Nuclear Spin–Spin Coupling between Directly Bound Tin Atoms Studied by a Novel Form of INDOR Spectroscopy

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Heteronuclear magnetic double-resonance experiments have been used to determine the signs and magnitudes of $^{1}J(^{119}\mathrm{Sn}^{119}\mathrm{Sn})$ and other coupling constants in $\mathrm{Li\{Sn(SnMe_3)_3\}\cdot 3thf}$, $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})\{\mathrm{P(OPh)_3}\}_2\{\mathrm{Sn(SnMe_3)_3}\}]$, and $\mathrm{SnMe_2(SnMe_3)_2}$. Values of *ca.* −5 000 Hz are found in the first of these compounds, and the results indicate that in general tin–tin coupling constants are determined mainly by changes in β_{SnSn}, the *s*-overlap integral for the Sn–Sn bond, brought about by changes in the substituents at the tin atoms. A new double-resonance method for recording the spectra of species in low abundance is also described.

It is generally the case that for the less electronegative elements indirect (electron-mediated) nuclear spin–spin reduced coupling constants $^{1}K(\mathrm{XY})$ can be discussed satisfactorily on the basis that the Fermi-contact mechanism dominates, and that the mean electronic excitation-energy approximation can be used.[1,2] In these circumstances changes in the coupling constants can be ascribed to variations in the *s* character of the hybrid orbitals used to form the X–Y bond and to changes in the effective nuclear charges of X and Y. In general, this type of behaviour is observed when both X and Y have an (accessible) open valence *s*-shell electronic configuration.[3] However, when the electronic configuration involves a closed valence *s* shell (*i.e.* a lone pair) as commonly occurs when X and/or Y is more electronegative, then the mean excitation-energy approximation becomes invalid. In this case a fuller treatment[4] shows that the coupling constant will also depend on the *s*-overlap integral, β_{XY}, for the X–Y bond and negative reduced coupling constants may arise. In addition, for very electronegative elements such as fluorine, coupling mechanisms other than Fermi contact may also become important, but this aspect will not be discussed here. The above type of behaviour is well exemplified by a recent discussion[5] of the couplings $^{1}K(\mathrm{C{-}X})$ and $^{1}K(\mathrm{Sn{-}X})$ (X = H, B, C, N, F, Si, P, Se, Sn, Te, or W), and also by the observation[6] that in trimethylstannyllithium, in which the tin atom can perhaps be regarded as having a lone pair of electrons, $^{1}K(\mathrm{SnC})$ is actually negative, whereas all other reported values of this coupling constant are positive.

It was reported[7] recently that in hexaorganoditin compounds, $\mathrm{R_3SnSnR_3}$, the magnitude of $^{1}J(^{119}\mathrm{Sn}^{119}\mathrm{Sn})$ shows a remarkable range of variation according to the nature of the organic groups attached to tin. This behaviour was attributed to changes in the effective nuclear charge of tin arising from different inductive effects of the organic groups (*i.e.* the mean electronic excitation-energy approximation was tacitly assumed to be valid), but the range of variation recorded (from 764 to 4 460 Hz) seems to be too large to be accounted for by this alone. A plot of $^{1}J(^{119}\mathrm{Sn}^{119}\mathrm{Sn})$ against the amount of α-chain branching in the alkyl groups attached to tin indicates that in hexa-t-butylditin (which has not yet been studied) the tin–tin coupling constant should be very small or even negative, a result which could not be accounted for if the mean electronic excitation-energy approximation is valid.

There are various difficulties in determining the sign of $^{1}J(^{119}\mathrm{Sn}^{119}\mathrm{Sn})$ in $\mathrm{Sn_2Bu^t_6}$ itself, and we have therefore studied three other species with tin–tin bonds in which it might be possible to confirm a breakdown of the mean

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[1] W. McFarlane, *Quart. Rev.*, 1969, **23**, 187.

[2] J. N. Murrell, *Progr. N.M.R. Spectroscopy*, 1971, **6**, 1.

[3] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1969, **51**, 2790.

[4] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.

[5] J. D. Kennedy, W. McFarlane, G. S. Pyne, and B. Wrackmeyer, *J.C.S. Dalton*, 1975, 386.

[6] J. D. Kennedy and W. McFarlane, *J.C.S. Chem. Comm.*, 1974, 983.

