Binuclear Organometallic Compounds. Part IX.[1] Nuclear Magnetic Double Resonance Studies of Tin-119 Chemical Shifts in Compounds with Transition Metal-to-Tin Bonds

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The magnetic shieldings determined by heteronuclear double resonance are reported for 35 organotin compounds containing transition-metal atoms. Exceptionally low-field chemical shifts in species with light transition-metal atoms were attributed to a large paramagnetic contribution arising from small average excitation energies associated with d_π–d_π bonding. Heavier transition metals increase the tin shielding but there is no apparent correlation with the *s*-electron density on the tin atom.

THIS work derives from complementary interests in two laboratories. At Sussex, numerous compounds having bonds between a transition-metal M and a Group IV Main Group metal M′ (Si, Ge, or Sn) have been prepared and studied and the nature of the M–M′ bond in the series of compounds $[(cp)M(CO)_3M'Me_3]$ ($cp = \eta\text{-}C_5H_5$) (Table 1) assessed. At Sir John Cass College heteronuclear double resonance has been extensively used to obtain n.m.r. data, including studies of $^1H\text{-}\{^{119}Sn\}$ double resonance in organotin compounds.

Although many ^{119}Sn chemical shifts of organotin compounds appear in the literature, measured either by direct observation [2] or by heteronuclear double-resonance spectroscopy,[3-5] only one organotin–transition-metal species $[Mn(CO)_5SnMe_3]$ has been examined.[2b] We report in this paper ^{119}Sn chemical shifts of 35 organotin–transition-metal compounds measured by heteronuclear $^1H\text{-}\{^{119}Sn\}$ double resonance. This technique for determining chemical shifts has been well established for many of the naturally occurring isotopes with nuclear spin $I = \frac{1}{2}$ (*e.g.* ^{13}C, ^{15}N, ^{31}P, ^{77}Se, ^{103}Rh, ^{183}W, ^{195}Pt, and ^{199}Hg).[6-13] The greater precision and inherent gain in sensitivity of the double-resonance

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[1] Part VIII, M. F. Lappert and G. Speier, *J. Organometallic Chem.*, 1974, **80**, 329.

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[3] A. G. Davies, P. G. Harrison, J. D. Kennedy, T. N. Mitchell, R. J. Puddephatt, and W. McFarlane, *J. Chem. Soc.* (*C*), 1969, 1136.

[4] P. G. Harrison, S. E. Ulrich, and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1971, **93**, 5398.

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[6] J. K. Becconsall and P. Hampson, *Mol. Phys.*, 1965, **10**, 21.

[7] D. W. W. Anderson, J. E. Bentham, and D. W. H. Rankin *J.C.S. Dalton*, 1973, 1215.

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

[9] W. McFarlane and R. J. Wood, *J.C.S. Dalton*, 1972, 1397.

[10] W. McFarlane, *Chem. Comm.*, 1969, 700.

[11] W. McFarlane and D. S. Rycroft, *J.C.S. Chem. Comm.*, 1973, 336.

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[13] W. McFarlane, *Chem. Comm.*, 1971, 609.

technique has permitted ^{119}Sn chemical-shift determinations on moderately weak solutions, so that effects due to solvents and/or auto-association can be allowed for.[14] Attention has been confined to the ^{119}Sn isotope ($I = \frac{1}{2}$) because it has a somewhat higher abundance (*ca.* 8·7%) than ^{117}Sn (*ca.* 7·6%) and isotope effects upon the shielding are known to be very small and certainly negligible in the present context.[5]

TABLE 1

Spectroscopic data for compounds (7), (8), and (14) [(cp)M(CO)$_3$SnMe$_3$] (M = Cr, Mo, or W)

