Mössbauer Spectra and Bonding in Four-co-ordinate Tin Compounds Containing a Tin–Cobalt Bond

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^{119}Sn Mössbauer spectra are reported for organometallic tin compounds of the type $R_lX_mSn[Co(CO)_4]_n$ (R = Me or Ph; X = Cl or Br; $l + m + n = 4$). From the quadrupole splitting of the compound $ClSn[Co(CO)_4]_3$ (1·42 mm s^{-1}), we have derived a partial quadrupole-splitting value for the $Co(CO)_4$ moiety of −0·71 mm s^{-1}. Using this value, signs and magnitudes of the quadrupole splittings for 25 compounds containing tin–cobalt bonds have been predicted. Except for two compounds, the observed magnitudes of the quadrupole-splitting parameters are in good agreement (within ±0·4 mm s^{-1}) of these predicted values. The partial quadrupole-splitting value for $Co(CO)_4$ indicates that the moiety is an appreciably poorer donor ligand than $Mn(CO)_5$ or $Fe(CO)_2$(cp) (cp = π-cyclopentadienyl). Centre-shift trends are rationalized by considering that the Sn–Co bond has a large amount of *s* character. This treatment is consistent with known *X*-ray structural information, and with correlations of the centre shift with both ^{59}Co n.q.r. data, and $^2J(^{119}Sn–CH_3)$ for compounds containing methyl groups.

^{119}Sn MÖSSBAUER spectra of compounds containing at least one tin–transition-metal bond have been the subject of a number of recent studies (refs. 1—3 and references therein). The additivity model,[4,5] involving the use of partial quadrupole-splitting (p.q.s.) values for ligands, has been particularly successful in correlating and predicting quadrupole splittings (q.s.) for these and other simple tin compounds.[5,6] This model can be derived from either a molecular-orbital[4,6] or a 'point-charge' approach; both lead to similar conclusions. In this paper, we have used the p.q.s. approach to predict signs and magnitudes of $\frac{1}{2}e^2qQ$, and the magnitude of η for 25 compounds of the type $R_lX_mSn[Co(CO)_4]_n$ (R = Me or Ph; X = Cl, Br, or I; $l + m + n = 4$). We have used the derived p.q.s. value for $Co(CO)_4$ to compare the Sn–Co bond with those of Sn–Mn and Sn–Fe in $SnMn(CO)_5$ and $SnFe(CO)_2$(cp) (cp = π-cyclopentadienyl) compounds.

Centre shifts (c.s.) in tin–transition-metal compounds have been successfully interpreted in terms of the large 5*s* character of the tin–metal bond relative to other ligands about the tin atom.[1,7-9] This approach is

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[1] G. M. Bancroft, K. D. Butler, A. T. Rake, and B. Dale, *J.C.S. Dalton*, 1972, 2025 and refs. 1—16.

[2] S. Ichiba, M. Katada, and H. Negita, *Bull. Chem. Soc. Japan*, 1972, **45**, 1679.

[3] B. Liengme, J. R. Sams, and J. C. Scott, *Bull. Chem. Soc. Japan*, 1972, **45**, 2956.

[4] G. M. Bancroft, M. J. Mays, and B. E. Prater, *Discuss. Faraday Soc.*, 1969, **47**, 136; *J. Chem. Soc.* (*A*), 1970, 956.

[5] R. V. Parish and R. H. Platt, *J. Chem. Soc.* (*A*) 1969, 2145; *Inorg. Chim. Acta*, 1970, **4**, 65.

[6] M. G. Clark, A. G. Maddock, and R. H. Platt, *J.C.S. Dalton*, 1972, 281.

[7] D. E. Fenton and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1968, **90**, 6226.

[8] S. R. A. Bird, J. D. Donaldson, A. F. Le C. Holding, B. J. Senior, and M. J. Tricker, *J. Chem. Soc.* (*A*), 1971, 1616.

[9] R. V. Parish, *Progr. Inorg. Chem.*, 1972, **15**, 101.

successful once again for our Sn–Co compounds in rationalizing variations in c.s., and the relative structural distortions found[10,11] for compounds containing the Sn–Co bond, compared to those with Sn–Mn and Sn–Fe bonds. Correlations of c.s. values with both ^{59}Co n.q.r. results[12-14] and $^{2}J(^{119}Sn-CH_3)$ data[7,15] are also rationalized in terms of the concentration of *s* character in the Sn–Co bond.

