Mössbauer Spectra of Four-co-ordinate Tin Compounds Containing a Tin–Iron or Tin–Manganese Bond

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Tin-119 Mössbauer spectra are reported for 15 Sn-organometallic compounds which contain Sn–Fe or Sn–Mn bonds. Using recently derived partial quadrupole splitting (p.q.s.) values for Ph, R (Me, Et, *etc.*) and X (F, Cl, Br), we have derived new p.q.s. values for C_6F_5, $Mn(CO)_5$, and $Fe(CO)_2(cp)$ and have predicted the magnitude of $\frac{1}{2}e_2qQ$ (q.s.) and η, and the sign of the q.s. for 40 compounds containing Sn–Fe or Sn–Mn bonds. Except for four compounds, agreement between predicted and observed q.s. values is within 0·4 mm s^{-1}, and the signs of the q.s. agree with the known signs, and those determined in this study for $Me_2ClSnMn(CO)_5$ (–ve) and $MeCl_2SnMn(CO)_5$ (+ve). The predicted η value for $Me_2ClSnMn(CO)_5$ (0·41) agrees well with that determined (0·35) from magnetic spectra, whereas for $MeCl_2SnMn(CO)_5$ the predicted (0·89) and observed (0·46) values of η are not in good agreement. Calculations indicate that η should be much more sensitive than the q.s. to variations in p.q.s. values. The derived p.q.s. values show that the *p* donor capacity of the ligands increase in the order Cl, Br < C_6F_5 < $Mn(CO)_5$ < $Fe(CO)_2(cp)$ < Ph < R.

The centre shifts for the compounds $X_nR_{3-n}SnM$ [X = Cl, Br, or C_6F_5; R = Me or Ph; M = $Mn(CO)_5$ or $Fe(CO)_2(cp)$] generally increase as *n* increases. This trend is largely due to the concentration of *s* electron density in the Sn–M bond, and the high *p* character in the Sn–X bonds. The *s* character in Sn–L bonds increases in the order L = Cl, Br < C_6F_5 < Ph < Me < $Mn(CO)_5$ < $Fe(CO)_2(cp)$. The known tetrahedral distortions about Sn can be rationalized using this series.

TIN-119 Mössbauer spectra of compounds containing Sn–transition metal bonds of general formula $R_lX_mSnM_n$ [$l + m + n = 4$; R = Me, Et, Bu, or Ph; X = Cl, Br, I, NCS, HCO_2, or OAc; M = $Cr(CO)_3(cp)$, $Mn(CO)_5$, $Fe(CO)_2(cp)$, $Co(CO)_4$, $Mo(CO)_3(cp)$, $W(CO)_3(cp)$, $Re(CO)_5$ (cp = π-C_5H_5)] have been the subject of a number of recent papers.[1-16] Partial quadrupole splittings (p.q.s.)[17-20] have been very useful in rationalizing the sign and magnitude of the quadrupole splitting (q.s.) in some of these compounds.[11-14] The initial p.q.s. values of Parish and Platt[19] were used in the above papers. Clark, Maddock, and Platt[21] have recently shown that different p.q.s. values should be used for tetrahedral and octahedral Sn compounds. They have

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reported precise p.q.s. values * for alkyl and phenyl groups relative to halides (X = F, Cl, or Br) and more tentative values for a number of other moieties including C_6F_5, $Mn(CO)_5$, and $Fe(CO)_2(cp)$. We have calculated better p.q.s. values for the latter three moieties and have calculated quadrupole splittings for 40 compounds containing Sn–Mn and Sn–Fe bonds. Agreement between predicted and observed q.s. and η values is generally good.

The interpretation of organotin centre shift (c.s.) values has met with difficulties (for reviews see ref. 22 and 23). For octahedral and tetrahedral Sn^{IV} halides, the c.s. values decrease with increasing electronegativity.[24-28] Electronegative ligands withdraw both 5*s* and 5*p* electron density from the Sn, but since the c.s. is most sensitive to changes in 5*s* electron density,[29] and $\delta R/R$ is positive, a net withdrawal of *s* electrons by an electronegative ligand decreases the c.s. However, for tin–transition-metal compounds, the expected trend on the basis of the above argument no longer holds. For example, in the series of compounds X_nSnM_{4-n} [X = Cl or Br; M = $Mn(CO)_5$ or $Fe(CO)_2(cp)$] the c.s. increases as *n* increases,[6,8,10,12] despite the much greater electronegativity of X relative to M. These trends have been interpreted [6,8,10,12] in terms of the large 5*s* character of the Sn–M bond relative to the other ligands about Sn. Thus, if the Sn–Cl bond involves little Sn 5*s* character, Cl would be expected to increase $[\Psi(0)_s]^2$ by removal of *p* electron density (*i.e.* deshielding), and the c.s. increases—in contrast to the decrease noted earlier if the Sn–X bond involves appreciable 5*s* character. The structural data (refs. 6, 13, 21) lend strong support to this interpretation. It should also be noted that in Xe and I compounds such as $XeXe_4$, IX_4^- (X = halide) and the alkali iodides, $[\Psi(0)_s]^2$ also increases as the electronegativity of the ligand increases because the bonds have essentially pure *p* character.[22,30,31] It does not seem necessary to invoke Parish and Platt's loss of charge concept [28] to explain any of this data.

