# Nuclear Spin–Spin Coupling between Tin and Other Directly Bound Elements

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Heteronuclear double-resonance experiments are used to determine the signs and magnitudes of the spin-coupling constants between tin and the directly bound elements boron, nitrogen, silicon, tin, tellurium, and tungsten in some trimethylstannyl derivatives. These and other coupling constants involving tin are compared with the corresponding couplings involving carbon and it is found that for X = H, B, C, F, Si, Sn, Te, and W, $^{1}K$(Sn–X) is approximately nine times $^{1}K$(C–X) whereas for X = N, $P^{III}$, $P^{V}$, and Se this is not so. For X = N and $P^{V}$ the reduced couplings to carbon and tin are of opposite sign. The results are consistent with a molecular orbital theory which does not use the mean excitation energy approximation and, in general, it is concluded that the *s*-overlap integral $\beta_{Sn-X}$ is smaller than $\beta_{C-X}$ which leads to larger negative contributions to the mutual polarizability in the case of tin compounds.

THEORIES of the origin of spin–spin coupling between the nuclei of directly bound elements suggest that there should be marked similarities in the patterns of the behaviour of the group IV elements carbon and tin.[1,2] In order to test the general conclusions of these theories and to assess their range of applicability throughout the periodic table, it is useful to make a detailed comparison of the magnitudes and particularly the signs of coupling constants involving directly bound carbon or tin in analogous situations.[3,4] The signs and magnitudes of coupling constants between carbon [5] and many other elements are now available in series of representative molecules, but the amount of corresponding data for tin is much more limited. Previously the signs of the following coupling constants have been reported: Sn–H,[6] Sn–C,[7] Sn–F,[8] Sn–P,[9] Sn–Se,[10] and Sn–Sn,[11] and in this paper we report measurements of the signs and magnitudes of $^{1}K$(Sn–B), $^{1}K$(Sn–N), $^{1}K$(Sn–Si), $^{1}K$(Sn–Te), and $^{1}K$(Sn–W), and also of $^{1}K$(C–B) which is needed for comparison. These additional data make it possible to survey spin coupling involving tin or carbon and elements throughout the periodic table, and to delineate the region in which the coupling constants change sign.

Since many of the isotopes of interest in this work occur in only low natural abundance ($^{13}$C, 1·1%; $^{15}$N, 0·35%; $^{29}$Si, 4·6%; $^{119}$Sn, 8·6%; $^{125}$Te, 8%; $^{183}$W, 14%) the $^{1}$H-{X} double-resonance method was used to get adequate sensitivity and also to permit unambiguous determinations of relative signs. It also has the advantage of versatility and makes it possible to determine n.m.r. parameters for many different nuclei in a short space of time.[12]

## EXPERIMENTAL

All proton spectra were recorded at 60 MHz using a modified JEOL C60-H spectrometer with methylene chloride or benzene added to each sample to provide a field-frequency locking signal. $^{1}$H-{$^{11}$B}, $^{1}$H-{$^{13}$C}, $^{1}$H-{$^{15}$N}, $^{1}$H-{$^{29}$Si}, $^{1}$H-{$^{77}$Se}, $^{1}$H-{$^{119}$Sn}, $^{1}$H-{$^{125}$Te}, and $^{1}$H-{$^{183}$W} Double-resonance experiments were performed as described elsewhere [10,13] using a Schlumberger FS-30 frequency synthesizer which also controlled the spectrometer r.f. oscillator. The method of preparation and conditions of measurement of each sample were as follows. Criteria of purity were correct physical properties and the absence of spurious peaks in the proton n.m.r. spectrum.

$MeB(NMe_2)_2$.—Prepared by the reaction between methyllithium and $(Me_2N)_2BCl$ in diethyl ether followed by distillation under reduced pressure; examined as a neat liquid.

$Me_3SnB(NMe_2)_2$.—Prepared by the reaction between $Me_3SnLi$ and $(Me_2N)_2BCl$ in tetrahydrofuran followed by distillation under reduced pressure; examined as a neat liquid.

$Me_3SnB(NMe_2)Cl$.—Prepared by the reaction of $Me_3SnB(NMe_2)_2$ with two equivalents of gaseous hydrogen chloride followed by distillation under reduced pressure; examined as a neat liquid.

$Me_3Sn^{15}NHPh$.—$Me_3SnNEt_2$ (from $Me_3SnCl$ and $Et_2NLi$ in diethyl ether) was mixed with half a molar equivalent of aniline to give $(Me_3Sn)_2NPh$ which was purified by distillation. This was mixed with one molar equivalent of $Ph^{15}NH_2$ (96% isotopic purity) when heat was evolved and the resulting $Me_3SnNHPh$ (containing 48% of the required $^{15}$N species) was distilled. It was examined with *ca.* 10% benzene added to provide a locking signal.