EXPERIMENTAL

The preparation of compounds (1)—(16), (19), and (20) (Table 1) closely followed published methods.[16,17] Compound (17) was synthesized by the addition of one mole equivalent of $Co(CO)_4^-$ [formed by dissolving $Co_2(CO)_8$ in methanol] to a $Me_2ClSnMn(CO)_5$ solution in tetrahydrofuran, under an atmosphere of nitrogen. The solvent was removed under vacuum, and the compound recrystallized twice from pentane with cooling. Compound (18) was prepared by adding one mole equivalent of Ph_3P to solid $PhClSn[Co(CO)_4]_2$ and heating the reactants together on a steam-bath under vacuum for 15 min. The crude product was extracted with pentane, the volume reduced, and the product precipitated by cooling; recrystallization was from pentane. The identity and purity of all the compounds was checked by colour, melting points, and i.r. and Mössbauer spectra. The new compounds were verified by elemental analysis {Found: C, 25·9; H, 1·35. $Me_2Sn[Co(CO)_4][Mn(CO)_5]$ requires C, 25·65; H, 1·20. Found: C, 47·1; H, 2·15; Cl, 4·8. $PhClSn[Co(CO)_4)][Co(CO)_3(Ph_3P)]$ requires C, 46·1; H, 2·5; Cl, 4·4%}. All compounds were stored under an atmosphere of nitrogen and carefully recrystallized in deoxygenated solvents immediately before spectra were run.

TABLE 1

^{119}Sn Mössbauer parameters (mm s^{-1}; c.s. relative to $BaSnO_3$ at 80 K)

	Compound	c.s.*	q.s.*	$\Gamma_{1,2}$ †
(1)	$MeSn[Co(CO)_4]_3$	1·79	1·29	1·01, 1·01
(2)	$Me_2Sn[Co(CO)_4]_2$	1·57	1·53	1·04, 1·02
(3)	$Me_3SnCo(CO)_4$	1·39	1·73	1·05, 1·05
(4)	$Me_2ClSnCo(CO)_4$	1·49	2·73	1·20, 1·24
(5)	$MeClSn[Co(CO)_4]_2$	1·74	2·38	1·07, 1·34
(6)	$Ph_2Sn[Co(CO)_4]_2$	1·60	1·27	1·07, 1·07
(7)	$Ph_3SnCo(CO)_4$	1·41	1·20	1·01, 1·01
(8)	$Ph_2ClSnCo(CO)_4$	1·48	2·18	1·00, 1·02
(9)	$PhClSn[Co(CO)_4]_2$	1·70	1·88	1·10, 1·05
(10)	$Sn[Co(CO)_4]_4$	2·04	0·00	1·11
(11)	$FSn[Co(CO)_4]_3$	1·75	0·97	1·05, 1·05
(12)	$ClSn[Co(CO)_4]_3$	2·05	1·42	1·02, 0·98
(13)	$Cl_2Sn[Co(CO)_4]_2$	1·75	1·44	1·01, 1·11
(14)	$Cl_3SnCo(CO)_4$	1·42	1·20	1·02, 1·02
(15)	$Br_2Sn[Co(CO)_4]_2$	1·75	1·46	1·03, 1·03
(16)	$I_2Sn[Co(CO)_4]_2$	1·86	1·07	1·12, 1·12
(17)	$Me_2Sn[Co(CO)_4][Mn(CO)_5]$	1·55	1·46	0·97, 1·00
(18)	$PhClSn[Co(CO)_4][Co(CO)_3(Ph_3P)]$	1·67	2·00	1·07, 1·15
(19)	$Cl_3SnMn(CO)_4(Ph_3P)$	1·70	1·69	0·91, 0·95
(20)	$Ph_3SnMn(CO)_4(Ph_3P)$	1·42	$<0·30$	1·26

* Errors are ±0·02 mm s^{-1}. † Errors are ±0·05 mm s^{-1}.

The Mössbauer spectra were recorded at 80 K using an Austin Science Associates spectrometer with a 512 channel analyser, and a 5 mCi $BaSnO_3$ source. The spectra were calibrated using Fe foil and a laser interferometer. Approximately 250 000 counts per channel were accumulated for all spectra and absorptions were in the range 4—9%. χ^2 Values were in the range 450—550. All spectra were fitted to Lorentzian line shapes using methods described previously.[18] The spectrum of the compound $Ph_3SnMn(CO)_4(Ph_3P)$ could not be resolved into two peaks without using position constraints.

RESULTS

Mössbauer parameters for 18 compounds containing a Sn–Co bond and two compounds containing a Sn–Mn bond are reported in Table 1. Parameters for 10 of these compounds have not been previously reported, and our results for compounds (3), (6)—(8), (10), and (13)—(16) are in good agreement with those published previously.[2,7,9,19] Compound (6), $Ph_2Sn[Co(CO)_4]_2$, has been widely studied and a variety of c.s. and q.s. values reported.[7,9,19] Our results for this compound are in excellent agreement with those given by Parish.[9] The parameters we measured for $ClSn[Co(CO)_4]_3$ [compound (12)] are not in good agreement with the previously reported[2] c.s. (1·93 mm s^{-1}) and q.s. (1·18 mm s^{-1}) values.