[7] T. N. Mitchell, *J. Organometallic Chem.*, 1974, **70**, C1.

electronic excitation-energy approximation. These are $\mathrm{Sn_AMe_2(Sn_BMe_3)_2}$, (I), $\mathrm{[Fe(\eta\text{-}C_5H_5)\{P(OPh)_3\}_2\{Sn_A(Sn_BMe_3)_3\}]}$, (II), and $\mathrm{Li[Sn_A(Sn_BMe_3)_3]\cdot 3thf}$, (III), and in all cases $^{1}\mathrm{H}\text{-}\{^{117/119}\mathrm{Sn}\}$ double-resonance experiments were used to obtain the required data (thf = tetrahydrofuran). In (III) the small value of $^{3}J(\mathrm{Sn\cdots H})$, together with the low abundance of species containing two magnetically active tin isotopes, necessitated the use of a modified form of INDOR spectroscopy, and this is also described in the present paper.

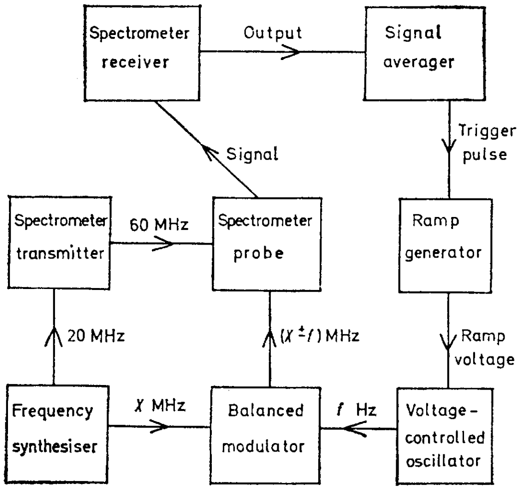

FIGURE 1 Instrumental arrangements used for averaging INDOR spectra produced by decoupling

EXPERIMENTAL

Tetrahydrofuran solutions of trimethylstannyl-lithium, and of (I), (II), and (III) were prepared essentially according to the literature,[8-10] and the last three species were examined as concentrated solutions in benzene at 23 °C. All spectra were recorded at constant magnetic field, B_0, and standard heteronuclear $^{1}\mathrm{H}\text{-}\{^{117/119}\mathrm{Sn}\}$ double-resonance experiments were made as described previously [11] using a JEOL spectrometer operating at a proton frequency of 60 MHz. The electronic arrangement used to acquire the time-averaged modified INDOR spectra was as shown in Figure 1. A pulse provided by the JEOL SB3 signal averager as it began to sweep triggered the time base of a Tel-equipment model D53 cathode-ray oscilloscope which provided a ramp voltage to drive the Exact Instruments model 196 voltage-controlled oscillator. The output from this (normally a sine wave with a frequency f in the range 500—100 000 Hz) was mixed in the balanced modulator with the radiofrequency (r.f.) output (X MHz) from the Schlumberger model FS-30 frequency synthesizer to give slowly varying radio frequencies $\nu_2 = (X + f)$ and $(X - f)$ which were then supplied to the probe of the spectrometer *via* a power amplifier. Normally X and f were chosen so that only one of $(X + f)$ and $(X - f)$ was in a range expected to give spectral perturbation, and experiments were made at several combinations of X and f to ensure the absence of spurious effects. Calibration was achieved by altering X by known amounts and allowing f to sweep through the same range. It was shown experimentally that the accuracy of linearity in frequency of the system is better than 2% of the total sweep width.

RESULTS

The results are given in the Table in which the signs of the coupling constants are based on the assumption that $^{2}J(^{117/119}\mathrm{Sn}\cdots\mathrm{H})$ is positive in all cases. It is to be noted that $\gamma(^{117}\mathrm{Sn})$ and $\gamma(^{119}\mathrm{Sn})$ are both negative. This assumption is justified in the Discussion section. In the case of (I) the couplings $^{2}J(^{117/119}\mathrm{Sn}\cdots\mathrm{H})$ and $^{3}J(^{117/119}\mathrm{Sn}\cdots\mathrm{H})$ were all large enough to yield clearly resolved satellites in the proton spectra and there was no difficulty in detecting lines due to species containing magnetic tin at two sites. Thus the double-resonance experiments and their interpretation were straightforward.[12]