M	Cr	Mo	W
Mössbauer spectrum: quadrupole splitting (Δ) and isomer shift (δ/mm s^{-1}) [a]	Δ, 1·36; δ, 1·41	Δ, 1·25; δ, 1·43	Δ, 0·79; δ, 1·36
D(M–Sn)/kcal mol^{-1} [b]	50	67	72
ν(M–Sn) far i.r./cm^{-1} [b,c,d]	183	170	166
^{1}H N.m.r., δ (cp)/p.p.m.[c,e,f]	4·75	5·24	5·33
^{119}Sn N.m.r.; δ(^{119}Sn)/p.p.m.[g]	161	121	42
^2J(^{119}Sn $\cdots$ H)/Hz [g]	48·1	48·3	48·5

[a] Relative to SnO$_2$ at *ca.* 20 °C, from S. R. Bird, J. D. Donaldson, S. A. Keppie, and M. F. Lappert, *J. Chem. Soc.* (*A*), 1971, 1311. [b] Mass spectrometric or i.r. data from D. J. Cardin, S. A. Keppie, M. F. Lappert, M. R. Litzow, and T. R. Spalding, *J. Chem. Soc.* (*A*), 1971, 2262. [c] D. J. Cardin, S. A. Keppie, and M. F. Lappert, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 365. [d] In Polythene disc. [e] D. J. Cardin, S. A. Keppie, and M. F. Lappert, *J. Chem. Soc.* (*A*), 1970, 2594. [f] CDCl$_3$ solution. [g] See Table 2, this work.

Most previous work in this area has been interpreted in terms of variations in inductive electron withdrawal from the tin atom by its substituents by d_π–p_π bonding or dispersion force effects.[2-5] Possible changes in electronic excitation energies have generally been ignored which is probably reasonable for the species studied hitherto, but in our compounds this neglect may be unjustified owing to d_π–d_π overlap, and ^{119}Sn n.m.r. may be a useful probe into this type of interaction between tin and a transition metal.

EXPERIMENTAL

Samples were generally prepared as saturated benzene solutions, although in cases of low solubility chlorinated solvents were used. The proton spectra were recorded in either frequency sweep mode (*i.e.* constant B_0) or field sweep mode, with or without the field-frequency locking circuits actuated by the solvent, in order to achieve the optimum conditions for each individual sample. Data were obtained using a JEOL C-60-H instrument, operating at a proton frequency of 60 MHz containing an extra coil within the probe. The ^{119}Sn frequency (*ca.* 22·4 MHz) was provided by a Schlumberger frequency synthesiser model FS 30, and the frequency of the nominal 60 MHz oscillator was locked to the synthesiser. ^{119}Sn INDOR spectra were obtained by monitoring a suitable satellite line and driving the free-running oscillator of the frequency synthesiser as described previously.[15] The ^{119}Sn resonance frequencies obtained were first corrected to a field strength appropriate to a SiMe$_4$ proton resonance at 60 MHz and then multiplied by 10/6 to give Ξ(^{119}Sn) values.[16] The Ξ value has been defined as the resonant frequency in a polarising magnetic field of strength such that SiMe$_4$ gives a proton resonance at exactly 100 MHz.[16] The convention is adopted that a positive value for δ(^{119}Sn) corresponds to a shift to low field of the reference compound, tetramethyltin, *i.e.* to reduced shielding. Tetramethyltin is taken as having Ξ(^{119}Sn) = 37·290665 MHz.

Compounds (2)—(5) were supplied by Mr. M. Webb,[17] (7), (8), (14),[18] and (28) [19] by Dr. S. A. Keppie, (33)—(36) by Dr. J. McMeeking,[20] and (37) by Dr. C. J. Cardin,[21] research colleagues at the University of Sussex. Preparations of the compounds (6), (9)—(13), (15)—(19),[22] (20),[23,24] (22) and (23),[25] (24),[24] (25),[25] (26) and (27),[26] (29),[27] (30) and (31),[28] and (32) [20] were in accordance with published methods.