As with the $Mn(CO)_5$ and $Fe(CO)_2(cp)$ (cp = π-cyclopentadienyl) compounds reported previously,[1,20] low-symmetry species of the type $R_lX_mSn[Co(CO)_4]_n$ (R = Me or Ph; X = Cl or Br; l,m,n = 1 or 2) had much larger q.s. values than either $R_3SnCo(CO)_4$ or $X_3SnCo(CO)_4$. Thus the compounds $Me_3Sn[Co(CO)_4]$ and $Cl_3Sn[Co(CO)_4]$ had |q.s.| values of 1·73 and 1·20 mm s^{-1}, while those of $Me_2ClSn[Co(CO)_4]$ and $MeClSn[Co(CO)_4]_2$ were 2·73 and 2·38 mm s^{-1} respectively. All the $R_{4-n}Sn[Co(CO)_4]_n$ and $X_{3-n}Sn[Co(CO)_4]_n$ compounds had substantially larger and smaller |q.s.| values respectively than their $Mn(CO)_5$ and $Fe(CO)_2(cp)$ analogues.

In the $R_{4-n}Sn[Co(CO)_4]_n$ and $X_{4-n}Sn[Co(CO)_4]_n$ compounds, the c.s. increased with increase in n, as with the analogous $Mn(CO)_5$ and $Fe(CO)_2(cp)$ compounds. The c.s. values for the $R_{4-n}SnM_n$ compounds [M = $Mn(CO)_5$ or $Fe(CO)_2(cp)$] were very similar, but those for the halogen-containing $Co(CO)_4$ compounds, such as $X_{4-n}Sn[Co(CO)_4]_n$, were substantially smaller than their $Mn(CO)_5$ and $Fe(CO)_2(cp)$ analogues. Thus, c.s. values for the compounds $Cl_3SnMn(CO)_5$, $Cl_2MeSnMn(CO)_5$, $ClMe_2SnMn(CO)_5$, and $Me_3SnMn(CO)_5$ are 1·65, 1·62, 1·52, and 1·41 mm s^{-1}; values for the corresponding $Co(CO)_4$ compounds $Cl_3SnCo(CO)_4$, $ClMe_2SnCo(CO)_4$, and $Me_3SnCo(CO)_4$ are 1·42, 1·49, and 1·39 mm s^{-1} respectively. It is also interesting to note that the c.s. for the compound $Sn[Fe(CO)_2(cp)]_4$ (2·14 mm s^{-1})[9] is substantially larger than that for $Sn[Co(CO)_4]_4$

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[10] B. P. Bir'yukov, E. A. Kukhtenkova, Yu. Y. Struchkov, K. N. Anisimov, N. E. Kolobova, and V. I. Khandozhko, *J. Organometallic Chem.*, 1971, **27**, 337.

[11] B. P. Bir'yukov, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, O. P. Osipova, and M. Ya. Zakharov, *Chem. Comm.*, 1967, 749.

[12] D. D. Spencer, J. L. Kirsch, and T. L. Brown, *Inorg. Chem.*, 1970, **9**, 235.

[13] J. D. Graybeal, S. D. Ing, and M. W. Hsu, *Inorg. Chem.*, 1970, **9**, 678.

[14] T. L. Brown, P. A. Edwards, C. B. Harris, and J. L. Kirsch, *Inorg. Chem.*, 1969, **8**, 763.

[15] W. R. Cullen, J. R. Sams, and J. A. J. Thompson, *Inorg. Chem.*, 1971, **10**, 843.

[16] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 2222; 1967, **6**, 981; 1968, **7**, 771.

[17] R. D. Gorsich, *J. Amer. Chem. Soc.*, 1962, **84**, 2486.

[18] G. M. Bancroft, W. K. Ong, A. G. Maddock, R. H. Prince, and A. J. Stone, *J. Chem. Soc.* (*A*), 1967, 1966.

[19] A. N. Karasev, N. E. Kolobova, L. S. Polak, V. S. Shpinel, and K. N. Anisimov, *Teor. i. eksp. Khim.*, 1966, **2**, 126.

[20] G. M. Bancroft, K. D. Butler, and A. T. Rake, *J. Organometallic Chem.*, 1972, **34**, 137.

(2·04 mm s^{-1}). The parameters for the phosphine-substituted compounds [(18)—(20)] are all within 0·15 mm s^{-1} of those of their carbonyl parent compounds.[1,20]

DISCUSSION

Structures.—*X*-Ray structures of the compounds $ClSn[Co(CO)_4]_3$ and $Ph_2Sn[Co(CO)_4][Mn(CO)_5]$ have been reported.[10,11] The Sn atom in both structures appears to be unambiguously four co-ordinate. With the possible exception of the two asterisked compounds in Table 4, there is no reason to suppose that the remainder of the compounds we have studied contain other than four-co-ordinate tin. The bond angles (Table 2) indicate that the $Co(CO)_4$ compounds are substantially less distorted from tetrahedral geometry than their $Mn(CO)_5$ analogues. However, like the $Mn(CO)_5$ compounds, the $SnCo(CO)_4$ compounds have M–Sn–M or M–Sn–L (Table 2) bond angles greater than the regular tetrahedral value of 109° 28′.