$Me_3SnSiMe_3$.—Prepared by the addition of lithiumtrimethyltin in tetrahydrofuran to trimethylchlorosilane in diethyl ether at −70 °C and distillation of the product; examined as a 90% solution in benzene.

$Me_3SnSnPh_3$.—Prepared similarly from $Ph_3SnLi$ and $Me_3SnCl$; examined as a saturated solution in $CH_2Cl_2$.

$(Me_3Sn)_2Se$.—Prepared by dissolving elemental selenium in a solution of lithiumtrimethyltin in tetrahydrofuran at 0 °C, and then adding trimethyltin chloride and distilling at 61—63 °C/0·9 Torr; examined as a 50% solution in $CH_2Cl_2$.

$(Me_3Sn)_2Te$.—Prepared by stirring elemental tellurium with a solution of lithiumtrimethyltin at room temperature for 72 h, adding trimethyltin chloride, and distilling at 97—

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

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

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

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

[5] J. B. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, 1972.

[6] C. Schumann and H. Dreeskamp, *J. Magnetic Resonance*, 1970, **3**, 204.

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

[8] W. McFarlane and R. J. Wood, *Chem. Comm.*, 1969, 262.

[9] H. Elser and H. Dreeskamp, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 619.

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

[11] W. McFarlane, *J. Chem. Soc.* (*A*), 1968, 1630.

[12] W. McFarlane, *Det. Org. Struct. Phys. Meth.*, 1971, **4**, 139.

[13] W. McFarlane and D. S. Rycroft, *J.C.S. Dalton*, 1973, 2162.

99 °C/3 Torr; examined as a 70% solution in dichloromethane.

[$Me_3SnW(CO)_3(\pi$-$C_5H_5)$].—This compound was kindly loaned by Professor M. F. Lappert and was examined as a *ca.* 50% solution in benzene.

## RESULTS

As each of the compounds examined presented different problems and therefore required a different approach the double-resonance experiments are discussed individually. In all cases for which sign determinations have been made $^{2}J(^{119}Sn$–C–H) in trimethylstannyl groups has been found to be positive and is known to increase algebraically as the electronegativity of the groups attached to tin increases.[7] Only when the effective nuclear charge on tin is high as in $Me_3SnLi$ or $MeSnH_2^-$ must the possibility of a sign reversal for this coupling be contemplated,* and in none of our compounds (including the boron derivatives) does this arise. Most of the signs of coupling constants given below are therefore based on the assumption that $^{2}J(^{119}Sn$–C–H) is positive. It should be noted that of the nuclides considered here $^{15}N$, $^{29}Si$, $^{119}Sn$, and $^{125}Te$ have negative magnetogyric ratios and this was allowed for in the interpretation of the experiments. $\Xi$(X) Is the resonant frequency of X at a magnetic field strength such that $Me_4Si$ would give a proton resonance at exactly 100 MHz,[12] and the chemical shifts are quoted in the convention that a high-field resonance is given a negative sign. The chemical shift standards used for the various nuclei are as follows: $^{1}H$, $Me_4Si$; $^{11}B$, $BF_3{\cdot}Et_2O$; $^{13}C$, $Me_4Si$; $^{15}N$, $Me_4N^+I^-$ in $(CD_3)_2SO$; $^{29}Si$, $Me_4Si$; $^{31}P$, 85% $H_3PO_4$; $^{77}Se$, $Me_2Se$; $^{119}Sn$, $Me_4Sn$; $^{125}Te$, $Me_2Te$; $^{183}W$, $WF_6$.

We have generally attributed observed increases in peak heights during double-resonance experiments to the collapse of unresolved satellite lines rather than to nuclear Overhauser enhancements. In view of the low magnetogyric ratios of many of the nuclei involved this is probably correct; however, this in no way affects the signs of the coupling constants derived from these experiments.

$MeB(NMe_2)_2$.—The B-methyl proton resonance was *ca.* 3 Hz wide at half-height as a result of incompletely averaged coupling to $^{11}B$ and its height could be increased by a factor of *ca.* 2 by $^{1}H$–{$^{11}B$} decoupling. This gave the boron resonance frequency to ±5 Hz. Of the two $^{13}C$ satellites of the B-methyl proton resonance, that at low field was hidden by other lines and therefore the high-field one was used in the determination of $^{1}J(^{11}B-^{13}C)$. $^{1}H$–{$^{11}B$} Experiments then gave the magnitude of the coupling constant and showed it to be of the same sign as $^{1}J(^{13}C-H)$ which is known to be positive.[4] Attempts to use changes of line shape in $^{1}H$–{$^{13}C$} experiments to give the sign of $^{2}J(^{11}B \cdots {}^{1}H)$ were unsuccessful owing to the low signal-to-noise ratio at which the satellite line was observed. There was some broadening of the *N*-methyl resonance as a result of interaction with $^{11}B$.