Considerable confusion in the very recent literature has arisen due to the loose use of electron donor ability, and the lack of a consistent interpretation of q.s. data. Onaka *et al.*[10] noted that from c.s. data the 'Mn(CO)$_5$ group is a stronger electron donor than methyl or phenyl' and Greenwood *et al.*[13] have noted that 'the electron density in the tin region of the bonds decreases in the order Sn–M > Sn–R > Sn–X'. However, Parish noted [23] that the M groups from q.s. data are *poorer p donors* than Me or Ph and he first recognized the apparent discrepancy between donor strengths from c.s. and q.s. values.[23] We show that the p.q.s. values depend on *both* the *p* donor strength of ligand L and the *p* character of the metal orbital. We also develop the rehybridization concept for c.s. values to rationalize the apparent discrepancy between c.s. and q.s. results and show that the *s* character in the Sn–L bonds obtained from the c.s. results is entirely consistent with the bond angles in these and other Sn compounds containing Sn–M bonds.

EXPERIMENTAL

The preparation of compounds (2)—(10) in Table 1 will be reported elsewhere.[32] All other compounds were prepared by previously published methods.[33-36] M.p.s and i.r., n.m.r., and Mössbauer spectra were used as criteria of purity; for new compounds this was verified by chemical analysis.

TABLE 1

^{119}Sn Mössbauer parameters (relative to $BaSnO_3$ at 78 K)

	Compound	C.s.†	Q.s.†	Γ_1 ‡	Γ_2 ‡
(1)	$Ph_3SnMn(CO)_5$	1·35	0·41 ± 0·10	0·97	1·04
(2)	$Ph_2(C_6F_5)SnMn(CO)_5$	1·45	0·95	1·11	1·02
(3)	$Ph(C_6F_5)_2SnMn(CO)_5$	1·45	1·06	1·15	1·01
(4)	$(C_6F_5)_3SnMn(CO)_5$	1·44	0·99	1·04	1·08
(5)	$Ph_2(C_6F_5)SnFe(CO)_2(cp)$	1·48	0·93	1·21	1·03
(6)	$Ph(C_6F_5)_2SnFe(CO)_2(cp)$	1·48	1·37	1·14	0·99
(7)	$(C_6F_5)_3SnFe(CO)_2(cp)$	1·39	1·21	0·86	1·11
(8)	$Ph_2BrSnFe(CO)_2(cp)$	1·61	2·52	1·27	1·17
(9)	$PhBr_2SnFe(CO)_2(cp)$	1·73	2·65	0·98	1·04
(10)	$Br_3SnFe(CO)_2(cp)$	1·86	1·63	1·14	0·92
(11)	$Ph_2ClSnMn(CO)_5$	1·61	2·50	1·13	1·11
(12)	$PhCl_2SnMn(CO)_5$	1·63	2·52	1·26	1·23
(13)	$Ph_2BrSnMn(CO)_5$	1·58	2·31	1·12	1·06
(14)	$PhBr_2SnMn(CO)_5$	1·75	2·65	1·09	1·00
(15)	$Br_3SnMn(CO)_5$	1·76	1·53	1·23	0·98

† Errors are ±0·02 mm s^{-1} except where indicated. ‡ Errors are ±0·05 mm s^{-1}.

The Mössbauer spectra were taken at 80 K using an Austin Science Associates spectrometer and a 5 mCi $BaSnO_3$ source. The spectrometer was calibrated using Fe foil and a laser interferometer. All spectra were fitted to Lorentzians using methods previously described.[16,37] The constraint facility in this computer program enabled the detection of very small visually unresolved quadrupole splittings.

The magnetic spectra of $(C_6F_5)_3SnMn(CO)_5$, $Me_2ClMn(CO)_5$, and $MeCl_2Mn(CO)_5$ were taken at the PCMU Harwell.