TABLE 2

Bond-angle data for some selected tetrahedral tin compounds

	Bond angles/° *		
Compound	Cl–Sn–L	L–Sn–L	Ref.
$[Mn(CO)_5]_3SnCl$	101·0	116·5	*a*
$[Co(CO)_4]_3SnCl$	104	114	10
Ph_3SnCl	106·4	112·3	*b*
Cl_4Sn	109·5	109·5	*c*
	Mn–Sn–L		
$Ph_2Sn[Mn(CO)_5]_2$	117		*d*
$Ph_2Sn[Co(CO)_4][Mn(CO)_5]$	114		11
$Ph_3Sn[Mn(CO)_5]$	112·7		*e*

* Average values given where there is more than one such angle in the compound.

[a] J. H. Tsai, J. J. Flynn, and J. P. Boer, *Chem. Comm.*, 1967, 702. [b] N. G. Bokii, G. N. Zakharova, and Yu. T. Struchkov, *Zhur. strukt. Khim.*, 1970, **11**, 895. [c] R. L. Livingston and C. N. R. Rao, *J. Chem. Phys.*, 1959, **30**, 339. [d] B. T. Kilbourn and H. M. Powell, *Chem. and Ind.*, 1964, 1578. [e] H. P. Weber and R. F. Bryan, *Chem. Comm.*, 1966, 443.

Quadrupole Splittings.—To calculate q.s. values, we assumed tetrahedral geometry for all the compounds and used the p.q.s. values for F, Cl, Br, I, Me, Ph,[6] $Fe(CO)_2(cp)$, and $Mn(CO)_5$ [1] (Table 3) derived previously.

TABLE 3

Partial quadrupole splittings

Ligand	p.q.s./mm s^{-1}	Ref.
F,Cl,Br	0·00	6
I	−0·17	6
Ph	−1·26	6
Me	−1·37	6
$Mn(CO)_5$	−0·97	1
$Fe(CO)_2(cp)$	−1·08	1
$Co(CO)_4$	−0·71	This work

cp = π-Cyclopentadienyl.

A p.q.s. value of −0·76 mm s^{-1} has been assigned to the $Co(CO)_4$ moiety,[6] but we have derived a new value for $Co(CO)_4$, using the q.s. in the compound $ClSn[Co(CO)_4]_3$, because its structure is known to deviate little from regular tetrahedral geometry.[10] Taking the q.s. of $ClSn[Co(CO)_4]_3$ to be negative, the p.q.s. of $Co(CO)_4$ was calculated to be −0·71 mm s^{-1}. {The known positive signs for the compounds $Cl_3SnFe(CO)_2(cp)$ and $Cl_3SnMn(CO)_5$ [8,21] make it almost certain that the sign of the q.s. for the compound $ClSn[Co(CO)_4]_3$ will be negative.[5,9,20]}

Using the expressions for the electric-field gradient components derived previously [5,20] and the above p.q.s. values, we have calculated $\frac{1}{2}e^2qQ$ and η for 25 compounds (Table 4). Except for the compounds $Me_3SnCo(CO)_4$ and $FSn[Co(CO)_4]_3$, the agreement between predicted and observed q.s. values is good (within ±0·4 mm s^{-1}). It is interesting to note that the order of q.s. values for the mixed species $R_2ClSnCo(CO)_4$ and $RClSn[Co(CO)_4]_2$ (R = Me or Ph) is correctly predicted. The $RCl_2Sn[Co(CO)_4]$ compounds have not yet been examined, but they should have very similar |q.s.| values to the $R_2ClSn[Co(CO)_4]$ compounds, but with opposite sign.[1] The very large predicted η values for the $RClSn[Co(CO)_4]_2$ compounds (Table 4) suggest that the sign of e^2qQ could be either negative or positive, especially since observed η values will quite probably differ appreciably from the calculated values due to distortions or small variations in p.q.s. values.[1] For example, the measured η value for the compound $MeCl_2SnMn(CO)_5$ (0·46) is in substantial disagreement with the predicted value (0·89), presumably due to distortion, even though the predicted and observed q.s. values are in close agreement.[1] The