In (III) the relevant isotopically substituted species are as follows: (*a*) $\mathrm{Li\{Sn(^{119}SnMe_3)(SnMe_3)_2\}}$; (*b*) $\mathrm{Li\{Sn(^{117}SnMe_3)(SnMe_3)_2\}}$; (*c*) $\mathrm{Li\{^{119}Sn(SnMe_3)_3\}}$; (*d*) $\mathrm{Li\{^{117}Sn(SnMe_3)_3\}}$; (*e*) $\mathrm{Li\{^{119}Sn(^{119}SnMe_3)(SnMe_3)_2\}}$; (*f*) $\mathrm{Li\{^{117}Sn(^{119}SnMe_3)(SnMe_3)_2\}}$; (*g*) $\mathrm{Li\{^{119}Sn(^{117}SnMe_3)(SnMe_3)_2\}}$; (*h*) $\mathrm{Li\{^{117}Sn(^{117}SnMe_3)(SnMe_3)_2\}}$. The three thf molecules are omitted in each case and the absence of a superscript indicates a tin isotope other than $^{117}\mathrm{Sn}$ or $^{119}\mathrm{Sn}$, which have $I = \frac{1}{2}$ and abundances of 7.7 and 8.7% respectively.

N.m.r. parameters of species with tin–tin bonds

		Species				
Parameter		$\mathrm{Sn_AMe_2(Sn_BMe_3)_2}$	$\mathrm{[Fe(\eta\text{-}C_5H_5)\{P(OPh)_3\}_2\{Sn_A(Sn_BMe_3)_3\}]}$	$\mathrm{Li\{Sn_A(Sn_BMe_3)_3\}\cdot 3thf}$ Sample 1 [a]	$\mathrm{Li\{Sn_A(Sn_AMe_3)_3\}\cdot 3thf}$ Sample 2 [a]	$\mathrm{(SnMe_3)_2}$ [b]
$^{1}J(^{119}\mathrm{Sn}\text{–}^{119}\mathrm{Sn})$/Hz [c]		$2\,900 \pm 50$	0 ± 20	$-5\,200 \pm 20$	$-4\,445 \pm 40$	$4\,460$
$^{2}J(^{119}\mathrm{Sn}\cdots\mathrm{H})$/Hz [c]	A	43.0 ± 0.5	41.9 ± 0.2	37.3 ± 0.1	38.4 ± 0.2	49.5
	B	46.5 ± 0.5				
$^{3}J(^{119}\mathrm{Sn}\cdots\mathrm{H})$/Hz [c]	A	-14.5 ± 0.3	$(-)\ 7.9 \pm 0.1$	$\mp 1.3 \pm 0.1$ [d]	$\mp 2.1 \pm 0.1$ [d]	-17.3
	B	-21.5 ± 0.3				
$\delta(^{119}\mathrm{Sn_A})$/p.p.m. [e]		-263 ± 1.5	-401.1 ± 0.5	$-1\,042.1 \pm 0.5$	$-1\,031.2 \pm 0.5$	
$\delta(^{119}\mathrm{Sn_B})$/p.p.m. [e]		-100.8 ± 2	-103 ± 0.5	-104.6 ± 0.1	-107.1 ± 0.5	-113
$\delta(^{1}\mathrm{H})$/p.p.m.	A	0.46 ± 0.02	0.69 ± 0.02	0.71 ± 0.01	0.71 ± 0.05	0.35 ± 0.12
	B	0.35 ± 0.02				

[a] The parameters for these species vary considerably according to sample conditions (*e.g.* concentration, age, *etc.*); the samples cited here gave parameters lying at the extreme ends of approximately linear ranges (see text). [b] Taken from W. McFarlane, *J. Chem. Soc.* (*A*), 1968, 1630. [c] Signs of coupling constants are based on $^{2}J(^{119}\mathrm{Sn}\cdots\mathrm{H})$ being positive. [d] Probably negative (see text). [e] To low field of $\mathrm{SnMe_4}$ [$\Xi(^{119}\mathrm{Sn})$ 37 290 665 Hz].

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[8] W. L. Wells and T. L. Brown, *J. Organometallic Chem.*, 1968, **11**, 271.

[9] R. Sommer, B. Schneider, and W. P. Neumann, *Annalen*, 1966, **692**, 12.