$Me_3SnBCl(NMe_2)$.—Initially, attempts were made to determine the sign of $^{1}J(^{11}B-^{119}Sn)$ in the molecule $Me_3SnB(NMe_2)_2$, but the rate of quadrupolar relaxation of the $^{11}B$ nucleus ($I = 3/2$) was so great (as indicated by a measured [14] width at half-height for the $^{11}B$ spectrum of *ca.* 200 Hz) that there was no detectable residual broadening of the Sn–methyl resonance and therefore $^{1}H$–{$^{11}B$} experiments produced no result. In the chloro-compound, however, the relaxation rate is somewhat slower (half-height width [14] of the boron spectrum <150 Hz) and $^{1}H$–{$^{11}B$} experiments gave a *ca.* 10% increase in the height of the Sn–methyl resonances. Observations of the $^{119}Sn$ satellites of the Sn–methyl resonance then showed that $^{2}J(^{119}Sn \cdots {}^{1}H)$ and $^{1}J(^{119}Sn-^{11}B]$ were of opposite sign and an accurate value for $^{1}J(^{119}Sn-^{11}B)$ was obtained from $^{1}H$–{$^{119}Sn$} experiments.

In $Me_3SnB(NMe_2)_2$ the magnitude of $^{1}J(^{119}Sn-^{11}B)$ was obtained from $^{1}H$–{$^{119}Sn$} experiments using the Sn–methyl resonance and the sign is assumed to be the same as in $Me_3SnBCl(NMe_2)$.

TABLE 1

N.m.r. parameters of $MeB(NMe_2)_2$

| | |
|---|---|
| $^{1}J(^{11}B-^{13}C)$ | +59 ± 5 Hz |
| $^{1}K$(B–C) | +6·1 $nm^{-3}$ |
| $^{1}J(^{13}C-^{1}H)$ (B) | +115 ± 0·5 Hz |
| $\Xi(^{11}B)$ | 32 085 058 ± 8 Hz |
| $\delta(^{11}B)$ | +33·5 ± 0·3 p.p.m. |
| $\Xi(^{13}C)$ | 25 144 980 ± 10 Hz |
| $\delta(^{13}C)$ | −1 ± 1 p.p.m. |
| $\delta(^{1}H)$ (B–Me) | +0·12 ± 0·01 p.p.m. |
| $\delta(^{1}H)$ (N–Me) | +2·65 ± 0·01 p.p.m. |

TABLE 2

N.m.r. parameters of $Me_3SnBCl(NMe_2)$ and $Me_3SnB(NMe_2)_2$

| | $Me_3SnBCl(NMe_3)$ | $Me_3SnB(NMe_2)_2$ |
|---|---|---|
| $^{1}J(^{119}Sn-^{11}B)$/Hz | −1007 ± 10 | −953 ± 10 |
| $^{1}K$(B–Sn)/$nm^{-3}$ | +70·1 | +66·3 |
| $^{2}J(^{119}Sn \cdots {}^{1}H)$/Hz | +49·2 ± 0·2 | +42·3 ± 0·2 |
| $\Xi(^{11}B)$/Hz | 32 085 388 ± 10 | 32 085 205 ± 10 |
| $\delta(^{11}B)$/p.p.m. | +44·4 ± 0·3 | +39·0 ± 0·3 |
| $\Xi(^{119}Sn)$/Hz | 37 285 488 ± 30 | 37 285 068 ± 30 |
| $\delta(^{119}Sn)$/p.p.m. | −139 ± 1 | −150 ± 1 |
| $\delta(^{1}H)$(Sn–Me)/p.p.m. | +0·18 ± 0·01 | 0·0 |
| $\delta(^{1}H)$(N–Me) (i)/p.p.m. | +2·73 ± 0·01 | +2·67 ± 0·1 |
| $\delta(^{1}H)$(N–Me) (ii)/p.p.m. | +2·75 ± 0·01 | |

There was also some broadening of the $NMe_2$ proton resonances in this molecule which was removed by irradiation at the $^{11}B$ frequency and it was observed that the two inequivalent methyl resonances (rotation about the B–N bond is slow on an n.m.r. time scale at room temperature) had different widths, indicating that the two $^{11}B$–$^{1}H$ coupling constants are not equal.

$Me_3Sn^{15}NHPh$.—This compound was obtained as a 1 : 1 mixture with the $^{14}N$($I = 1$) species in which spin coupling interactions are averaged to zero by the nuclear quadrupole moment. No $^{14/15}N$ isotope effects were noticed in the proton spectrum and the $^{14}N$ containing species is ignored in the following discussion. There was a very small coupling [$^{3}J(^{15}N \cdots {}^{1}H)$ ~0·2 Hz] between the $^{15}N$ and the protons of the methyl groups which gave a slight broadening of their resonance, and removal of this by $^{15}N$ irradiation gave a *ca.* 10% increase in their intensity. From the differential effects obtained in this way on the high- and low-field $^{119}Sn$ satellites of the methyl groups $^{1}J(^{15}N-^{119}Sn)$ and $^{2}J(^{119}Sn \cdots {}^{1}H)$ were found to be of opposite sign and the former had a magnitude of 25 ± 1 Hz. Since $^{2}J(^{119}Sn \cdots {}^{1}H)$ in a Sn–methyl group is generally positive (and certainly so when the tin is bound to an electronegative atom such as nitrogen) it follows that $^{1}J(^{15}N-^{119}Sn)$ is negative, as is the corresponding reduced coupling constant. The magnitude of $^{1}J(^{15}N-^{119}Sn)$ was confirmed by $^{1}H$–{$^{15}N$} experiments using the Sn satellites of the N–H resonance and these also showed $^{2}J(^{119}Sn$–N–$^{1}H)$ to be