TABLE 4

Predicted and observed values for $\frac{1}{2}e^2qQ$ and η for tetrahedral Sn–Co compounds

	q.s.			η
Compound	calc.	obs.	Ref.	calc.
$PhSn[Co(CO)_4]_3$	+1·10	1·28	7	0·00
$Ph_2Sn[Co(CO)_4]_2$	1·27	1·27	*a*	1·00
$Ph_3SnCo(CO)_4$	−1·10	1·20	*a*	0·00
$Ph_2ClSnCo(CO)_4$	−2·39	2·18	*a*	0·60
$PhCl_2SnCo(CO)_4$	+2·45	*b*		0·76
$PhClSn[Co(CO)_4]_2$	−2·07	1·88	*a*	0·83
$MeSn[Co(CO)_4]_3$	+1·32	1·29	*a*	0·00
$Me_2Sn[Co(CO)_4]_2$	1·52	1·53	*a*	1·00
$Me_3SnCo(CO)_4$	−1·32	1·73 *	*a*	0·00
$Me_2ClSnCo(CO)_4$	−2·62	2·73	*a*	0·66
$MeCl_2SnCo(CO)_4$	+2·63	*b*		0·71
$MeClSn[Co(CO)_4]_2$	−2·27	2·38	*a*	0·99
$FSn[Co(CO)_4]_3$	−1·42	0·97 *	*a*	0·00
$ClSn[Co(CO)_4]_3$	*c*	1·42	*a*	0·00
$Cl_2Sn[Co(CO)_4]_2$	1·64	1·44	*a*	1·00
$Cl_3SnCo(CO)_4$	+1·42	1·20	*a*	0·00
$BrSn[Co(CO)_4]_3$	−1·42	1·06	2	0·00
$Br_2Sn[Co(CO)_4]_2$	1·64	1·46	*a*	1·00
$Br_3SnCo(CO)_4$	+1·42	1·29	2, 9	0·00
$ISn[Co(CO)_4]_3$	−1·08	0·95	2	0·00
$I_2Sn[Co(CO)_4]_2$	1·25	1·07	*a*	1·00
$I_3SnCo(CO)_4$	+1·08	0·71	2	0·00
$Sn[Co(CO)_4]_4$	0·00	0·00	*a*	0·00
$Me_2Sn[Co(CO)_4][Mn(CO)_5]$	−1·30	1·46	*a*	0·80
$Ph_2Sn[Co(CO)_4][Mn(CO)_5]$	−1·06	1·15	19	0·72
$Cl_2Sn[Co(CO)_4][Mn(CO)_5]$	−1·83	*b*		0·37

[a] This work. [b] Not reported. [c] Compound used to calculate p.q.s.$[Co(CO)_4]$.

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[21] B. A. Goodman, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc. (A)*, 1971, 1868.

q.s. for the compound $Me_3SnCo(CO)_4$ is certainly abnormally large when compared with the corresponding Ph derivatives and the other $Me_nSn[Co(CO)_4]_{4-n}$ compounds. For example, using the point-charge model, the |q.s.| of the compounds $MeSn[Co(CO)_4]_3$ and $Me_3Sn[Co(CO)_4]$ should be equal, and that of $Me_2Sn[Co(CO)_4]_2$ 15% larger. It is possible that the anomalously large value for the $Me_3SnCo(CO)_4$ compound is due to large distortions from tetrahedral geometry.

The small q.s. for the compound $FSn[Co(CO)_4]_3$ could be due to distortion or association. Clark *et al.*[6] decided that the p.q.s. of F^- was very close to those of Cl^- and Br^-, and assigned all three a zero value. Thus we would expect that the compounds $ClSn[Co(CO)_4]_3$ and $FSn[Co(CO)_4]_3$ would have very similar q.s. values. Indeed for the compound $(neophyl)_3SnF$ [neophyl = $PhC(Me)_2CH_2$], which should contain four-co-ordinate Sn because of the steric barrier to fluorine bridging presented by the bulky neophyl groups, the observed q.s. is *larger* by 0·14 mm s^{-1} than those for the analogous chloride and bromide compounds.[22] This is consistent with a slightly *positive* p.q.s. value for F^-, while our result for a four-co-ordinate $FSn[Co(CO)_4]_3$ species would suggest a p.q.s. value for F^- of —0·23 mm s^{-1}. These results strongly suggest either that the compound $FSn[Co(CO)_4]_3$ has a very distorted four-co-ordinate structure, or that there is intermolecular fluorine bridging. Clark[23] has shown that a five-co-ordinate bridging structure involving one axial and one equatorial atom (F in this case) would give a smaller q.s. than the four-co-ordinate structure. Using his treatment, the predicted |q.s.| for the above five-co-ordinate structure is 1·14 mm s^{-1}, in good agreement with the observed value of 0·97 mm s^{-1}. These results suggest an associated structure, but it is still possible that a very distorted four-co-ordinate structure could give rise to the low observed q.s.