RESULTS

Mössbauer parameters for 15 compounds are given in Table 1. For compounds (10)—(15), the agreement between our results and those previously published is generally

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* p.q.s. = $\frac{1}{2}e^2|Q|[L]$ where $[L]$ = partial field gradient.[21]

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good.[5,8–13] For $Ph_3SnMn(CO)_5$, quadrupole splitting had not been reported previously. χ^2 Values for two peak fits were over 50 smaller than for one peak fits for this compound, as was the case for $Ph_3SnFe(CO)_2(cp)$ reported previously.[14] The error in these small q.s. values is, of course, rather large.

The magnetic spectra of $Me_2ClSnMn(CO)_5$ and $MeCl_2SnMn(CO)_5$ at 4 K are shown in Figure 1. The best fits to these spectra gave a q.s. of $-2{\cdot}70$ mm s^{-1} and $\eta = 0{\cdot}30$ for $Me_2ClSnMn(CO)_5$; and q.s. of $+2{\cdot}66$ mm s^{-1} and $\eta = 0{\cdot}46$ for $MeCl_2SnMn(CO)_5$. The errors in the η values are considered to be $\pm 0{\cdot}05$.

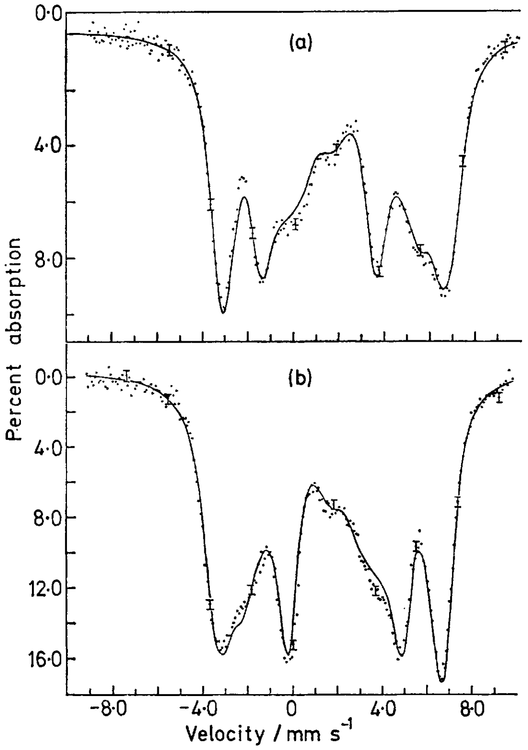

FIGURE 1 Mössbauer spectra of: (a) $MeCl_2SnMn(CO)_5$ and (b) $Me_2ClSnMn(CO)_5$ at 4·2 K in a magnetic field of 42 kG. The solid line gives the best fit to the spectrum

As for the compounds reported previously,[14] the q.s. of the intermediate members of any $R_{3-n}X_nSnM$ (n = 1 or 2) series are usually larger than those for $n = 0$ or $n = 3$. For the C_6F_5 derivatives, the q.s. values for $n = 0, 1, 2$ are quite similar.

The trend in c.s. values for the compounds is indicated in Table 1. For X = Cl or Br, the c.s. increases as n increases, although the trend is not linear with n. For X = C_6F_5, an initial increase in the c.s. for $n = 1$ is followed by a decrease for $n = 3$.

DISCUSSION

Structures.—The *X*-ray structures of $Me_3SnMn(CO)_5$,[38] $Ph_3SnMn(CO)_5$,[39] $Ph_3SnFe(CO)_2(cp)$,[40] $Cl_3SnFe(CO)_2(cp)$,[41] $Br_3SnFe(CO)_2(cp)$,[42] and $PhCl_2SnFe(CO)_2(cp)$,[43] have been reported and all show that the Sn atom is four-co-ordinate with no abnormally short non-bonded distances. The distortion from tetrahedral geometry about the Sn atom increases in the order given above. Thus in $Me_3SnMn(CO)_5$, the Me–Sn–Me and Me–Sn–Mn bond angles vary from 106·9 to 112·2°, but in $PhCl_2SnFe(CO)_2(cp)$, the corresponding angles vary from 99·1 to 129·7°. No crystal structures of the C_6F_5 compounds or analogues have yet appeared, but these compounds almost certainly contain four-co-ordinate Sn also.