RESULTS AND DISCUSSION

The tin-119 chemical shifts relative to Me$_4$Sn are given in Table 2, a positive sign indicating a shift to low field of the reference. The coupling constant ^2J(^{119}Sn $\cdots$ H) is also given as it can be used to assess the degree of inductive electron withdrawal from tin by its substituents. A large positive value of this coupling arises when the tin atom has substituents of high electronegativity and is due to an increased effective nuclear charge of the tin atom and/or diversion of *s*-character into the Sn–Me bonds.[29] Similarly, small values are found when the tin atom has electropositive substituents, *e.g.* in Me$_3$SnLi ^2J(^{119}Sn $\cdots$ H) varies from 5 to 8 Hz according to conditions.[4] Selected chemical shifts are presented graphically in the Figure together with results for Me$_{4-n}$SnCl$_n$ for comparison. Four of the species examined here (2)—(5) do not have a direct tin–transition-metal bond and give tin chemical shifts in the region to be expected for substituted tetra-alkyltin derivatives, *i.e.* close to $\delta = 0$. The remaining compounds have chemical shifts covering a range of more than 700 p.p.m. which is as great as that previously recorded for all types of organotin compound.[2-5] In fact, the ^{119}Sn chemical shifts for (23), (27), (30), and (31) are the highest yet reported by substantial margins.[4]

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[14] *E.g.*, V. N. Torocheshnikov, A. P. Tupčiauskas, N. M. Sergeyev, and Yu. A. Ustynuk, *J. Organometallic Chem.*, 1972, **35**, C25.

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[16] W. McFarlane, *Ann. Rev. N.M.R. Spectroscopy*, 1968, **1**, 131.

[17] M. F. Lappert and M. Webb, unpublished work.

[18] D. J. Cardin, S. A. Keppie, and M. F. Lappert, *J. Chem. Soc.* (*A*), 1970, 2594.

[19] R. B. King and K. H. Pannell, *Inorg. Chem.*, 1968, **7**, 1510.

[20] B. Çetinkaya, M. F. Lappert, J. McMeeking, and D. E. Palmer, *J.C.S. Dalton*, 1973, 1202.

[21] C. J. Cardin, D. J. Cardin, and M. F. Lappert, *J. Organometallic Chem.*, 1973, **60**, C70.

[22] D. H. Harris, S. A. Keppie, and M. F. Lappert, *J.C.S. Dalton*, 1973, 1653; and earlier papers in this series.

[23] H. C. Clark and J. H. Tsai, *Inorg. Chem.*, 1966, **5**, 1407.

[24] W. A. G. Graham, W. Jetz, P. B. Simons, and J. A. J. Thompson, *Inorg. Chem.*, 1966, **5**, 2217.

[25] W. A. G. Graham and J. A. J. Thompson, *Inorg. Chem.*, 1967, **6**, 1365.

[26] M. Bigorgne and O. Kahn, *J. Organometallic Chem.*, 1967, **10**, 137; H. Behrens and R. Weber, *Z. anorg. Chem.*, 1955, **281**, 190.

[27] E. W. Abel and S. Moorhouse, *J. Organometallic Chem.*, 1970, **24**, 687.

[28] W. A. G. Graham and D. J. Patmore, *Inorg. Chem.*, 1967, **6**, 981.

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

This range of shielding is accompanied by values of $^2J(^{119}\mathrm{Sn}\cdots\mathrm{H})$ lying within the limits of 24 to 53 Hz, which suggests that the tin chemical shift cannot be dominated by the inductive effect of its substituents, because in general a shift to low field (positive δ) is associated with a *large* value of $^2J(^{119}\mathrm{Sn}\cdots\mathrm{H})$ in compounds Me$_3$SnX or Me$_2$SnX$_2$ without tin–transition-metal bonds.[30] One of the most striking features of the results is the large differences in shielding observed for compounds in which tin is bound to different transition metals in the same Group of the Periodic Table: there is no reason to doubt that apparently analogous pairs of compounds [*e.g.* (10) and (16)] have similar structures.