The p.q.s. value for $Co(CO)_4$ is substantially less negative than those for $Mn(CO)_5$ and $Fe(CO)_2(cp)$. This accounts for the considerably larger q.s. values for the $R_{4-n}Sn[Co(CO)_4]_n$ compounds, and the substantially smaller q.s. values for the $X_{4-n}Sn[Co(CO)_4]_n$ compounds, compared with the $Mn(CO)_5$ and $Fe(CO)_2(cp)$ analogues. Since Clark *et al.*[6] have shown that the q.s. is not sensitive to π bonding, the less-negative p.q.s. value for $Co(CO)_4$ indicates that it is an appreciably poorer donor to the Sn *p* orbitals than $Mn(CO)_5$ and $Fe(CO)_2(cp)$. Considering all the ligands in Table 3, the order of *p*-donor ability to Sn increases in the order Cl,Br $<$ I $<$ $Co(CO)_4 < Mn(CO)_5 < Fe(CO)_2(cp) <$ Ph $<$ Me. This order is similar to the well established order of basicities and nucleophilicities.[9,24,25]

Centre Shifts and N.m.r. Data.—In our previous paper,[1] we indicated that the tin *s* character in the Sn–L bond increases in the order L = Cl $< C_6F_5 <$ Ph $<$ Me $< Mn(CO)_5 < Fe(CO)_2(cp)$. The c.s. results for the $Co(CO)_4$ compounds show that $Co(CO)_4$ lies between Me and $Mn(CO)_5$ in this series. Thus, the c.s. increases markedly as *n* increases in the series $R_{4-n}Sn[Co(CO)_4]_n$ (R = Ph or Me), as it does for the analogous $Mn(CO)_5$ and $Fe(CO)_2(cp)$ compounds. These results strongly indicate that the Sn–M bonds [M = $Co(CO)_4$, $Mn(CO)_5$, and $Fe(CO)_2(cp)$] involve considerably more Sn 5*s* character than the Sn–R bonds. Three pieces of evidence suggest that the Sn–$Co(CO)_4$ bond involves less Sn 5*s* character than the Sn–Mn or Sn–Fe bonds. First, the c.s. values for most of the $Co(CO)_4$ compounds are smaller than their $Mn(CO)_5$ or $Fe(CO)_2(cp)$ analogues. The poorer *p*-donor ability of $Co(CO)_4$ relative to $Mn(CO)_5$ and $Fe(CO)_2(cp)$ would give the opposite trend. Secondly, the $Co(CO)_4$ halide compounds have much lower c.s. values than their $Mn(CO)_5$ and $Fe(CO)_2(cp)$ analogues. This is largely due to the higher Sn 5*s* character in the Sn–Cl bonds (and therefore lower 5*s* character in the Sn–Co bond) in the $Co(CO)_4$ compounds. The electronegative chlorines therefore withdraw more *s* electron density in the $Co(CO)_4$ compounds than the $Mn(CO)_5$ and $Fe(CO)_2(cp)$ analogues, and thus decrease the c.s. Thirdly, in the $R_{3-n}X_nSnCo(CO)_4$ compounds, the c.s. only increases marginally with increase in *n*, and then decreases, in contrast to the $Mn(CO)_5$ and $Fe(CO)_2(cp)$ analogues in which a large increase occurs. For example, the c.s. values for the compounds $Ph_3Sn[Co(CO)_4]$, $Ph_2ClSnCo(CO)_4$, and $Cl_3SnCo(CO)_4$ are 1·41, 1·48, and 1·42 mm s^{-1}; values for the analogous $Fe(CO)_2(cp)$ compounds are 1·39, 1·58, and 1·75 mm s^{-1} (ref. 20). This difference can be attributed again to an increase in *s* character of the Sn–Cl bonds in the $SnCo(CO)_4$ compounds with a concomitant decrease in the 5*s* character of the Sn–Co bond, relative to the Sn–Fe bond.

The above *s*-character series is consistent with the known *X*-ray structural data (Table 2). We would expect that distortion from regular tetrahedral geometry would increase as the difference in *s* character between the different tin–ligand bonds in four-co-ordinate compounds became greater. Thus for the series of compounds $ClSnL_3$, bond angles deviate further and further from the tetrahedral value of 109·5° in the order L = Cl $<$ Ph $< Co(CO)_4 < Mn(CO)_5$, as would be predicted from the *s*-character series (Table 2). In addition, the Mn–Sn–L angle in $Ph_2[Mn(CO)_5]SnL$ compounds increases in the order Ph $< Co(CO)_4 < Mn(CO)_5$ (Table 2) as would be expected. Patmore and Graham[16] have also proposed, on the basis of intensity ratios of the A_1 and B_1 ν(CO) bands for the series of compounds $Ph_nCl_{2-n}Sn[Co(CO)_4]_2$, that the Co–Sn–Co angle increases from $n = 2$ to $n = 0$ (*i.e.* as Ph ligands are successively replaced by Cl). This trend is, once more, consistent with our *s*-character series.