[10] W. Kläui and H. Werner, *J. Organometallic Chem.*, 1973, **54**, 331.

[11] J. D. Kennedy and W. McFarlane, *J.C.S. Dalton*, 1973, 2134.

[12] W. McFarlane, *Ann. Rep. N.M.R. Spectroscopy*, 1968, **1**, 135; 1972, **5**, 353.

Figure 2 shows schematically the positions of certain lines in the proton spectra given by these species; in the cases of (*e*) and (*h*) these lines are not in the positions expected on a first-order basis because $^{1}J(^{119}\mathrm{Sn}^{119}\mathrm{Sn})$ and $^{1}J(^{117}\mathrm{Sn}^{117}\mathrm{Sn})$ are not small compared with the differences in tin resonance frequencies $\nu(^{119}\mathrm{Sn_A}) - \nu(^{119}\mathrm{Sn_B})$ and $\nu(^{117}\mathrm{Sn_A}) - \nu(^{117}\mathrm{Sn_B})$. An adapted version of the computer program UEA BASIC (available from the University of East Anglia) was used, together with appropriate values (from preliminary experiments) of $^{1}J(^{119}\mathrm{Sn}{-}^{119}\mathrm{Sn})$, $^{1}J(^{117}\mathrm{Sn}{-}^{117}\mathrm{Sn})$, and the resonance frequencies, to calculate the proton spectra of species (*e*) and (*h*) shown in Figure 2. Because of the small value of $^{3}J(^{117/119}\mathrm{Sn}\cdots\mathrm{H})$ the lines *c*, *d*, *c'*, and *d'* were incompletely resolved and appeared as shoulders of the central peak in the proton spectrum (in the position indicated by a broken line in Figure 2), and the corresponding lines *e*, *f*, *etc.* from species containing two magnetically active tin isotopes were undetectable in the noise. However, irradiation at the resonance frequencies $\nu(^{117}\mathrm{Sn_A})$ or $\nu(^{119}\mathrm{Sn_A})$ caused $^{3}J(^{117}\mathrm{Sn}\cdots\mathrm{H})$ or $^{3}J(^{119}\mathrm{Sn}\cdots\mathrm{H})$ to collapse and gave a *ca.* 3% increase in the height of the central proton resonance, and thus made it possible to determine $\nu(^{117}\mathrm{Sn_A})$ and $\nu(^{119}\mathrm{Sn_A})$ to ± 10 Hz. In the cases of the species (*e*)—(*h*) the expected height increases of *a*, *b*, *etc.* were lost in the noise. This difficulty could be avoided in principle by accumulating a sufficient number of INDOR spectra,[13] *i.e.* by monitoring a proton transition and sweeping the irradiating frequency ν(Sn) through an appropriate range. However, the requirements of instrumental stability when many spectra are to be accumulated are extremely stringent, especially when the monitored line is a shoulder of, or is hidden by, a much stronger peak. The following alternative procedure was therefore developed, using the instrumental arrangements described in the Experimental section.

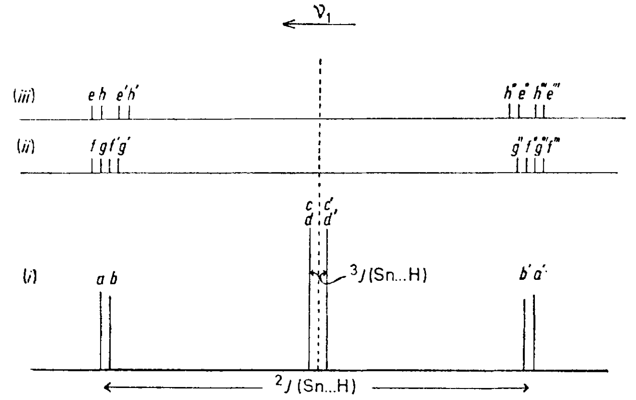

FIGURE 2 Schematic partial proton spectra of (III) for species containing magnetic tin. The vertical broken line is the position of the signal from molecules containing tin isotopes with $I = 0$. Species: (*i*) containing one magnetic tin nucleus; (*ii*) containing one ^{119}Sn and one ^{117}Sn nucleus, first-order spectra; (*iii*) containing two ^{119}Sn or two ^{117}Sn nuclei, second-order spectra. The relative intensities in (*i*)—(*iii*) are not drawn to scale and other lines near the centre arising from protons in methyl groups not attached to magnetic tin in (*ii*) and (*iii*) are not shown