Quadrupole Splittings.—In the calculation of q.s. values, we assume tetrahedral geometry and take the p.q.s. values for X, Ph, and R to be 0·00, $-1{\cdot}26$, and $-1{\cdot}37$ (all in mm s^{-1}) respectively from the previous careful analysis of Sn quadrupole splittings.[21] Although deviations from tetrahedral geometry can be considered,[12–14,16,21] Clark *et al.*[21] concluded that small distortions should be ignored, and our results in this paper indicate that even for highly distorted compounds, the good agreement between observed and calculated results strongly supports the use of the idealized geometry. Clark *et al.*[21] also calculated working p.q.s. values for C_6F_5, $Mn(CO)_5$, and $Fe(CO)_2(cp)$ from the q.s. values of $Me_3SnC_6F_5$, $Cl_3SnMn(CO)_5$, and $Cl_3SnFe(CO)_2(cp)$ respectively. We have recalculated what we consider to be better p.q.s. values using the q.s. values in Table 2. For C_6F_5, we have averaged the p.q.s. values calculated from the first six compounds taking $(\text{p.q.s.})_{Ph}$ and $(\text{p.q.s.})_{Me}$ to be $-1{\cdot}26$ and $-1{\cdot}37$ mm s^{-1} respectively.[21] There is good internal consistency between the six calculated values, and the average value [$(\text{p.q.s.})_{C_6F_5} = -0{\cdot}76$ mm s^{-1}] gives better agreement between predicted and observed values than the previous value of $-0{\cdot}70$ mm s^{-1}.

TABLE 2

Q.s. values used in calculating p.q.s. values for C_6F_5, $Mn(CO)_5$, and $Fe(CO)_2(cp)$

Compound	Q.s.	Ref.
(1) $Ph_3Sn(C_6F_5)$	−0·95	21
(2) $Ph_2Sn(C_6F_5)_2$	1·11	21
(3) $PhSn(C_6F_5)_3$	(+)0·92	21
(4) $Me_3Sn(C_6F_5)$	−1·35	21
(5) $Me_2Sn(C_6F_5)_2$	1·51	21
(6) $MeSn(C_6F_5)_3$	(+)1·14	21
(7) $Me_3SnMn(CO)_5$	(−)0·80	14
(8) $Bu_3SnFe(CO)_2(cp)$	−0·59	13

For the $Mn(CO)_5$ and $Fe(CO)_2(cp)$ moieties, it is desirable, as Clark *et al.* pointed out,[21] to derive p.q.s. values from compounds which are relatively close to ideal geometry. However, they chose the very distorted chlorides to calculate p.q.s. values for these metal moieties—probably because the signs of the q.s. were known. It seemed desirable to calculate p.q.s. values from the alkyl compounds, since $Me_3SnMn(CO)_5$ is known to be only slightly distorted from tetrahedral geometry, and the recently determined negative sign

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of the q.s. for $Bu_3SnFe(CO)_2(cp)$ [13] makes it highly probable that the sign of e^2qQ for $Me_3SnMn(CO)_5$ is also negative. We assume with Clark *et al.* that $(p.q.s.)_{Me} = (p.q.s.)_{Bu}$ and calculate $(p.q.s.)_{Mn(CO)_5}$ and $(p.q.s.)_{Fe(CO)_2(cp)}$ from the q.s. of compounds (7) and (8) respectively in Table 2. The values of $-0{\cdot}97$ mm s^{-1} for $(p.q.s.)_{Mn(CO)_5}$ and $-1{\cdot}08$ mm s^{-1} for $(p.q.s.)_{Fe(CO)_2(cp)}$ obtained differ considerably from those given by Clark *et al.*,[21] but generally give much better agreement between predicted and observed values for the compounds in Tables 4 and 5.

TABLE 3

Partial quadrupole splittings

Ligand	P.q.s.	Ref.
X (F, Cl, Br)	0·00	21
Ph	−1·26	21
R	−1·37	21
C_6F_5	−0·76	This work
$Mn(CO)_5$	−0·97	This work
$Fe(CO)_2(cp)$	−1·08	This work

