$ values in $CDCl_3$ rise when the phenyls in Ph_4Sn are successively replaced by chlorines (Table 1), and correlate linearly ($r = 0.932$) with the number of chlorines present (Fig. 2b).

With tetraorganotin compounds (Table 2), e.g. the series Me_xSnPh_{4-x} with $x = 0-4$, as the number of phenyl groups increases, the $\delta(Me)$ values decrease by ca. 0.4 ppm for each step and the $^1J(C(Me)-^{119}Sn)$ values increase by ca. 14 Hz for each step. Large differences can be seen between the data for, e.g., $MeSnPh_3$ ($\delta = -10.6$ ppm, $^1J(C(Me)-^{119}Sn)$ 376.6 Hz) and $MeSnCl_3$ (δ 11.0 ppm, $^1J(C(Me)-^{119}Sn)$ 701.5
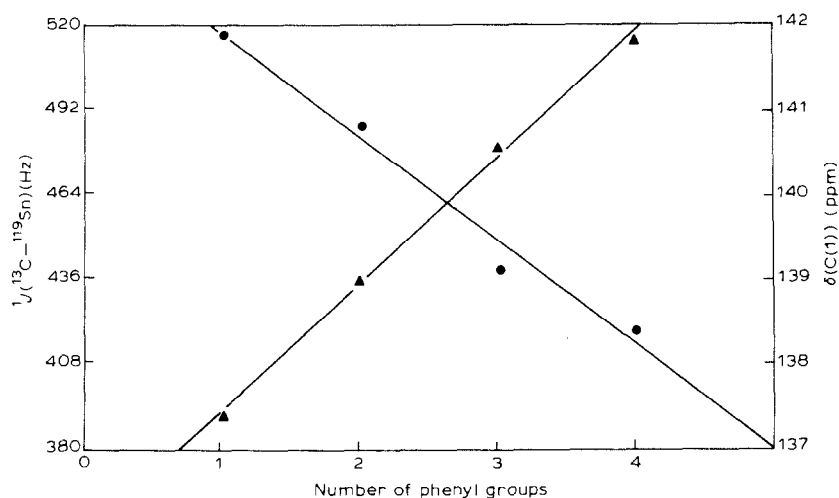

Fig. 3. Linear relationships between number of phenyl groups and either (a) $^1J(C-Sn)$ (▲) ($r = 0.998$) or (b) $\delta(C(1))$ (⊙) ($r = 0.978$), for the phenyl group in Ph_xSnBu_{4-x} ($x = 1-4$) in $CDCl_3$.

Hz) in $CDCl_3$, and likewise with other members of the two series. This can be attributed to greater electronegativity of Cl than of Ph. Similarly, as the number of phenyl groups of the same series increases, the $\delta(Ph)$ values decrease and $^1J(C(Ph)-^{119}Sn)$ values increase. Linear relationships are observed between the number of phenyl groups in the series Me_xSnPh_{4-x} with $x = 0$–4 and either of the $\delta(Me)$ ($r = 0.992$), $^1J(C(Me)-^{119}Sn)$ values ($r = 0.999$), or $\delta(Ph)$ values ($r = 0.973$). Similarly for the series Bu_xSnPh_{4-x} with $x = 0$–4 both $\delta(Ph)$ and $^1J(C(Ph)-^{119}Sn)$ values correlate linearly with the number of phenyl groups in the compounds (the r values are 0.978 and 0.998, respectively) (Fig. 3a and b). There are no significant variations for the series Me_xSnBu_{4-x} with $x = 0$–4.

The ^{13}C data of Me_3SnX, where X is a pseudo halide group, were obtained for solutions in DMSO-d_6, this being used to insure larger $^1J(C-Sn)$ values and so larger differences between the compounds (Table 3). It seems that as the electronegativity of the substituent (X) increases the $^1J(C-^{119}Sn)$ values increase, and the effects of the groups increase in the following sequence: $OH \ll Cl < NO_3 \leqslant CN \leqslant OCOMe < N_3 < NCS < NCO$.