TABLE 2

^{119}Sn Chemical shifts in organotin–transition metal compounds

Compound no.	Compound	$^2J(^{119}\mathrm{Sn}\cdots\mathrm{H})$/Hz	$\delta(^{119}\mathrm{Sn})$/p.p.m.[a]	Conditions
(1)	Me$_4$Sn	53·9	0	+5% CH$_2$Cl$_2$
(2)	[(cp)$_2$Ti(Cl)CH$_2$SnMe$_3$]	52·3	+14 ± 1	Satd. C$_6$H$_6$ soln.
(3)	[(cp)$_2$Ti(CH$_2$SiMe$_3$)CH$_2$SnMe$_3$]	50·0	+4 ± 2	Satd. C$_6$H$_6$ soln.
(4)	[(cp)$_2$Zr(Cl)CH$_2$SnMe$_3$]	50·9	+15 ± 1	Satd. C$_6$H$_6$ soln.
(5)	[(cp)$_2$Hf(Cl)CH$_2$SnMe$_3$]	50·8	+16·5 ± 2	Satd. C$_6$H$_6$ soln.
(6)	[(cp)$_2$Ta(H)$_2$SnMe$_3$]	35·7	+53 ± 2	Satd. C$_6$H$_6$ soln.
(7)	[(cp)Cr(CO)$_3$SnMe$_3$]	48·1	+161 ± 0·5	C$_6$H$_6$ soln.
(8)	[(cp)Mo(CO)$_3$SnMe$_3$]	48·3	+121 ± 0·5	C$_6$H$_6$ soln.
(9)	[(cp)$_2$Mo(H)SnMe$_3$]	38·2	+123 ± 2	Satd. C$_6$H$_6$ soln.
(10)	[(cp)$_2$Mo(Cl)SnMe$_3$]	42·5	+90 ± 2	Satd. C$_6$H$_6$ soln.
(11)	[(cp)$_2$Mo(Br)SnMe$_3$]	42·5	+90 ± 2	Satd. C$_6$H$_6$ soln.
(12)	[(cp)$_2$Mo(I)SnMe$_3$]	42·0	+96 ± 2	Satd. C$_6$H$_6$ soln.
(13)	[(cp)$_2$Mo{C(CO$_2$Me)=C(CO$_2$Me)H}SnMe$_3$]	38·9	+119 ± 1	Satd. C$_6$H$_6$ soln.
(14)	[(cp)W(CO)$_3$SnMe$_3$]	48·5	+42 ± 0·5	C$_6$H$_6$ soln.
(15)	[(cp)$_2$W(H)SnMe$_3$]	38·3	−41 ± 2	Satd. C$_6$H$_6$ soln.
(16)	[(cp)$_2$W(Cl)SnMe$_3$]	42·5	−70 ± 5	Satd. C$_6$H$_6$ soln.
(17)	[(cp)$_2$W(Br)SnMe$_3$]	42·5	−74 ± 2	Satd. C$_6$H$_6$ soln.
(18)	[(cp)$_2$W(I)SnMe$_3$]	42·2	−74 ± 2	Satd. C$_6$H$_6$ soln.
(19)	[(cp)$_2$W{C(CO$_2$Me)=C(CO$_2$Me)H}SnMe$_3$]	38·1	−40 ± 2	Satd. C$_6$H$_6$ soln.
(20)	[Mn(CO)$_5$SnMe$_3$]	48·5	+63 ± 1	C$_6$H$_6$ soln.
(21)	[Mn(CO)$_5$SnMe$_3$] [b]	48·5	+66·3	Cyclohexane soln.
(22)	[{Mn(CO)$_5$}$_2$SnMe$_2$]	37·0	+150 ± 1	Satd. C$_6$H$_6$ soln.
(23)	[{Mn(CO)$_5$}$_3$SnMe]	24	+284 ± 2	Satd. CDCl$_3$ soln.
(24)	[Re(CO)$_5$SnMe$_3$]	47·0	−89 ± 1	Satd. C$_6$H$_6$ soln.
(25)	[{Re(CO)$_5$}$_2$SnMe$_2$]	36·6	−223 ± 2	Satd. CDCl$_3$ soln.
(26)	[Fe(CO)$_4$(SnMe$_3$)$_2$]	49·5	+79 ± 1	C$_6$H$_6$ soln.
(27)	[{Fe(CO)$_4$SnMe$_2$}$_2$]	51·8	+257 ± 2	CDCl$_3$ soln.
(28)	[(cp)Fe(CO)$_2$SnMe$_3$]	49	+147 ± 0·5	C$_6$H$_6$ soln.
(29)	[Co(CO)$_4$SnMe$_3$]	52·8	+151 ± 0·2	C$_6$H$_6$ soln.
(30)	[{Co(CO)$_4$}$_2$SnMe$_2$]	46·1	+293 ± 1	Satd. C$_6$H$_6$ soln.
(31)	[{Co(CO)$_4$}$_3$SnMe]	33·8	+483 ± 1	Satd. C$_6$H$_6$ soln.
(32)	[(Ph$_3$P)$_2$Rh(C≡CPh)$_2$SnMe$_3$] [c]	50·0	+172 ± 2	Satd. CH$_2$Cl$_2$ soln.
(33)	[(Ph$_3$P)$_2$Ir(CO)(C≡CPh)$_2$SnMe$_3$] [c]	46·5	−106 ± 2	Satd. CH$_2$Cl$_2$ soln.
(34)	[(Me$_2$PhP)$_2$Ir(CO)(C≡CPh)$_2$SnMe$_3$] [c]	46·0	−123 ± 2	Satd. CH$_2$Cl$_2$ soln.
(35)	*cis*-[(Ph$_3$P)$_2$Pt(C≡CPh)SnMe$_3$]	43·5	−46 ± 2	Satd. CH$_2$Cl$_2$ soln.
(36)	*cis*-[(MePh$_2$P)$_2$Pt(C≡CPh)SnMe$_3$]	43·0	−48 ± 1	Satd. [^{2}H$_8$]toluene soln.
(37)	*cis*-[(Ph$_3$P)$_2$Pt(CF=CF$_2$)SnMe$_3$]	43·9	0 ± 2	Satd. CDCl$_3$ soln.