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* In $Me_3SnLi$,3THF the coupling $^{2}J(^{119}Sn \cdots H)$ varies from −3 to −15 Hz according to conditions. J. D. Kennedy and W. McFarlane, *J.C.S. Chem. Comm.*, 1974, 983.

[14] H. Nöth, personal communication.

positive. In principle it should have been possible to use $^{1}\mathrm{H}$-{$^{119}\mathrm{Sn}$} experiments to compare the signs of $^{1}J(^{15}\mathrm{N}{-}^{1}\mathrm{H})$ and $^{1}J(^{119}\mathrm{Sn}{-}^{15}\mathrm{N})$ but the overall complexity of the tin spectrum and the small size of $^{1}J(^{119}\mathrm{Sn}{-}^{15}\mathrm{N})$ prevented this.

$(\mathrm{Me_3Sn})_2\mathrm{Se}$ *and* $(\mathrm{Me_3Sn})_2\mathrm{Te}$.—In the tellurium compound $^{3}J(^{125}\mathrm{Te}\cdots{}^{1}\mathrm{H})$ is large enough for the $^{125}$Te satellites to be clearly resolved in the proton spectrum and the experiments used to determine the signs of the various coupling constants were straightforward. In the selenium compound owing to the smaller magnetogyric ratio of $^{77}$Se the coupling $^{3}J(^{77}\mathrm{Se}\cdots{}^{1}\mathrm{H})$ is smaller and no $^{77}$Se satellites were observed; however, peak heights could be increased by *ca.* 6% by irradiation at the appropriate $^{77}$Se frequency and so the magnitude of $^{1}J(^{77}\mathrm{Se}{-}^{119}\mathrm{Sn})$ and its sign relative to that of $^{2}J(^{119}\mathrm{Sn}{-}^{1}\mathrm{H})$ could be determined.

TABLE 3

N.m.r. parameters of $\mathrm{Me_3Sn^{15}NHPh}$

| | |
|---|---|
| $^{1}J(^{119}\mathrm{Sn}{-}^{15}\mathrm{N})$ | −26·3 ± 0·5 Hz |
| $^{1}K(\mathrm{Sn{-}N})$ | −5·86 nm$^{-3}$ |
| $^{1}J(^{15}\mathrm{N}{-}^{1}\mathrm{H})$ | −73·3 ± 0·3 Hz |
| $^{2}J(^{119}\mathrm{Sn{-}C}{-}^{1}\mathrm{H})$ | +54·2 ± 0·2 Hz |
| $^{2}J(^{119}\mathrm{Sn{-}N}{-}^{1}\mathrm{H})$ | +22·5 ± 0·2 Hz |
| $^{3}J(^{15}\mathrm{N}\cdots{}^{1}\mathrm{H})$ | *ca.* 0·2 Hz |
| $\Xi(^{119}\mathrm{Sn})$ | 37 292 360 ± 90 Hz |
| $\delta(^{119}\mathrm{Sn})$ | +46·4 ± 2 p.p.m. |
| $\Xi(^{15}\mathrm{N})$ | 10 133 446 ± 1 Hz |
| $\delta(^{15}\mathrm{N})$ | −9·4 ± 0·1 p.p.m. |
| $\delta(^{1}\mathrm{H})(\mathrm{Me})$ | + 0·21 ± 0·01 p.p.m. |
| $\delta(^{1}\mathrm{H})(\mathrm{NH})$ | +2·82 ± 0·1 p.p.m. |

TABLE 4

N.m.r. parameters of $(\mathrm{Me_3Sn})_2\mathrm{E}$

| | E = $^{77}$Se | E = $^{125}$Te |
|---|---|---|
| $^{1}J(^{119}\mathrm{Sn{-}E})$/Hz | +1060 ± 10 | −1385 ± 10 |
| $^{1}K(^{19}\mathrm{Sn{-}E})$/nm$^{-3}$ | −124·0 | −98·1 |
| $^{2}J(^{119}\mathrm{Sn}\cdots{}^{1}\mathrm{H})$/Hz | +56·2 ± 0·2 | +55·3 ± 0·1 |
| $^{3}J(\mathrm{E}\cdots{}^{1}\mathrm{H})$/Hz | $\lvert J\rvert < 1{\cdot}5$ | −2·9 ± 0·1 |
| $\Xi(^{119}\mathrm{Sn})$/Hz | 32 292 327 ± 8 | 37 288 173 ± 3 |
| $\delta(^{119}\mathrm{Sn})$/p.p.m. | +44·5 | −66·8 |
| $\Xi(\mathrm{E})$/Hz | 19 061 097 ± 8 | 31 511 513 ± 8 |
| $\delta(\mathrm{E})$/p.p.m. | −546·7 | −1214 |