TABLE 4

Predicted and observed values of e^2qQ and η

		Q.s.		η	
	Compound	Calc.	Obs.	Calc.	Obs.
(1)	$Ph_3SnMn(CO)_5$	−0·58	0·41	0·00	
(2)	$Ph_2(C_6F_5)SnMn(CO)_5$	−0·97	0·95	0·78	
(3)	$Ph(C_6F_5)_2SnMn(CO)_5$	+0·95	1·06	0·58	
(4)	$(C_6F_5)_3SnMn(CO)_5$	+0·42 *	+0·99	0·00	
(5)	$Ph_3SnFe(CO)_2(cp)$	−0·36	0·32	0·00	
(6)	$Ph_2(C_6F_5)SnFe(CO)_2(cp)$	−0·94	0·93	0·50	
(7)	$Ph(C_6F_5)_2SnFe(CO)_2(cp)$	+0·99	1·37	0·84	
(8)	$(C_6F_5)_3SnFe(CO)_2(cp)$	+0·64 *	1·21	0·00	
(9)	$Ph_2BrSnFe(CO)_2(cp)$	−2·42	2·52	0·20	
(10)	$PhBr_2SnFe(CO)_2(cp)$	+2·72	2·65	0·98	
(11)	$Br_3SnFe(CO)_2(cp)$	+2·16 *	1·63	0·00	
(12)	$Ph_2ClSnMn(CO)_5$	−2·39	2·50	0·32	
(13)	$PhCl_2SnMn(CO)_5$	+2·62	2·52	0·94	
(14)	$Cl_3SnMn(CO)_5$	+1·94	+1·60 [a]	0·00	
(15)	$Ph_2BrSnMn(CO)_5$	−2·39	2·31	0·32	
(16)	$PhBr_2SnMn(CO)_5$	+2·62	2·65	0·94	
(17)	$Br_3SnMn(CO)_5$	+1·94 *	1·53	0·00	
(18)	$Me_2ClSnMn(CO)_5$	−2·59	−2·60	0·41	0·35
(19)	$MeCl_2SnMn(CO)_5$	+2·79	+2·62	0·89	0·46
(20)	$Ph_2ClSnFe(CO)_2(cp)$	−2·42	2·54 [c]	0·20	
(21)	$PhCl_2SnFe(CO)_2(cp)$	+2·72	2·84 [c]	0·98	
(22)	$Cl_3SnFe(CO)_2(cp)$	+2·16	+1·83 [b]	0·00	

[a] Sign determined in ref. 13. [b] Sign determined in refs. 12 and 13. [c] Liengme *et al.*[15] have recently reported much smaller q.s. values. We have remeasured our q.s. values and they are certainly accurate.

TABLE 5

Predicted and observed q.s. values for other Sn–Fe and Sn–Mn compounds

		Q.s.			η
	Compound	Calc.	Obs.	(Ref.)	Calc.
(1)	$Me_2Sn[Mn(CO)_5]_2$	0·92	0·92	8	1·00
(2)	$MeSn[Mn(CO)_5]_3$	+0·80	0·95	8	0·00
(3)	$Ph_2Sn[Mn(CO)_5]_2$	0·67			1·00
(4)	$PhSn[Mn(CO)_5]_3$	+0·58			0·00
(5)	$Cl_2Sn[Mn(CO)_5]_2$	2·24	2·10	23	1·00
(6)	$ClSn[Mn(CO)_5]_3$	−1·94	1·55	1	0·00
(7)	$Br_2Sn[Mn(CO)_5]_2$	2·24	2·12	23	1·00
(8)	$BrSn[Mn(CO)_5]_3$	−1·94			0·00
(9)	$Me_3Sn[Fe(CO)_2(cp)]$	−0·58	0·46	9	0·00
(10)	$Me_2Sn[Fe(CO)_2(cp)]_2$	0·67	0	3	1·00
(11)	$MeSn[Fe(CO)_2(cp)]_3$	+0·58			0·00
(12)	$Ph_2Sn[Fe(CO)_2(cp)]_2$	0·42	0	2	1·00
(13)	$PhSn[Fe(CO)_2(cp)]_3$	+0·36	0	2	0·00
(14)	$Cl_2Sn[Fe(CO)_2(cp)]_2$	2·50	+2·39	13	1·0
(15)	$ClSn[Fe(CO)_2(cp)]_3$	−2·16			0·00
(16)	$Br_2Sn[Fe(CO)_2(cp)]_2$	2·50	2·42	23	1·00
(17)	$BrSn[Fe(CO)_2(cp)]_3$	−2·16			0·00
(18)	$ClSn[Mn(CO)_5][Fe(CO)_2(cp)]_2$	−2·10	2·02	2	0·14

Using these p.q.s. values (Table 3), we have calculated the q.s. and η for the compounds in this and our previous preliminary study [14] (Table 4), as well as the q.s. values and η for other Sn–Mn and Sn–Fe compounds (Table 5). The expressions for the EFG components in terms of the point-charge model are given in our previous paper [14] for tetrahedral geometry. Except for the four compounds asterisked in Table 4, the agreement between predicted and observed q.s. values is within the value $\pm 0{\cdot}4$ mm s^{-1} considered by Clark *et al.*[21] to be satisfactory considering the approximations involved.[21,22] [We consider that compounds (10), (12), and (13) in Table 5 will all have a small q.s. which have not yet been observed.] Indeed, calculated and observed q.s. values for the great majority of compounds in Tables 4 and 5 are within $0{\cdot}2$ mm s^{-1}. However, the lack of agreement for the four asterisked compounds makes it sometimes dangerous to infer degrees of association [44] from fairly small changes in q.s. values. Consideration of distortions using either the point-charge model or the MO treatment [21] does not improve agreement for the four asterisked compounds.