[a] A positive sign indicates a shift to low field of tetramethyltin. [b] Ref. 2. [c] Precise stereochemistry not yet established.

Tin chemical shifts are known to be very sensitive to the co-ordination number of the tin atom; typically an increase from four to five is accompanied by a decrease in $\delta(^{119}\mathrm{Sn})$ of 100—200 p.p.m.[2,3] In the present work donor solvents which might co-ordinate to the tin atom and so produce such changes have been avoided, and intermolecular association is unlikely as the shifts were obtained in dilute solutions and were essentially independent of concentration. Thus it is reasonable to assume that all of the compounds examined here contained four-co-ordinate tin.

The major contributions to tin shielding (and that of other heavy nuclei) are the diamagnetic (σ^d) and the paramagnetic (σ^p) terms: other factors which might be important such as the magnetic and electric anisotropies of the solvent have effects which are small compared with the overall range of tin chemical shifts.[31] The diamagnetic contribution arises largely from the inner electrons of the atom in question and variations in response to changes in chemical environment are generally neglected. However, it has been suggested recently[32] that the diamagnetic contribution due to nearest neighbours of the nucleus is important, and satisfactory interpretations of carbon-13 chemical shifts have been obtained on this basis.[32] This contribution is proportional to Z/r, where Z is the atomic number of the contributing atom and r is its distance from the relevant nucleus.[33] For series of organotin sulphides this can account for some of the trends observed,[34] but it must be realised that the term is linear with respect