(ii) Solvent effects

In donor solvents, e.g., DMSO-d_6, the data for the tetraorganotin compounds, R_4Sn and $R_xSnR'_{4-x}$ showed no significant change from those in $CDCl_3$, and this is as expected for tetra-coordinate tin. The marked increase in both the δ and $^1J(C-^{119}Sn)$ values for the chlorine derivatives R_xSnCl_{4-x} ($R = Me$, Bu^n, Ph; $x = 1$–3) on going from ($CDCl_3$) to the donor solvent DMSO-d_6 can be attributed to the coordination of donor solvent to tin. The considerable increase in $^1J(C-^{119}Sn)$ for Me_3SnCl (129 Hz), Bu_3SnCl (120 Hz), and Ph_3SnCl (197 Hz), is to be associated with penta-coordinate tin in the complexes $R_3SnCl \cdot DMSO$. The large increase in $^1J(C-^{119}Sn)$ values for Me_2SnCl_2 (533 Hz), Bu_2SnCl_2 (433 Hz) and Ph_2SnCl_2 (762 Hz) are attributed to formation of the hexa-coordinate tin complexes $R_2SnCl_2 \cdot 2DMSO$. Similarly the increases in $^1J(C-^{119}Sn)$ values for $MeSnCl_3$ (316 Hz), $BuSnCl_3$ (174 Hz) and $PhSnCl_3$ (506 Hz) are consistent with hexa-coordination of the tin in the complexes $RSnCl_3 \cdot 2DMSO$. The results obtained for the methyl series in solution are in agreement with those reported previously for solid $Me_3SnCl \cdot L$, $Me_2SnCl_2 \cdot 2L$, and $MeSnCl_3 \cdot 2L$ with $L = DMSO$ or DMF [10]. To provide confirmation of the results obtained from the solutions, the complexes $Me_3SnN_3 \cdot DMSO$, $Me_3SnOCOMe \cdot DMSO$, $Ph_3SnCl \cdot DMSO$, $Ph_2SnCl_2 \cdot 2DMSO$, and $PhSnCl_3 \cdot 2DMSO$ were isolated from their DMSO solutions as white solids and characterized by elemental analysis. Furthermore, the complex $Ph_2SnCl_2 \cdot 2DMSO$ has been previously prepared and shown by X-ray diffraction to contain hexa-coordinate tin [11b].

To provide another check on a correlation between $^1J(C-^{119}Sn)$ and the coordination number of tin, the spectra of Me_3SnCl and Ph_3SnCl were recorded in various solvents (Table 4). There is only a small change in δ on going from one solvent to another, but the $^1J(C-Sn)$ values for the C atom of the methyl group and those for C(1) of the phenyl group were found to increase with increasing donor ability of the solvent. The coupling constants for the other carbon atoms of the phenyl group remain essentially constant throughout. If the $^1J(C-Sn)$ value is taken as a measure of the donor ability of the solvent, this ability rises in solvents in the sequence: $CDCl_3 \leqslant C_6H_6$-$d_6 < CH_3NO_2$-$d_3 <$ dioxane-$d_8 < CH_3CN$-$d_3 \leqslant$ actone-$d_6 \ll$

TABLE 4

CARBON-13 NMR DATA; δ(ppm) AND ^nJ(C–^{119}Sn) (Hz) FOR TIN COMPOUNDS Me$_3$SnCl AND Ph$_3$SnCl IN VARIOUS SOLVENTS[b]

| Solvent | Me$_3$SnCl | | Ph$_3$SnCl | | | | | | | |
| | | | C(1) | | C(2) | | C(3) | | C(4) | |
	δ[a]	J(C–Sn)	δ[a]	J(C–Sn)	δ[a]	^2J(C–Sn)	δ[a]	^3J(C–Sn)	δ[a]	^4J(C–Sn)
C$_6$H$_6$-d_6	−1.04	385.3	137.6	613.3	136.5	52.4	128.0	88.2	130.6	13.2
CH$_3$NO$_2$-d_3	−0.6	395.4	139.1	625.1	137.5	50.0	130.6	63.6	131.4	23.6
dioxane-d_8	0.0	421.2	139.1	644.2	136.8	48.5	129.6	64.7	130.7	13.3
acetone-d_6	0.6	430.9	140.6	660.4	136.9	48.5	129.5	64.8	130.6	14.8
CH$_3$CN-d_3	0.8	428.1	140.4	675.1	137.1	48.5	129.9	67.7	131.0	14.6
CH$_3$OH-d_4	0.0	491.7	142.5	759.0	137.2	47.1	129.6	67.7	130.4	14.7
DMF-d_7[c]	2.4	505.5	144.0	797.2	136.9	47.1	129.0	72.1	129.6	16.2

[a] Downfield from internal TMS. [b] For the data in CDCl$_3$ and DMSO-d_6, see Table 1. [c] DMF = dimethylformamide.