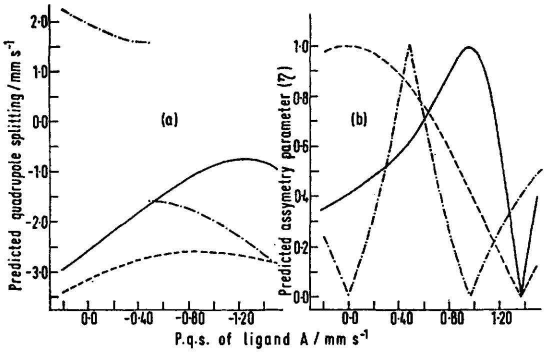

FIGURE 2 Variation of calculated values of (a) q.s. and (b) η with p.q.s. values of the ligands for $Me_2ClSnMn(CO)_5$: — — — = Me_2ClSnA, — • — • — = $A_2ClSnMn(CO)_5$, —— = $Me_2ASnMn(CO)_5$

The signs of the predicted quadrupole splittings are in agreement with those observed for compounds (4), (14), (18), (19), and (22) in Table 4, and the generally good agreement for the magnitude of the q.s. values makes it highly probable that the predicted signs in Tables 4 and 5 are correct. Even the predicted relative values of η for compounds (18) and (19) in Table 4 agree with the observed values, although the observed η value for compound (19) is appreciably smaller than that predicted.

An examination of $R_{3-n}X_nSnM$ ($n = 1$ or 2) quadrupole splittings indicates that as Clark *et al.* pointed out,[21] η should be much more sensitive to changes in p.q.s. values than the q.s., and this is illustrated in Figure 2. The three graphs in each figure illustrate the behaviour of the q.s. and η as the p.q.s. value of each ligand in

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[44] R. H. Platt, *J. Organometallic Chem.*, 1970, **24**, C23; A. G. Maddock and R. H. Platt, *J. Chem. Soc.* (*A*), 1971, 1191.

$Me_2ClMn(CO)_5$ is varied in turn through the range of p.q.s. values likely to be encountered for real ligands, while the p.q.s. values of the other two ligands are held to their values given in Table **3**. For $Me_2XSnMn(CO)_5$ and Me_2ClSnM, the magnitude of the q.s. is a minimum when the variable p.q.s. becomes equal to that of the other singly present ligand, so that the stoicheiometry of the system effectively becomes $SnAB_3$. On the $A_2ClSnMn(CO)_5$ curves, this situation occurs twice, but the point of minimum magnitude of q.s. occurs at a point where the variable ligand p.q.s. is equal to the average of the other two ligand p.q.s. values. It is interesting to note that a change of sign of q.s. occurs at this point, causing a discontinuity in the curve; and, from Figure 2(b), that $\eta = 1$ there. As would be expected, $\eta = 0$ at all points on the graph where the variable p.q.s. causes the stoicheiometry to become effectively $SnAB_3$, and $\eta = 1$ wherever the stoicheiometry is effectively SnA_2B_2. From the slope of the q.s. and η curves, it is apparent that η changes much more rapidly than q.s. for small changes in p.q.s. values, and the large discrepancy between predicted and observed η values for $MeCl_2SnMn(CO)_5$ is not surprising. Clark [45] has also recently shown for Co^{III} compounds, that small distortions will effect η values more significantly than q.s.

The p.q.s. values in Table **3** can also be used to rationalize bonding properties of ligands.[17-21] Since Clark *et al.*[21] have shown that any π bonding involving the Sn $5d$ orbitals would have no observable effect on the q.s., we need just consider σ bonding. The more negative the p.q.s. value, the greater is the Sn $5p_z$ orbital population.[17] Following Clark's treatment,[21] it is readily seen that this population will depend on *both* the donor strength of the ligand *and* the p character of the metal hybrid orbital. For example, if we consider an MO (α) to be a linear combination of a metal orbital h_L and a ligand orbital χ_L, then:

$$\alpha_L = c_1 h_L + c_2 \chi_L$$

Clark [21] showed that the p.q.s. values are proportional to c_1^2 which increases as the donor ability of the ligand increases. In addition, however, the population of the Sn $5p_z$ orbital will depend on the p character of the metal orbital.† Thus the order of donor ability plus p character of the bond increases in the order $Cl, Br < C_6F_5 < Mn(CO)_5 < Fe(CO)_2(cp) < Ph < Me$. Since it is known that the Sn–Cl bond has a larger Sn p character than the Sn–M or Sn–R bonds (see next section), it would appear that the above order reflects mainly the donor ability of the ligand. However, because of the smaller p character in Sn–M bond than in the Sn–R bond, it is possible that the metal moieties are comparable or better donors than Ph or Me.