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[30] R. C. Poller, 'The Chemistry of Organotin Compounds,' Logos Press, London, 1970, p. 234 *et seq.*

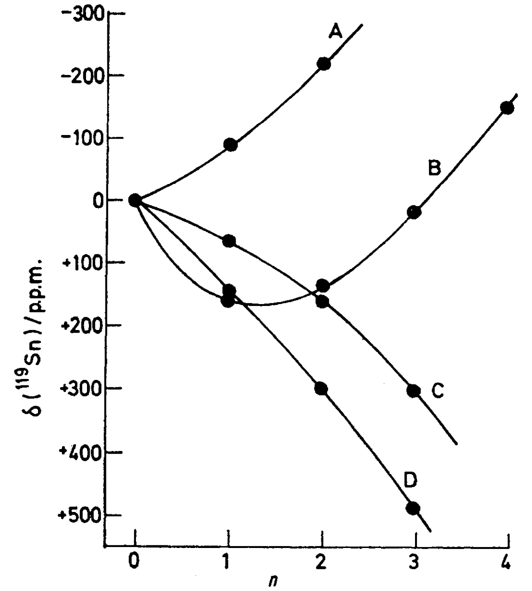
[31] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution N.M.R. Spectroscopy,' Pergamon Press, Oxford, 1965.

[32] J. Mason, *J. Chem. Soc.* (*A*), 1971, 1038.

[33] W. H. Flygare and J. Goodisman, *J. Chem. Phys.*, 1968, **49**, 3122.

[34] J. D. Kennedy and W. McFarlane, *J.C.S. Perkin II*, 1974, 146.

to the number of contributing atoms and cannot account for non-linear relationships. Using the approach of ref. 33, the diamagnetic contributions to $\delta(^{119}Sn)$ of a single manganese or rhenium atom directly bound to tin are calculated to be 84 and 227 p.p.m. to high field respectively on the assumption of metal–tin bond lengths calculated to be 0·28 and 0·31 nm. The difference of 143 p.p.m. between these two contributions is close to the difference in $\delta(^{119}Sn)$ found for (20) and (24) and is in the correct direction, thus suggesting that this term largely accounts for the difference in tin shielding associated with bonding to transition elements in different rows of the Periodic Table. The observed chemical-shift difference of 372 p.p.m. between (22) and (25) is, however, substantially larger than that predicted (286 p.p.m.) on this basis, and it appears that multiple heavy-atom substitution leads to non-linearity in the tin chemical-shift trends, as has been observed for other series of tin compounds.[34] This may arise from the high polarisability of the heavier atoms which will affect the mobility of the outer electrons of the nucleus in question and so alter the paramagnetic contribution.[35] Such an effect would then be greater for the heavier nuclei (*vide infra*).



Graphical representation of $\delta(^{119}Sn)$ for $Me_{4-n}SnX_n$: X = A, $Re(CO)_5$; B, Cl; C, $Mn(CO)_5$; D, $Co(CO)_4$

The paramagnetic contribution to the shielding is given by an expression of the form (1) in which ΔE is an average electronic excitation energy and Q_p and Q_d depend upon the size of and electron imbalance in the valence *p*- and *d*-orbitals respectively. In addition,

$$\sigma^{p} = -\frac{1}{\Delta E}\cdot(Q_p + Q_d) \qquad (1)$$

external factors such as neighbouring electric fields (arising from polar groups or bonds) and dispersion forces (arising from adjacent polarisable atoms) may also deform the periphery of the electronic cloud and so affect the terms in this expression. Chemical shifts involving tin have generally been interpreted on the assumption that ΔE in equation (1) is constant,[3–5] and this is reasonable for many series. The observed variations in $\delta(^{119}Sn)$ are then considered to be due to changes in Q_p and Q_d which can be seen as a change in the degree of electron imbalance in the bonds to tin. In compounds of the type $R_{4-n}SnX_n$ where R and X are of significantly different effective electronegativities, the imbalance will be a maximum for $n = 2$ and this accounts for the characteristic non-linear appearance of plots of $\delta(^{119}Sn)$ against n in such series, as typified by the data for R = Me and X = Cl shown in the Figure. When $n = 1$ there is a linear correlation with the electronegativity of X, the more electronegative groups giving shifts to low field, in accord with the prediction of equation (1).