The centre of the proton spectrum (*i.e.* the mid-point of *c*–*c'* or *d*–*d'*) was monitored with the amplitude, B_1, of the observing r.f. field set *ca.* 10 dB higher than for normal unsaturated observation. The irradiating frequency ν_2 [amplitude given by $\gamma(^{119}\mathrm{Sn})B_2/2\pi > 3|^{3}J(^{119}\mathrm{Sn}\cdots\mathrm{H})|$] was swept through an appropriate range at a rate of *ca.* 100 Hz s^{-1}, the signal averager being swept simultaneously. As ν_2 passed through $\nu(^{119}\mathrm{Sn_A})$ decoupling occurred and a positive perturbation was recorded by the signal averager as shown in Figure 3 for a typical sample of (III). The ringing pattern is a consequence of the high sweep rate used. The main peak in Figure 3 is flanked by satellites: those marked G and G' are symmetrically disposed about the main peak and arise from species (*g*) of which one is monitoring the resonance of the protons in methyl groups attached to non-magnetic isotopes of tin. The fact that these responses are obtained at all when the centre of the proton spectrum is monitored indicates that $^{4}J(^{117/119}\mathrm{Sn}\cdots\mathrm{H})$ must be zero or very nearly so. The separation G–G' gives the magnitude of $^{1}J(^{119}\mathrm{Sn}{-}^{117}\mathrm{Sn})$ as 4 950 Hz which corresponds to a value of 5 185 Hz for $|^{1}J(^{119}\mathrm{Sn}{-}^{119}\mathrm{Sn})|$. The chemical-shift difference between $^{119}\mathrm{Sn_A}$ and $^{119}\mathrm{Sn_B}$ is 20 950 Hz so that the ^{119}Sn spectrum of species (*e*) should not be first order. This accounts for the fact that the signals marked E and E' in Figure 3 are not placed symmetrically about the central peak; this is predicted in the spectrum calculated using UEA BASIC, and the positions of E and E' yield a value of 5 210 Hz for $|^{1}J(^{119}\mathrm{Sn}{-}^{119}\mathrm{Sn})|$, in good agreement with that deduced from $^{1}J(^{119}\mathrm{Sn}{-}^{117}\mathrm{Sn})$ above.

In order to compare the sign of the tin–tin coupling constant with that of $^{2}J(^{117/119}\mathrm{Sn}\cdots\mathrm{H})$ it was necessary to monitor lines such as *a* or *b* in the proton spectrum. The results were that when *b* was monitored a weak but sharp response was obtained in the high-frequency part (at 2 480 Hz relative to the centre) of the $^{119}\mathrm{Sn_A}$ spectrum, and when *b'* was monitored the response was at −2 480 Hz as illustrated in the upper traces of Figure 3. These responses were due to collapse of $^{3}J(^{119}\mathrm{Sn}\cdots\mathrm{H})$ in species (*g*) and show that $^{1}J(^{119}\mathrm{Sn}{-}^{117}\mathrm{Sn})$ is of opposite sign to $^{2}J(^{117}\mathrm{Sn}\cdots\mathrm{H})$. It is to be noted that $\gamma(^{119}\mathrm{Sn})$ is negative. However, when

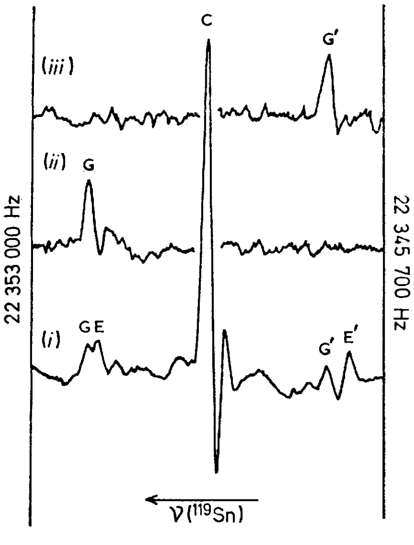

FIGURE 3 ^{119}Sn INDOR spectra of (III) produced by collapsing $^{3}J(^{119}\mathrm{Sn}\cdots\mathrm{H})$. These spectra were obtained by accumulating 32 scans, each of 25 s duration: (*i*) central line in proton spectrum monitored; (*ii*) line *b* (see Figure 2) monitored; (*iii*) line *b'* monitored

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[13] E. B. Baker, *J. Chem. Phys.*, 1962, **37**, 911.

a or *a′* was monitored either no response at all or only an extremely weak one was obtained in $^{1}H-\{^{119}Sn\}$ experiments. This was again a consequence of the second-order features of the spectrum arising from species (*e*) which leads to positions of the proton resonances *e* and *e′* which are not symmetrical about *a* and *a′*.