$\mathrm{Me_3SnSiMe_3}$ *and* $\mathrm{Me_3SnSnPh}$.—In the first of these compounds the coupling constants were such that most of the $^{119}$Sn and $^{29}$Si satellites were visible in the proton spectrum and therefore standard double-resonance experiments using lines from the species $\mathrm{Me_3{}^{119}Sn^{29}SiMe_3}$ which was present in 0·4% abundance gave all the required relative signs. In $\mathrm{Me_3SnSnPh_3}$ no coupling was observed between the protons of the phenyl groups and the more distant tin nucleus but this did not prevent determination of the required relative signs of the other coupling constants. The large tin chemical-shift difference (61·5 p.p.m. = 1380 Hz at our magnetic field strength) made it possible to obtain $^{1}J(^{119}\mathrm{Sn}{-}^{119}\mathrm{Sn})$ directly in the species $\mathrm{Me_3{}^{119}Sn^{119}SnMe_3}$ but in view of the second-order character of the tin spectrum of this molecule it was found better to measure $^{1}J(^{119}\mathrm{Sn}{-}^{117}\mathrm{Sn})$ and multiply the result by 1·046(5). The large tin chemical-shift difference also made it possible to assign unequivocally the two couplings $^{2}J$ and $^{3}J$ between $^{119}$Sn and the protons of the methyl groups and thus justify the assumptions made in other work.[11,15]

$[\mathrm{Me_3SnW(CO)_3}(\pi\text{-}\mathrm{C_5H_5})]$.—The couplings between both tin and tungsten and the cyclopentadienyl protons in this compound are small, but it was just possible to resolve a double set of satellites at the base of the $\pi$-$\mathrm{C_5H_5}$ resonance and double-resonance experiments were used to assign these as arising from the presence of $^{117/119}$Sn and $^{183}$W. It was not possible to observe any $\pi$-$\mathrm{C_5H_5}$ resonance from the species $\mathrm{Me_3{}^{117/119}Sn^{183}W(CO)_3}(\pi\text{-}\mathrm{C_5H_5})$ however. No $^{183}$W satellites of the methyl resonance were observed, but irradiation at the appropriate $^{183}$W frequency gave a *ca.* 7% increase in the height of this peak and similar selective irradiation experiments using the $^{119}$Sn satellites of the methyl resonance gave the magnitude of $^{1}J(^{119}\mathrm{Sn}{-}^{183}\mathrm{W})$ and its sign relative to that of $^{2}J(^{119}\mathrm{Sn}\cdots{}^{1}\mathrm{H})$.

TABLE 5

N.m.r. parameters of $\mathrm{Me_3SnXR_3}$

| | $\mathrm{XR_3} = {}^{29}\mathrm{SiMe_3}$ | $\mathrm{XR_3} = {}^{119}\mathrm{SnPh_3}$ |
|---|---|---|
| $^{1}J(^{119}\mathrm{Sn{-}X})$/Hz | +656 ± 10 | +4240 ± 80 |
| $^{1}K(^{119}\mathrm{Xn{-}X})$/nm$^{-3}$ | +73·7 | +255 |
| $^{2}J(^{119}\mathrm{Sn}\cdots{}^{1}\mathrm{H})$/Hz | +46·75 ± 0·1 | +51·6 ± 0·2 |
| $^{3}J(^{119}\mathrm{Sn}\cdots{}^{1}\mathrm{H})$/Hz | −31·2 ± 0·1 | |
| $^{2}J(\mathrm{X}\cdots{}^{1}\mathrm{H})$/Hz | +6·74 ± 0·08 | |
| $^{3}J(\mathrm{X}\cdots{}^{1}\mathrm{H})$/Hz | $\lvert J\rvert < 1{\cdot}5$ | −17·7 ± 0·2 |
| $\Xi(^{119}\mathrm{Sn})$/Hz | 37 285 942 ± 50 | 37 287 263 ± 7 |
| $\delta(^{119}\mathrm{Sn})$/p.p.m. | −126·7 | −91·5 |
| $\Xi(\mathrm{X})$/Hz | 19 866 966 ± 3 | 37 284 950 ± 50 |
| $\delta(\mathrm{X})$/p.p.m. | −11·0 ± 0·2 | −153 ± 2 |
| $\delta(^{1}\mathrm{H})(\mathrm{Sn})$/p.p.m. | +0·065 | +0·42 |
| $\delta(^{1}\mathrm{H})(\mathrm{X})$/p.p.m. | +0·23 | +7·00 to 7·62 |
| $\Xi(^{13}\mathrm{C})(\mathrm{Sn})$/Hz | 25 144 714 ± 2 | 25 144 793 ± 2 |
| $\delta(^{13}\mathrm{C})(\mathrm{Sn})$/p.p.m. | −11·52 | −8·4 |
| $\Xi(^{13}\mathrm{C})(\mathrm{X})$/Hz | 25 145 032·5 ± 4 | |
| $\delta(^{13}\mathrm{C})(\mathrm{X})$/p.p.m. | +1·13 | |
| $^{1}J(^{13}\mathrm{C{-}H})(\mathrm{Sn})$/Hz | +128·0 ± 0·5 | +129·8 ± 0·2 |
| $^{1}J(^{13}\mathrm{C{-}H})(\mathrm{X})$/Hz | +120·15 ± 0·5 | |