The above *s*-character series is also entirely consistent with $|^2J(^{119}Sn–CH_3)|$ parameters measured for Me_3SnL

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[22] A. G. Maddock and R. H. Platt, *J. Chem. Soc.* (*A*), 1971, 1191.

[23] M. G. Clark, unpublished calculations.

[24] M. I. Bruce and F. G. A. Stone, *Angew. Chem. Internat. Edn.*, 1968, **7**, 747.

[25] D. F. Shriver, *Accounts Chem. Res.*, 1970, **3**, 231.

compounds (Table 5). The treatment described here is an extension of that used by Fenton *et al.*,[7] Cullen *et al.*,[15] and some other authors.[26,27] We assume that the main contribution to $^2J(^{119}\mathrm{Sn{-}CH_3})$ is from the Fermi-contact term. For a series of closely related compounds, such as those in Table 5, the only variables which will appreciably affect $^2J(^{119}\mathrm{Sn{-}CH_3})$ are α_{Sn}^2 (the *s* character in the Sn–C bond) and $[\psi(0)_s]^2$ (the *s*-electron density at the Sn nucleus). In Table 5, it is apparent that there is no correlation between the c.s. and $|^2J(^{119}\mathrm{Sn{-}CH_3})|$, and that the c.s. does not vary greatly from compound to compound. Both of these observations indicate that $^2J(^{119}\mathrm{Sn{-}CH_3})$ reflects changes in α_{Sn}^2 to a much greater extent that changes in $[\psi(0)_s]^2$. Hence the relative order of tin *s* character in the tin–methyl group bond will be the same as the order of the coupling constants. Conversely, the order of increasing *s* character in the tin–ligand bond will be the *reverse*, *i.e.* $C_6F_5 < C_6Cl_5 < Ph < Me < Co(CO)_4 < Mn(CO)_5 < Fe(CO)_2(cp)$. This is the same order as that of the *s*-character series derived from Mössbauer c.s. results previously. Although the difference in coupling constants between Me_3SnPh and Me_4Sn is not great, their relative order in the tin *s*-character series is unambiguous since the compound with the larger value of $|^2J(^{119}\mathrm{Sn{-}CH_3})|$ also has the smaller c.s. value. Hence the coupling constant increases despite the decrease in *s*-electron density at the tin nucleus.

TABLE 5

N.m.r. and ^{119}Sn c.s. data for some Me_3SnL compounds

Compound	$\lvert^2J(^{119}\mathrm{Sn{-}CH_3})\rvert$/Hz	Ref.	c.s./ mm s^{-1}	Ref.
$Me_3SnFe(CO)_2(cp)$	47·2	15	1·35	15
$Me_3SnMn(CO)_5$	48·8	28	1·41	20
$Me_3SnCo(CO)_4$	52·6	16	1·39	*a*
Me_4Sn	54·0	29	1·31	30
Me_3SnPh	54·6	29	1·21	30
$Me_3SnC_6Cl_5$	56·8	29	1·32	30
$Me_3SnC_6F_5$	58·8	29	1·27	30

cp = π-Cyclopentadienyl.

[a] This work.

As further confirmatory evidence of this interpretation, Figure 1 shows a plot of $|^2J(^{119}\mathrm{Sn{-}CH_3})|$ against c.s. for three series of compounds Me_nSnM_{4-n} [M = $Co(CO)_4$, $Mn(CO)_5$, and $Fe(CO)_2(cp)$]. Mössbauer and n.m.r. data are collected from refs. 1, 15, 16, and 28—31, as well as this work. It is apparent that if $^2J(^{119}\mathrm{Sn{-}CH_3})$ was determined predominantly by $[\psi(0)_s]^2$ (as is the c.s.), then the $|^2J|$ against c.s. plot should have a positive gradient. The gradients of the plots are negative, and this can be rationalized if $^2J(^{119}\mathrm{Sn{-}CH_3})$ is determined prdominantly by α_{Sn}^2. Thus, an *increase* in *s*-electron density at the tin nucleus is accompanied by a corresponding *decrease* in the tin *s* character of each tin–methyl group bond.

^{59}Co e^2qQ *Values*.—Several recent papers[12-14] have reported e^2qQ values for $L_nSn[Co(CO)_4]_{4-n}$ compounds