Centre Shifts.—Previous Mössbauer results, and our present results, indicate that the s character in the Sn–L bond increases in the order $L = Cl < C_6F_5 < Ph \leqslant Me < Mn(CO)_5 < Fe(CO)_2(cp)$. To establish this order the following results are considered, as noted in the Introduction. In the series X_nSnM_{4-n} and R_nSnM_{4-n}, the trend in c.s. values indicated that the order of s character in the Sn–L bond varied in the order $L = Cl, Br < R < M$.[6,8,10,12] ^{55}Mn N.m.r. and ^{1}H n.m.r. data support this interpretation [6,10] for these and other compounds. The generally larger c.s. for compounds containing the $Fe(CO)_2(cp)$ moiety compared with the analogous $Mn(CO)_5$ compounds (Table 1) strongly indicate that the Sn–Fe bond has a larger $5s$ character than the Sn–Mn bond, especially since the q.s. results indicate that $Fe(CO)_2(cp)$ is a better p donor than $Mn(CO)_5$; this would tend to decrease the c.s. of $Fe(CO)_2(cp)$ compounds relative to $Mn(CO)_5$ compounds. A similar argument applies to the relative s characters in the Sn–Me and Sn–Ph bonds. Me compounds generally have larger c.s. than Ph compounds [*e.g.* c.s. of Me_4Sn and Ph_4Sn are 1·31 and 1·22 mm s^{-1} (ref. 46) respectively]; this indicates the greater s character of the Sn–Me bond. Again the p donor strengths from p.q.s. values would give the opposite trend.

C_6F_5 lies before Ph in this s character series. For example, in the series of compounds $Ph_{4-n}Sn(C_6F_5)_n$,[47] the c.s. decreases from 1·22 mm s^{-1} for Ph_4Sn to 1·04 mm s^{-1} for $(C_6F_5)_4Sn$ indicating that the Sn–Ph bond has a higher s character than the Sn–C_6F_5 bond. Again, the relative donor strengths from p.q.s. values would give the opposite trend.

Having established this s character series, we can now rationalize trends in c.s. for our compounds and other organotin compounds, and also show that our series is entirely consistent with bond angle data for A_3SnB and A_2SnB_2 systems (Table 6). For our compounds of type $A_{3-n}B_nSnM$ and $A_{4-n}SnB_n$ ($A = Ph$ or Me; $B = Cl$, Br, or C_6F_5; and A is higher in the s character series than B),

TABLE 6

Bond angle data for some selected organotin compounds *

	Compound	β	α	Ref.
(1)	Ph_3SnCl	106·4	112·4	48
(2)	$Me_3SnMn(CO)_5$	111·6	107·3	38
(3)	$Ph_3SnMn(CO)_5$	112·7	106·0	39
(4)	$Ph_3SnFe(CO)_2(cp)$	113·4	105·2	40
(5)	$Cl_3SnFe(CO)_2(cp)$	119·2	98·3	41
(6)	$Ph_2Sn[Mn(CO)_5]_2$	117	100	*a*
(7)	$Ph_2Sn[Fe(CO)_2(cp)]_2$	116	95	*b*
(8)	$Me_2Sn[Fe(CO)_2(cp)]_2$	123	104	*c*
(9)	$Cl_2Sn[Fe(CO)_2(cp)]_2$	128·6	94·1	*d*
(10)	Ph_2SnCl_2	100	125·5	49

* For compounds (1)—(5) (A_3SnB compounds), α = A–Sn–A angle, and β = A–Sn–B angle: but for compounds (6)—(10) (A_2SnB_2 systems), then α = A–Sn–A angle, and β = B–Sn–B angle.

[a] B. T. Kilbourn and H. M. Powell, *Chem. and Ind.*, 1964, 1578. [b] B. P. Bir'yukov, Yu. T. Struchkov, K. H. Anisimov, N. E. Kolobova, and V. V. Skripkin, *Chem. Comm.*, 1968, 1193. [c] B. P. Bir'yukov, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, *Chem. Comm.*, 1968, 159. [d] J. E. O'Connor and E. R. Corey, *Inorg. Chem.*, 1967, **6**, 968.

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† The contribution from the p character may be reduced somewhat because we have derived our p.q.s. values assuming tetrahedral geometry.

[45] M. G. Clark, *Chem. Phys. Letters*, 1972, **13**, 316.