TABLE 6

N.m.r. parameters of $[\mathrm{Me_3SnW(CO)_3}(\pi\text{-}\mathrm{C_5H_5})]$

| | |
|---|---|
| $^{1}J(^{119}\mathrm{Sn}{-}^{183}\mathrm{W})$ | −150 ± 5 Hz |
| $^{1}K(\mathrm{Sn{-}W})$ | +81 nm$^{-3}$ |
| $^{2}J(^{119}\mathrm{Sn}\cdots{}^{1}\mathrm{H})$ | +48·7 ± 0·2 Hz |
| $^{3}J(^{119}\mathrm{Sn}\cdots{}^{1}\mathrm{H})$ | 0·85 ± 0·05 Hz |
| $^{2}J(^{183}\mathrm{W}\cdots{}^{1}\mathrm{H})$ | 1·40 ± 0·05 Hz |
| $^{3}J(^{183}\mathrm{W}\cdots{}^{1}\mathrm{H})$ | $\lvert J\rvert < 0{\cdot}6$ Hz |
| $\Xi(^{119}\mathrm{Sn})$ | 37 292 271 ± 8 Hz |
| $\delta(^{119}\mathrm{Sn})$ | +43·1 ± 0·3 p.p.m. |
| $\Xi(^{183}\mathrm{W})$ | 4 149 570 ± 1 Hz |
| $\delta(^{183}\mathrm{W})$ | +2933·9 ± 0·3 p.p.m. |
| $\delta(^{1}\mathrm{H})(\mathrm{Me})$ | +0·62 ± 0·01 p.p.m. |

## DISCUSSION

In Table 7 are compared the signs and magnitudes of reduced coupling constants $^{1}K$(defined[1] by $K(\mathrm{XY}) = 4\pi^2 J(\mathrm{XY})/\gamma_{\mathrm{X}}\gamma_{\mathrm{Y}}h$ to avoid dependence upon individual nuclear properties) involving tin or carbon directly bound to another element. Ideally the values of $^{1}K(\mathrm{C{-}X})$ in t-butyl derivatives should be used, but in many cases these are not available, and as the range of variation of $^{1}K(\mathrm{C{-}X})$ as the nature of the alkyl groups attached to carbon changes is small the use of results for methyl compounds should not seriously invalidate the comparison.

According to Pople and Santry's molecular orbital treatment[1] the Fermi contact interaction will dominate the coupling mechanism in most cases and the reduced coupling constant is then given by equation (1) in which

$$^{1}K_{\mathrm{XY}} = \frac{64\pi^2\beta^2}{9}\,\psi^2_{ns(\mathrm{X})}(0)\cdot\psi^2_{ns(\mathrm{Y})}(0)\cdot\pi_{\mathrm{XY}} \qquad (1)$$

$\psi_{ns}{}^2(0)$ is the valence *s*-electron density at the nucleus.

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[15] R. J. H. Clark, A. G. Davies, R. J. Puddephatt, and W. McFarlane, *J. Amer. Chem. Soc.*, 1969, **91**, 1334.