It is striking that the transition-metal derivatives studied here do not conform to this pattern of behaviour: the values of $^{2}J(^{119}Sn\cdots H)$ observed in these compounds are all rather less than in tetramethyltin, indicating that the effective electronegativity of the transition-metal moiety is less than that of a methyl group, as would be expected on general chemical grounds. That is, the *s*-electron density on tin is relatively high. However, replacement of a single methyl group by a first-row transition metal still gives a shift to low field (*i.e.* σ^{p} becomes greater), and multiple substitution does nothing to reverse the trend.

Additionally in the compounds $[(cp)_2Mo(X)SnMe_3]$ (9)—(12) and the tungsten analogues (15)—(18) a change in the electronegativity of X, and hence of the effective electronegativity of the transition metal, does not affect the tin shielding in the expected manner. Thus for X = Cl, Br, or I the tin chemical shifts are all approximately equal and replacement of a halogen by hydrogen which should be more electropositive gives a shift to low field instead of to high field. However, changes in X might also alter the degree of d_π–d_π bonding between the transition metal and tin and this could cause a shift to low field for reasons discussed later.

For all cases in the present study in which exceptionally low-field tin chemical shifts are observed, the transition metal is also bound to carbonyl groups which may therefore be responsible for the effect. It is known[36] that the electric field of an adjacent carbonyl group can change ^{13}C shielding by at least 5 p.p.m. in organic compounds, by affecting the paramagnetic term, and in view of the greater sensitivity of ^{119}Sn shieldings to changes of electron distribution an effect of more than 50 p.p.m. could reasonably arise from the presence of a single carbonyl group. Although some cancellation of the electric fields of a number of carbonyl groups would occur *at the centre of the tin atom* [*e.g.* in

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[35] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1964, **40**, 1714.

[36] W. McFarlane, *Chem. Comm.*, 1970, 418.

(31)] the residual effects upon the peripheral electron could still be large and might account for most of the observed shift. However, it is generally thought[37] that the dipole moments and hence the associated electric fields of carbonyl groups in transition-metal complexes are much smaller than in ketones and so the effects upon nuclear shielding would also be smaller. Unfortunately, we do not have available any species in which several transition-metal atoms are bound to the tin, and in which all the carbonyls are replaced by other π-bonding substituents such as cyclopentadienyl. However, the relatively low-field shifts of (9)—(13) which are accompanied by quite small values of $^2J(^{119}\text{Sn}\cdots\text{H})$ (implying high *s*-electron density on tin) do suggest that the abnormal shielding is not dependent upon the presence of carbonyl groups. Equation (1) was obtained[35] by using wave functions centred upon the atom in question (in our case, tin) and any π-bonding between tin and the transition metal would invalidate this treatment. In particular it might make available low-energy electronic-excited states which would reduce ΔE in an appropriately modified form of equation (1) and so give a much increased paramagnetic contribution to the shielding. The size of this contribution would not depend linearly upon ΔE or upon the amount of π-bonding, and thus the curved appearance of the plots in the Figure is reasonable. Measurements of ^{55}Mn n.m.r. line widths and of ^{59}Co chemical shifts in compounds with transition metal-to-tin bonds have shown that there is appreciable d_π–d_π interaction in such species.[38,39] Normally the chemical shifts of transition metals themselves display appreciable temperature dependence[40,41] (typically 1 p.p.m./°C) and this is attributed to the population of higher vibrational levels which reduces the appropriate ΔE by altering the strength of the effective ligand field. This effect should affect the tin shifts much less since the relevant ΔE would be associated with the π system and should be relatively insensitive to changes in vibrational level populations. The tin chemical shifts of (7) and (29) were measured at several different temperatures, but no appreciable temperature dependence was observed. The differences between cobalt and manganese compounds may be due to a combination of greater electronegativity [compare values of $^2J(^{119}\text{Sn}\cdots\text{H})$ and pK_a values of the relevant hydrides $[\text{HM(CO)}_n]$[42] in the two series] and greater d_π–d_π overlap leading to a smaller ΔE term in equation (1) for the former.