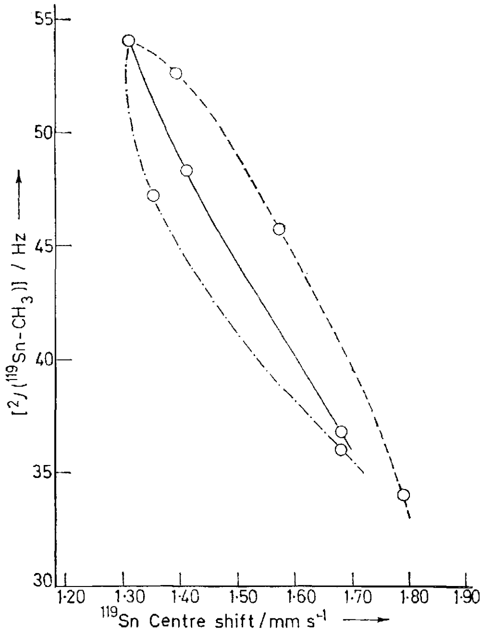

FIGURE 1 Plot of $|^2J(^{119}\mathrm{Sn{-}CH_3})|$ against ^{119}Sn centre shift for Me_nSnM_{4-n} compounds : (— — —), $Co(CO)_4$; (——), $Mn(CO)_5$; (–·–·–), $Fe(CO)_2(cp)$. ^{1}H N.m.r. data collected from refs. 1, 15, 16, and 28—31

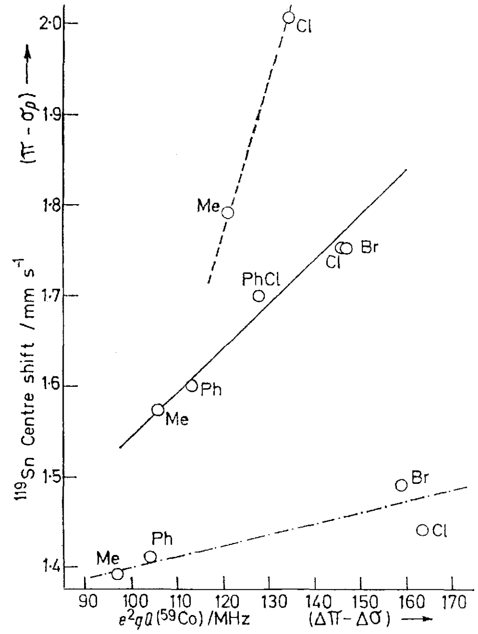

FIGURE 2 Plot of ^{119}Sn centre shift against $e^2qQ(^{59}\mathrm{Co})$ for $L_nSn[Co(CO)_4]_{4-n}$ compounds: (— — —), $n = 1$; (——), $n = 2$, (–·–·–), $n = 3$. ^{59}Co N.q.r. data collected from refs. 12—14

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[26] J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1961, **83**, 3903.

[27] T. F. Boles and R. S. Drago, *J. Amer. Chem. Soc.*, 1966, **88**, 5730.

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

[29] T. Chivers and J. R. Sams, *J. Chem. Soc.* (*A*), 1970, 928.

[30] G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 59.

[31] R. H. Herber and A. Hoffmann, *Progr. Inorg. Chem.*, 1967, **8**, 35.

(L = Me, Ph, Br, or Cl; $n = 1, 2$, or 3) and it is useful to rationalize the c.s. against e^2qQ correlations as given in Figure 2. As suggested in a recent publication,[32] the e^2qQ value for a hypothetical $Co(CO)_5^+$ species should be *ca.* +180 MHz. When the CO ligand along the Z electric-field gradient axis is replaced by a ligand L, e^2qQ will become more negative if L is a better σ donor than CO, and more positive if it is a better π acceptor than CO. Thus $e^2qQ(^{59}Co)$ is proportional to $\Delta\pi - \Delta\sigma$.

For the three series of compounds $L_nSn[Co(CO)_4]_{4-n}$ ($n = 1, 2$, or 3) shown in Figure 2, $e^2qQ(^{59}Co)$ increases as the c.s. increases. This correlation is readily rationalized in terms of σ effects, if the controlling factor in the c.s. variation is the large *s* character of the Sn–Co bond, as discussed earlier. Thus the c.s. becomes more negative as σ donation, largely to the Sn 5*p* orbitals, increases. It would become more positive if π acceptance of L increased. Thus the plot of c.s. against e^2qQ represents a plot of $(-\sigma_p + \pi)$ against $(\Delta\pi - \Delta\sigma)$, and gradients of the plots should be positive, as is observed. Thus these plots cannot distinguish σ and π effects, but both $e^2qQ(^{59}Co)$ results [12] and the ^{119}Sn centre shifts [1,7] indicate that both parameters are probably more sensitive to σ effects.

The greater sensitivity of the ^{119}Sn c.s. for small n (Figure 2) can also be rationalized using the *s*-character arguments given above. As n decreases, more Sn 5*s* character is used in the increasing number of Sn–Co bonds, and the Sn–L bonds will thus have a greater 5*p* character. This will of course make the c.s. more sensitive to variation in σ properties of L as n decreases, as is observed. The variation in Sn–Co bonding with variation in L is also felt by the carbonyl ligands as indicated by the ν(CO) against $e^2qQ(^{59}Co)$ correlation given previously.[12]

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[32] J. L. Slater, M. Pupps, and R. K. Sheline, *J. Chem. Phys.*, 1972, **57**, 2105.