CH_3OH-d_4 < DMF-d_7 < DMSO-d_6. The increase in the $^1J(C–Sn)$ value can be attributed to complexation in solution, which causes an increase in the s-character of hybrid tin-carbon orbitals. In agreement with conclusions reached on the basis of ^1H NMR data [1], the ^{13}C NMR data indicate that complexation does not affect the s-electron density on tin, but does raise it on the attached carbon.

Experimental

General

Natural abundance, proton-decoupled FT ^{13}C NMR spectra were recorded at 25°C on a Bruker-WH 90 DS spectrometer operating at 22.63 MHz. The pulse width of 6 s and 3 s delay were used, and between ca. 300 and 10000 Hz scans (depending on the nature of the compound) were accumulated with 16 K data points for a spectral width of 4807 Hz.

Preparation of compounds

The compounds Me_4Sn, Ph_4Sn, Bu_3SnCl, Ph_3SnCl and Bu_2SnCl_2 were commercial products. The compounds R_xSnCl_{4-x} (R = Me, x = 1, 2, 3; R = Bu, x = 1 and R = Ph, x = 1, 2) were prepared by standard methods [15,16].

The compounds $R_xSnR'_{4-x}$ (R = Me, Bu^n; R' = Ph and R = Me, R' = Bu^n; x = 3, 2, 1) were prepared from R_3SnCl or R_2SnCl_2 (R = Me, Bu^n, Ph) and the appropriate organolithium compound, RLi, in ether under nitrogen, as previously described [15].

The compounds Me_3SnX (X = OH, OCOMe, NO_3, CN, N_3, NCS) were prepared from Me_3SnCl and NaOH [17], $AgOCOMe/NO_3$ [18] and $NaCN/N_3/NCS$ [19], respectively, and Me_3SnNCO from Me_3SnOH and urea [20].

Preparation of DMSO complexes Ph_3SnCl, Ph_2SnCl_2, $PhSnCl_3$, Me_3SnN_3 and $Me_3SnOCOMe$

A. $Ph_2SnCl_2 \cdot 2DMSO$. A small amount of Ph_2SnCl_2 was dissolved in a minimum volume of DMSO. The mixture was allowed to stand for ca. 1 h and then ethanol was added dropwise. A white solid separated, and the liquid was decanted from this. The solid was washed twice with a small amount of ethanol and several times with hexane, than dried in vacuo. M.p. 132–134°C (Lit. [11a], 134–135°C). (Analysis. Found: C, 38.95; H, 4.41. $C_{16}H_{22}Cl_2S_2O_2Sn$ calcd.: C, 38.42; H, 4.40%).

B. $Ph_3SnCl \cdot DMSO$. This compound was prepared similarly as a white solid m.p. 106–108°C. (Analysis. Found: C, 51.63; H, 4.42. $C_{20}H_{21}ClSOSn$ calcd.: C, 51.81; H, 4.53%).

C. $PhSnCl_3 \cdot 2DMSO$. This compound was also prepared similarly as a white solid, m.p. 146–148°C. (Analysis. Found: C, 26.23; H, 3.60. $C_{10}H_{17}Cl_3S_2O_2Sn$ calcd.: C, 26.45; H, 3.71%).

D. $Me_3SnN_3 \cdot DMSO$ and $Me_3SnOCOMe \cdot DMSO$. These compounds were prepared by dissolving a small amount of the organotin compound in a minimum volume of DMSO then leaving the solution for several days at room temperature. The solid which appeared was separated by decantation and washed several times with small portions of ethanol and then with small portions of n-hexane, then dried under vacuum for several hours to give colourless cubic crystals of $Me_3SnN_3 \cdot DMSO$, m.p. 139–140°C (Analysis. Found: C, 20.92; H, 5.13; N, 14.61. $C_5H_{15}N_3SOSn$

calcd.: C, 21.15; H, 5.29; N, 14.80%), and colourless needles of $Me_3SnOCOMe \cdot$ DMSO, m.p. 164°C (with sublimation). (Analysis. Found: C, 28.32; H, 5.81. $C_7H_{18}SO_3Sn$ calcd.: C, 27.93; H, 6.00%).

Acknowledgement

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