TABLE 7

Reduced coupling constants involving tin or carbon and a directly bound element

| Element X | Tin compound | $^{1}K$(Sn–X) / nm$^{-3}$ | $^{1}K$(C–X) / nm$^{-3}$ | Carbon compound | $K$(Sn)/$K$(C) | Notes Sn, C |
|---|---|---|---|---|---|---|
| H | $Me_3SnH$ | +38·9 | +4·24 | $Me_3CH$ | 9·2 | *b, c* |
| B | $Me_3SnB(NMe_2)_2$ | +66·3 | +6·1 | $CH_3B(NMe_2)_2$ | 10·9 | *a, a* |
| C | $Me_4Sn$ | +29·3 | +4·3 | $CH_3CH_3$ | 6·8 | *d, e* |
| N | $Me_3SnNHPh$ | −5·85 | +1·47 | $CH_3NH_2$ | −4·0 | *a, f* |
| F | $(PhMe_2CCH_2)_3SnF$ | −54·6 | −5·88 | $Me_3CF$ | 9·3 | *g, c* |
| Si | $Me_3SnSiMe_3$ | +73·7 | +8·4 | $(CH_3)_4Si$ | 8·8 | *a, h* |
| $P^{III}$ | $Me_3SnPPh_2$ | −32·8 | −1·2 | $CH_3PPh_2$ | 27·3 | *i, j* |
| $P^{V}$ | $[Me_3SnPPh_2W(CO)_5]$ | −2·8 | +2·5 | $[CH_3PPh_2Cr(CO)_5]$ | −1·1 | *k, k* |
| Se | $(Me_3Sn)_2Se$ | −124 | −7·3 | $(CH_3)_3Se$ | 17·0 | *a, l* |
| Sn | $Me_3SnSnMe_3$ | +268 | +29·3 | $(CH_3)_4Sn$ | 9·1 | *m, d* |
| Te | $(Me_3Sn)_2Te$ | −98·1 | −11·5 | $(CH_3)_2Te$ | 8·5 | *a, l* |
| W | $[Me_3SnW(CO)_3(\pi\text{-}C_5H_5)]$ | +81 | (+) 10·6 | $[CH_3W(CO)_3(C_5H_5)]$ | 7·6 | *a, n* |

[a] This work. [b] Ref. 6. [c] Value based on results for several closely related molecules. [d] Ref. 7. [e] Ref. 16. [f] Ref. 17. [g] Ref. 8. [h] Ref. 18. [i] Ref. 9. [j] Ref. 19. [k] Ref. 20. [l] Ref. 21. [m] Ref. 11. [n] Kindly measured by Miss E. T. Hughes from $^{13}C$ spectrum.

$\pi_{XY}$ Is the mutual polarizability [22] of the atoms X and Y and is the change in electron density in the *s*-orbital of one atom which arises when the energy of the other *s*-orbital changes. The sign of $K$ resides in $\pi_{XY}$ which itself depends upon the relative energies of the various electronic excited states. In many cases (*e.g.* C–C, C–H) only the lowest excited state is important and it is then possible to make the mean excitation-energy approximation and replace $\pi_{XY}$ by $\alpha^2(X) . \alpha^2(Y)/\Delta E$ to give equation (2) in which $\alpha^2$ represents the *s*-character

$$^{1}K_{XY} = \frac{64\pi^2\beta^2}{9} . \psi^2_{ns(X)}(0) . \psi^2_{ns(Y)}(0) . \alpha^2(X)\alpha^2(Y)/\Delta E \quad (2)$$

of the hybrid orbital used to form the X–Y bond and $\Delta E$ is an average excitation energy.[1,23] This expression cannot yield a negative reduced coupling constant, so when these arise equation (1) *must* be used.

Measurements of C–H coupling constants have indicated that in most cases $\Delta E$ in equation (2) can be regarded as being approximately constant and most of the variation can be ascribed to changes in effective nuclear charge or of hybridization which affect $\psi^2_{ns}(0)$ and $\alpha^2$ respectively.[24] If neglect of changes in $\Delta E$ in an approximate treatment is justified then for analogous molecules coupling constants involving tin should be larger than those involving carbon by a factor of $\pi^2_{Sn}(0)/\psi_C{}^2(0)$. The data for the positive couplings listed in Table 7 support this to ±20% and suggest that equation (3) is valid in these cases, the factor of 9·0 also

$$^{1}K(Sn–X) = 9·0 \times {}^{1}K(C–X) \quad (3)$$

being a reasonable value for the ratio of the *s*-electron densities at the tin and carbon nuclei. Thus for the mean excitation energy approximation to be valid the requirements are that $K$ should be positive and that equation (3) should apply.

$\pi_{XY}$ Is related to the valence *s*-overlap integral $\beta$ between A and B and is positive when this is large. As $\beta$ becomes smaller, additional excitations, of which some make negative contributions, become important, and $\pi_{XY}$ passes through zero and becomes negative.[1] Thus for intermediate values of $\beta$ the mutual polarizability will be close to zero and will also be very sensitive to small changes in X and Y. Equation (1) must then be used to describe the coupling and it is not in general to be expected that there will be any simple relation between $^{1}K$(C–X) and $^{1}K$(Sn–X) in these circumstances. For small $\beta$, as is expected to occur for X = F, $\pi_{CX}$ and $\pi_{SnX}$ will have large negative values and again $^{1}K$ will not be very sensitive to changes in the excitation energies arising from changes in $\beta$. It will still be necessary to use equation (1) to describe the coupling, but variations in $^{1}K$ will be due largely to changes in $\psi^2(0)$ and $\alpha^2$ and equation (3) should again apply. The data of Table 7 support this view in that for X = F or Te the ratio $^{1}K$(Sn–X)/$^{1}K$(C–X) has values of 9·3 and 8·5 respectively.