[46] P. J. Smith, *Organometallic Chem. Rev.* (*A*), 1970, **5**, 373.

the further apart A and B are in the series, the greater is the increase of c.s. with increase in n. This trend is rationalized considering three factors. First, the q.s. data shows that the B groups are poorer donors than A. Considering *just* the effect of p electron density, replacement of A by B will increase $[\Psi(0)s]^2$ by deshielding and the c.s. will *increase*. Second, in opposition to the above effect, if there is appreciable s character in the Sn–B bond, withdrawal of s electrons will *decrease* the c.s. relative to A. Whether the c.s. decreases or increases then will depend on the relative s characters in the Sn–A and Sn–B bonds. Thirdly, in the $A_{3-n}B_nSnM$ system, replacement of A by B causes a concomitant increase in the s character of the Sn–M bond and the c.s. *increases* more markedly than might be expected from the first effect.

To examine the first two effects, we first consider the $Ph_{4-n}Sn(C_6F_5)_n$ and $Ph_{4-n}SnCl_n$ series. In the first series the c.s. decreases with n because the second effect is dominant. The s characters of the Sn–Ph and Sn–C_6F_5 bonds are similar, and C_6F_5 effectively withdraws s electron density. However, in the second series, the first effect is more important and the c.s. increases from Ph_4Sn (1·22 mm s^{-1}) [46,47] to Ph_2SnCl_2 [28] (1·38 mm s^{-1}). In the latter compound the Sn–Cl has comparatively little s character as evidenced by the Cl–Sn–Cl angle of 100°.[49]

In our $A_{3-n}B_nSnM$ compounds, the data in Table 1 indicates again that when B = Cl or Br, the c.s. increases much more markedly than for B = C_6F_5, and that the increase is much greater than for the $A_{4-n}SnB_n$ series. This much greater increase is attributed to the third effect. When Ph is replaced by Cl or C_6F_5, the Sn–M bond gains s character,[6] and this effect enhances the increase in the c.s. due to withdrawal of mostly p electron density by Cl, or the slight decrease due to substitution of Ph by C_6F_5.

Considering structural data, we would expect that the greater the difference in s characters of the Sn–L bonds in tetrahedral compounds, the greater would be the deviation from tetrahedral geometry, and the smaller the L–Sn–L bond angles for the L–Sn bonds of lowest s character. These expectations are borne out by the data in Table 6, and enlarge the initial ideas of Zuckerman [6] and Parish and Platt.[28] Thus, $Me_3SnMn(CO)_5$ is only slightly distorted from tetrahedral geometry and Me and $Mn(CO)_6$ have similar s characters. By contrast, $Cl_3SnFe(CO)_2(cp)$ is the most distorted of the $A_{3-n}SnB_n$ compounds in Table 6, and Cl and $Fe(CO)_2(cp)$ are the farthest apart in our s character series. The distortions in the other $A_{3-n}SnB_n$ compounds qualitatively agree with that predicted from the s character series: *i.e.* $Me_3SnMn(CO)_5 < Ph_3SnMn(CO)_5 \sim Ph_3SnCl < Ph_3SnFe(CO)_2(cp) < Cl_3SnFe(CO)_2(cp)$; and the angles in the Ph_3SnCl agree with those which might be expected for the four-co-ordinate species [47] with the s character concentrated in the Ph–Sn bonds.

Similarly, in the A_2SnB_2 compounds, the relative order of distortion is that expected from the s character series, although the distortion is greatly increased from the A_3SnB compounds. Thus, $Ph_2Sn[Mn(CO)_5]_2$ is the least distorted, while $Cl_2Sn[Fe(CO)_2(cp)]_2$ is the most distorted. It is difficult to assess qualitatively the other distortions, but it is interesting to note than the distortion in Ph_2SnCl_2 is similar to that in such compounds as $Me_2Sn[Fe(CO)_2(cp)]_2$ which also contains two non-nearest neighbour ligands in the s character series. This data is thus consistent with Ph_2SnCl_2 and Ph_3SnCl being four-co-ordinate with no unusual association as recently determined by Mössbauer [44,20] and X-ray analysis.[48,49]

Finally, it is interesting to note that the Fe–Sn bond length decreases as the proposed s character of the bond increases. Thus the Sn–Fe bond length decreases from 2·54 Å for $Ph_3SnFe(CO)_2(cp)$, to 2·50 Å for $Ph_2ClSnFe(CO)_2(cp)$ and to 2·47 Å for $PhCl_2SnFe(CO)_2(cp)$ and $Cl_3SnFe(CO)_2(cp)$. The bond length, like the centre shift, levels off for the latter two compounds. These results illustrate the large effect on the c.s. caused by variations in the nature of the metal–metal bond.

We thank the National Research Council of Canada for financial support, and Dr. H. C. Clark and Dr. T. G. Appleton for helpful discussions.

[2/907 *Received, 24th April,* 1972]

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[49] P. T. Greene and R. F. Bryan, *J. Chem. Soc.* (*A*), 1971, 2549.