The foregoing experiments were all repeated with irradiation in the neighbourhood of $\nu(^{117}Sn_A)$ instead of $\nu(^{119}Sn_A)$ with the expected results. Thus when the central peak in the proton spectrum was monitored the values of $|^{1}J(^{119}Sn-^{117}Sn)|$ and $|^{1}J(^{117}Sn-^{117}Sn)|$ obtained were 4 960 and 4 730 Hz respectively, and responses were obtained when *a* and *a′*, but not *b* and *b′*, were monitored. It should be noted that small variations in the chemical shifts and coupling constants were observed for different samples of (III) (see Figure 4 and the Table). These appeared to depend on the thf content of the solution and may have parallels in the behaviour of Li(SnMe$_3$) in solution (see below) in which similar changes can be attributed to variations in the co-ordination sphere of the lithium atom.

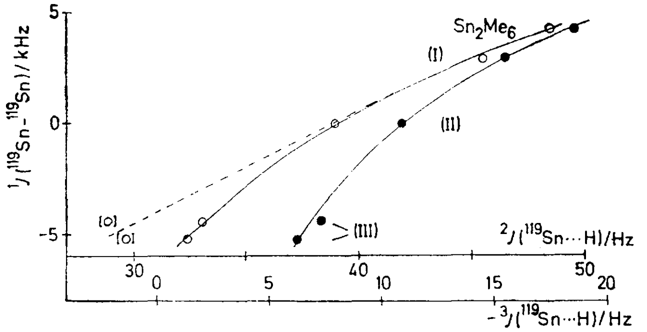

FIGURE 4 Plots of $^{1}J(^{119}Sn-^{119}Sn)$ against $^{2}J(^{119}Sn\cdots H)$ (●) and $^{3}J(^{119}Sn\cdots H)$ (○) for species with tin–tin bonds

The values of B_1, B_2, and rate of sweep, ν_2, used in the above experiments were those found experimentally to maximise the signal-to-noise ratio of the recorded responses. The high level of B_1 used had the additional effect of reducing the unwanted (constant) signal occurring at the monitoring point in the absence of B_2 by producing a substantial degree of saturation. It was possible to determine the positions of the responses in the tin spectra considerably more accurately by reducing B_2 and the sweep rate, although more scans were then needed to attain an adequate signal-to-noise ratio. The foregoing technique was not suitable for comparison of the signs of $^{3}J(^{117/119}Sn\cdots H)$ and $^{1}J(Sn-Sn)$ by irradiation at $\nu(^{119/117}Sn_B)$ because of the small value of the former coupling constant and the relatively large value of $^{2}J(^{117/119}Sn\cdots H)$. However, a consistent pattern of variation with sample conditions of the three coupling constants is established if it is assumed that the vicinal-tin–proton coupling constant is negative in (III).

In principle the spectra of (II) should be similar to those of (III), but as $^{3}J(^{117/119}Sn\cdots H)$ is considerably larger the satellites *c*, *d*, *c′*, and *d′* were clearly resolved from the central proton peak. It was also just possible to detect *e*, *f*, *h*, *etc.*, in a single scan of the proton spectrum, but it was still more convenient to use accumulated INDOR spectra to obtain the sign and magnitude of the tin–tin coupling constant. This is very small in (II) compared with $\nu(Sn_A) - \nu(Sn_B)$, and so second-order features were absent from the spectra of species corresponding to (*e*) and (*h*). The ^{117}Sn and ^{119}Sn spectra recorded in this way of Sn$_A$ were 1 : 2 : 1 triplets as a result of coupling to the two ^{31}P nuclei with $|^{2}J(^{119}Sn\cdots ^{31}P)|$ 500 ± 20 Hz. $^{1}H-\{^{31}P\}$ experiments showed that any coupling between phosphorus and the methyl protons was negligible, thus precluding a determination of the sign of $^{2}J(^{117/119}Sn\cdots ^{31}P)$, and any coupling $^{3}J(^{119}Sn\cdots ^{31}P)$ appeared to be small.