When X = N, $P^{III}$, $P^{V}$, or Se it is clear that equation (3) does not apply even approximately and that in all these cases there is a substantial additional negative contribution to $^{1}K$(Sn–X). That is, for any particular class of compound $\beta$ is smaller for the Sn–X than for the C–X bond so that the contributions from excitations to higher electronic states are greater and $\pi_{SnX}$ is generally more negative than $\pi_{CX}$.

In their rationale of nuclear spin–spin coupling between directly bound elements, Jameson and Gutowsky [2] suggest that when X belongs to a given group of the periodic table $K$(X–Y) should increase in magnitude regardless of its sign, as the atomic number of X increases, provided that X is an atom with, or which has accessible, an open *s*-shell configuration. Both carbon and tin come into this category and the accuracy with which equation (3) is obeyed for Y = H, B, C, F, Si, Sn, Te, and W supports their contention.

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[16] N. Sheppard and R. M. Lynden-Bell, *Proc. Roy. Soc.*, 1962, **A269**, 385.

[17] L. Paulillo and E. D. Becker, *J. Magnetic Resonance*, 1970, **3**, 200.

[18] R. R. Dean and W. McFarlane, *Mol. Phys.*, 1967, **12**, 289.

[19] W. McFarlane, *Proc. Roy. Soc.*, 1968, **A306**, 185.

[20] W. McFarlane and D. S. Rycroft, *J.C.S. Dalton*, 1974, 1977.

[21] W. McFarlane, *Mol. Phys.*, 1967, **12**, 243.

[22] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, 1947, **A191**, 39.

[23] H. M. McConnell, *J. Chem. Phys.*, 1956, **24**, 460.

[24] J. H. Goldstein, V. S. Watts, and L. S. Rattet, *Progr. N.M.R. Spectroscopy*, 1971, **8**, 103.

However, the results for Y = N, $P^{III}$, $P^{V}$, or Se are not in agreement with this and also contradict their view that for all X in group IV $K$(X–Y) should have the same sign for a given Y. We believe therefore that the approach of Pople and Santry [1] is better.

It has recently been found [25] that $^1J(^{119}Sn-^{119}Sn)$ in hexaorganodistannanes varies over a remarkably wide range as the nature of the organic groups bound to tin varies. For example,[11] in $Me_3SnSnMe_3$ this coupling constant is +4462 Hz whereas in $Pr^i_2Bu^tSnSnBu^tPr^i_2$ it is only (+) 780 Hz and molecules with intermediate values are known.[25] The variations have been attributed [25] to differences in the electron-donating abilities of the various alkyl groups which would presumably affect $\psi_{(Sn)}{}^2(0)$ in equation (1) or (2), but the magnitude of the effect appears to be much too great for this to be the major factor. We therefore suggest that in these species the presence of bulky ligands on tin leads to a reduced $\beta$ for the tin–tin bond so that negative contributions to $\pi_{SnSn}$ become significant and the coupling constant is smaller. Thus changes in $\alpha_{Sn}{}^2$ and $\psi_{Sn}{}^2(0)$ have only small effects upon $^1J$(Sn–Sn) and equation (1) must be used; it is even possible that species will exist in which $^1J$(Sn–Sn) is negative although in these $\beta$ may be so small that the stability is low.

The tin chemical shifts in the compounds studied are in accord with empirical trends which have been noted elsewhere.[26] The measurement of $\delta(^{119}Sn)$ in $Me_3SnB(NMe_2)Cl$ is the first report of a tin chemical shift in a compound with a B–Sn bond. The small electropositive boron atom [note the small value of $^1J$(C–H) in $CH_3B(NMe_2)_2$ as an indication of the $\sigma$-electron donating characteristics of the boron atom] can be expected to contribute to a high-field tin shift by analogy with the result for monomeric $Me_3SnLi$,3THF for which $\delta(^{119}Sn) = -180$ p.p.m. However, in the boron compound the possibility of $\pi$-bonding between tin and boron must also be taken into account: the large difference between the values of $^2J(^{119}Sn \cdots {}^1H)$ in $Me_3SnB(NMe_2)_2$ and $Me_3SnBCl(NMe_2)$ suggests that some such effect may be important and this is being investigated further. The values of $\delta(^{119}Sn)$ in $(Me_3Sn)_2E$ (E = S, Se, or Te) are +85, +44·5, and −66·8 p.p.m. and probably reflect the increasing bulk and polarizability of the chalcogen rather than changes in electronegativity. On this basis, however, the higher field tin shift in $Me_3SnSnPh_3$ is surprising.

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

[26] J. D. Kennedy and W. McFarlane, *Rev. Silicon, Germanium, Tin, and Lead Chem.*, 1974, **1**, 235.

[27] R. Schwerthöffer, Dissertation, University of Münich, 1974.