The relatively high-field shifts observed when tin is bound to a third-row transition metal may arise because of less d_π–d_π interaction leading to larger values of ΔE in equation (1) so that the paramagnetic term is smaller, but the combined effects of the neighbouring atom diamagnetic contribution[32] and the high polarisability of the bulkier transition metal should also lead to a high-field shift. In the absence of accurate information upon the magnitudes of these contributions it is not yet possible to use the ^{119}Sn chemical shift to estimate the extent of any d_π–d_π overlap, although this may be possible when data for a wider range of compounds are available.

Other attempts to relate d_π–d_π bonding in tin-to-transition-metal bonds to spectroscopic parameters (*e.g.* see Table 1) have not always been successful. Explanation of ^{119}Sn Mossbauer parameters for tin-to-transition metal complexes can involve either d_π–d_π bonding or the more widely accepted point-charge approximations. Quadrupole splittings determined for the series $[(\text{cp})\text{M(CO)}_3\text{SnMe}_3]$ (M = Cr, Mo, or W) show similar trends to the corresponding ^{119}Sn chemical shifts (Table 1) and have been explained similarly by d_π–d_π M–Sn interaction. In compounds of type $[\text{Me}_3\text{Sn–ML}]$ (L = all other ligands) the amount of Sn–M π-bonding is related to the *d*-electron imbalance as indicated by the quadrupole splitting. However, it is not possible to make a simple direct comparison between members of the series $[\text{Me}_{4-n}\text{Sn–(ML)}_n]$ (n = 1—4) due to the different symmetries. Thus the recently reported Mössbauer data on the complexes $[\text{Me}_{4-n}\text{Sn\{Co(CO)}_4\}_n]$ (n = 1—3)[43] is of little use in determining the relative amount of d_π–d_π bonding within the series. However, an earlier study on $[\text{Me}_{4-n}\text{Sn\{Co(CO)}_4\}_n]$ (n = 1—4) by ^{59}Co n.q.r. has indicated an increase in d_π–d_π M–Sn interaction with increasing values of n.[44] Furthermore, only small changes in d_π–d_π interaction may be necessary for large changes in the tin chemical shift so despite ^{119}Sn Mössbauer values which show that M–Sn bonds are predominantly σ in character,[45] sufficient variation in d_π–d_π bonding may occur to cause the wide variations in $\delta(^{119}\text{Sn})$. Similarly the effects upon bond lengths may be too small for *X*-ray studies to have a great deal of relevance.[45] However, using such data in related silyl-transition metal complexes, a reasonable case has been made out for the presence of d_π–d_π Si–M bonding,[46] and especially its absence[47] in the unusually long Si–Zr bond in the d^0 $[(\text{cp})_2\text{Zr(Cl)SiPh}_3]$.[48]

Our results suggest, therefore, that when tin is bound to one or more transition-metal atoms the tin magnetic shielding is not closely related to the *s*-electron density on the tin atom [as assessed by the magnitude of $^2J(^{119}\text{Sn}\cdots\text{H})$] but is dominated by the extent of

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electron delocalisation brought about by d_π–d_π overlap between tin and the transition metal. This reduces ΔE in equation (1) so that the paramagnetic contribution is larger and the total shielding is decreased. This effect is offset by heavy atoms so that shifts to high field are observed when a third-row transition element is present, and intermediate results are obtained for the second row metals.

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