DISCUSSION

It is known [6,14] that $^{2}J(^{117/119}Sn\cdots H)$ may be of either sign; however, only one species, Li(SnMe$_3$), has been reported in which the sign is actually negative.[6] Furthermore in this species the coupling is small (*ca.* −6 Hz in thf solution) and the tin atom is directly associated with a highly electropositive atom. This results in a high concentration of *s* character in the tin–lithium bond with a corresponding reduction of *s* character and also of β_{SnC} for the other bonds to tin. Replacement of thf in the lithium co-ordination sphere by the stronger donor tris(dimethylamino)phosphine oxide (tdpo) further satisfies the electronic requirements of lithium [equation (1)] and the tin-containing moiety approximates even more closely to a free [SnMe$_3$]$^-$ anion in which the tin atom may be regarded as having an electron lone pair. This

$$\mathrm{Li(SnMe_3){\cdot}3thf} \underset{\mathrm{thf}}{\overset{\mathrm{tdpo}}{\rightleftharpoons}} \mathrm{Li(SnMe_3){\cdot}3tdpo} \qquad (1)$$

behaviour is manifested by a further decrease in $^{2}J(^{119}Sn\cdots H)$ to *ca.* −19 Hz and an accompanying change in $^{1}J(^{119}Sn-^{13}C)$ on addition of tdpo to thf solutions of Li(SnMe$_3$). There has been some discussion [15] as to whether tdpo does cause ionisation of the tin–lithium bond. This would probably be best investigated by conductivity measurements. If ion separation does in fact occur then our results suggest that a large part of the available *s* character is in the lone pair of the [SnMe$_3$]$^-$ anion, which would imply a pyramidal structure as is observed in the isoelectronic SbMe$_3$.

We have also found that high dilutions of Li(SnMe$_3$) in tdpo lead to a sign reversal of $^{2}J(^{119}Sn\cdots H)$ (*i.e.* the coupling constant becomes positive, see Figure 5) and this is accompanied by a reduction in the tin-119 shielding. The significance of this is uncertain at present, but the behaviour may result from the catalytic formation [15] of species containing Li{Sn(SnMe$_3$)$_3$}. However, at the extreme dilutions the possibility of adventitious oxidation or hydrolysis cannot be completely excluded.

The environment of the trimethylstannyl groups in the other compounds, (I)—(III), examined in this work is on the other hand in no way abnormal: each tin is bound covalently to four other atoms, none of which is highly electropositive, and the coupling constants $^{2}J(^{117/119}Sn\cdots H)$ themselves all have a substantial magnitude. Thus there can be very little doubt that the assignment of a positive sign to these couplings is correct, and the

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[14] W. McFarlane, *J. Chem. Soc.* (*A*), 1967, **528**.

[15] A. T. Weibel and J. P. Oliver, *J. Organometallic Chem.*, 1974, **82**, 281.

other signs in the Table then follow from the double-resonance experiments.

Our results show that in (III) $^1K(\mathrm{SnSn})$ has a substantial negative value, and indeed the figure of -311 nm^{-3} appears to be the most negative reduced coupling constant yet reported. This can be attributed to the presence of a lone electron pair on one of the tin atoms which makes π_{SnSn}, the mutual polarisability of the valence *s* electrons of the tin atoms,[4] negative, together with the relatively large value [3] of $\psi(0)^2$ for tin (which is a fourth-row element) which leads to a large magnitude for the coupling. Figure 4 shows plots of $^1J(^{119}\mathrm{Sn}\text{–}^{119}\mathrm{Sn})$ for several species against $^2J(^{119}\mathrm{Sn}\cdots\mathrm{H})$ and $^3J(^{119}\mathrm{Sn}\cdots\mathrm{H})$, and it is apparent that either of the proton–tin coupling constants can be used as a guide to the magnitude and sign of $^1J(^{119}\mathrm{Sn}\text{–}^{119}\mathrm{Sn})$ in species with tin–tin bonds. A similar relation is already established [14] for $^1J(^{119}\mathrm{Sn}\text{–}^{13}\mathrm{C})$.

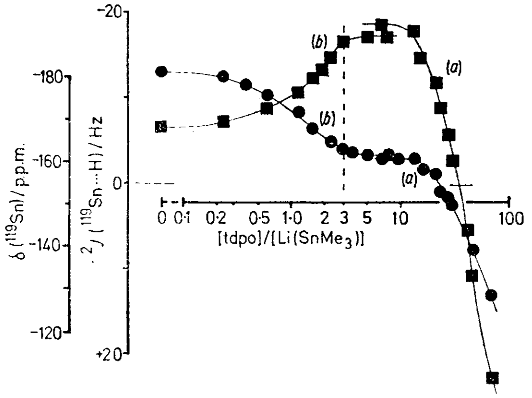

FIGURE 5 Effects on $\delta(^{119}\mathrm{Sn})$ (●) and $^2J(^{119}\mathrm{Sn}\cdots\mathrm{H})$ (■) of adding tdpo to (*a*) 7.5 mol % and (*b*) 8.3 mol % solutions of $\mathrm{Li(SnMe_3)}$ in thf in the absence of lithium halide. Deterioration of the solutions precluded a complete set of dilution experiments on a single sample and there are therefore small discrepancies in the overlap regions

It is impossible to account for our results without assuming that the use of the mean electronic excitation-energy approximation to describe the Fermi-contact contribution to $^1K(\mathrm{SnSn})$ is grossly invalid. This indicates that β_{SnSn} must be extremely sensitive to the substituents on the tin atoms. When one of the substituents is effectively a lone electron pair, as in (III), β_{SnSn} is very small indeed and π_{SnSn} has a substantial negative value; when one of the tin atoms is bound to iron, β_{SnSn} is small and π_{SnSn} appears to be approximately zero; and when each tin atom has only carbon and tin as its substituents β_{SnSn} is larger so that π_{SnSn} takes on a positive value. However, even in this last case β_{SnSn} appears to be very sensitive to some property (probably the bulk) of the substituents, and we believe it is this factor rather than changes in the effective nuclear charge of tin [7] which dominates the observed variations in $^1J(^{119}\mathrm{Sn}\text{–}^{119}\mathrm{Sn})$. This does not preclude changes in $\psi(0)^2$ and α_s^2 having some effect on the coupling constant, and as β_{SnSn} becomes large these two factors will become more important. This could well be the case for example in $[\{\mathrm{SnBu_2(O_2CMe)}\}_2]$ in which $^1J(^{119}\mathrm{Sn}\text{–}^{119}\mathrm{Sn}) =$ *ca.* 11 000 Hz, although the situation is complicated here by the bridging acetate groups.[16]

The technique used to record the tin spectra of (II) and (III) is very convenient in use and has affinities both with Freeman's [17] 'isotope filter' and with Ziessow's [18] transient nutation experiments. Its main advantages over them and conventional INDOR spectroscopy [13] are the superior sensitivity for nuclei of lower magnetogyric ratio than the proton, and much less stringent demands on instrumental stability which permits the accumulation of large numbers of scans. When B_2 is set high enough [typically $|\gamma(\mathrm{X})B_2/2\pi| > |3J(\mathrm{H}\cdots\mathrm{X})|$] to achieve maximum sensitivity the value of ν_{X} can be determined with a precision of *ca.* $\pm 3J(\mathrm{H}\cdots\mathrm{X})$ and the tolerable frequency drift of ν_1 (which is also the necessary setting accuracy of the position of the recorder pen) is *ca.* $J(\mathrm{H}\cdots\mathrm{X})/3$. The maximum permissible sweep rate of ν_2 depends on B_1 and $T_1(\mathrm{H})$, but not significantly on $T_1(\mathrm{X})$ when $|\gamma_{\mathrm{X}}| \ll \gamma_{\mathrm{H}}$: high levels of B_1 increase the suppression of the unwanted central proton signal from molecules containing non-magnetic isotopes of X and also give stronger responses. However, such high levels must be compensated for by using high values of $\mathrm{d}\nu/\mathrm{d}t$ which lead to distorted line shapes. A fuller account of this technique, together with applications to the study of other isotopes of low abundance (*e.g.* ^{15}N, ^{29}Si, and ^{57}Fe), will be given elsewhere.

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