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^{57}Fe and ^{119}Sn Mössbauer Spectra of Phosphine and Phosphite Derivatives of $Ph_{3-n}Cl_nSnFe(CO)_2(\pi\text{-}C_5H_5)$ Compounds

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The ^{119}Sn Mössbauer spectra of the series $Ph_{3-n}Cl_n SnFe(CO)_{2-x}cpL_x$ [$n = 0$–3, $x = 1$ for $L = PPh_3$, PEt_3, $P(OPh)_3$, and $x = 2$ for $L = P(OPh)_3$] are reported, together with the ^{57}Fe Mössbauer parameters, ν_{CO} stretching frequencies, and $\tau_{C_5H_5}$ nmr shifts for the series $Ph_{3-n}Cl_nSnFe(CO)cpL$ ($n = 0$ to 3, and $L = CO$ or PPh_3) and $Cl_3SnFe(CO)_{2-x}cpL_x$ [$x = 1$ for $L = PPh_3$, PEt_3, $P(OPh)$, $P(OEt)_3$ and $x = 2$ for $L = P(OPh)_3$]. The ^{57}Fe centre shifts show that there is a large Fe 4s character in the Fe–Sn bond, and that ($\sigma + \pi$) of the L ligands increase in the order $PPh_3 < PEt_3 < P(OPh)_3 < P(OEt)_3 < CO$. The change in substituents on the Fe atom results in considerable variation in the ^{119}Sn parameters. The ^{119}Sn quadrupole splittings indicate that the Fe–Sn bond has a smaller Sn 5s character in Fe(CO)cpL compounds than in the $Fe(CO)_2cp$ compounds. Together with results on phosphine-substituted $SnCo(CO)_4$ compounds, it is shown that discrepancies between predicted (using partial quadrupole splittings) and observed quadrupole splittings are substantially due to the variations in s character of the Sn–M (M = Fe, Co) bonds.

Introduction

In previous papers,[1,2,3] we have reported the ^{119}Sn Mössbauer parameters of a large number of four coordinate Sn compounds of the type $R_lX_mSnM_n$ ($l + m + n = 4$, R = Me, Ph, C_6F_5; X = Cl, Br, I; M = $Mn(CO)_5$, $Fe(CO)_2cp$ and $Co(CO)_4$). Partial quadrupole splittings[4] (pqs) have been used successfully to rationalize variations in signs and magnitudes of quadrupole splittings (Q.S.). From the pqs values, the donor strength of the ligands were determined, and from the centre shifts (C.S.), it was possible to deduce an s character series which was consistent with known structural data.

Although the agreement between predicted and observed quadrupole splittings is generally very good[1,2,3,5], the predicted quadrupole splittings for some compounds such as the Cl_3SnM (M = $Mn(CO)_5$, $Fe(CO)_2cp$) were substantially larger than those observed. For example, for $Cl_3SnFe(CO)_2cp$, the predicted and observed quadrupole splittings are +2.16 mm s^{-1} and +1.83 mm s^{-1} respectively. To try to understand why such differences arise, we have undertaken a detailed study of the ^{57}Fe and ^{119}Sn Mössbauer parameters for compounds of the type $Ph_{3-n}Cl_nSnFe(CO)_{2-x}cpL_x$[$n = 0$–$3$, $x = 1$ for L = PPh_3, PEt_3, $P(OPh)_3$ and $x = 2$ for L = $P(OPh)_3$] in which there should be small subtle changes in the Fe–Sn bond. Since this work was started, two papers on analogous Sn–Fe compounds of the types $R_3SnFe(CO)_{2-x}cpL_x$[6], $R_3SnFe(dppe)cp$ and $X_3SnFe(dppe)cp$[7] have been published. Because signs of quadrupole splittings were sometimes lacking, a complete interpretation in terms of partial quadrupole splittings could not be made. In addition, the interpretation of these two papers is often at variance with that proposed for similar $R_3SnMn(CO)_4L$ compounds.[8]

With the large amount of data in this paper along with previous ^{119}Sn spectra on similar compounds, we are able to rationalize differences in Mössbauer parameters in terms of changes in the Sn–Fe bond, and to propose a possible explanation for discrepancies between predicted and observed quadrupole splittings.

Experimental

All compounds in this work were prepared as described previously[9]. The ^{57}Fe Mössbauer spectra were obtained at 298 K using a 50 mCi ^{57}Co/Cu source, while the ^{119}Sn spectra were obtained at 80 K using a 5 mCi $BaSnO_3$ source at room temperature. A typical ^{119}Sn spectrum is given in the Figure. Calibration was performed using the ^{57}Fe spectrum of a 99.99% Fe foil at room temperature, and the scan centre method[10,11] Spectra were computed to Lorentzian line shapes using A. J. Stone's program as outlined previously.[10] In some Sn spectra, no quadrupole splitting was visually resolvable, but χ^2 decreased by over 50 on fitting two peaks. Infrared spectra and H nmr spectra were obtained as described previously.[9]

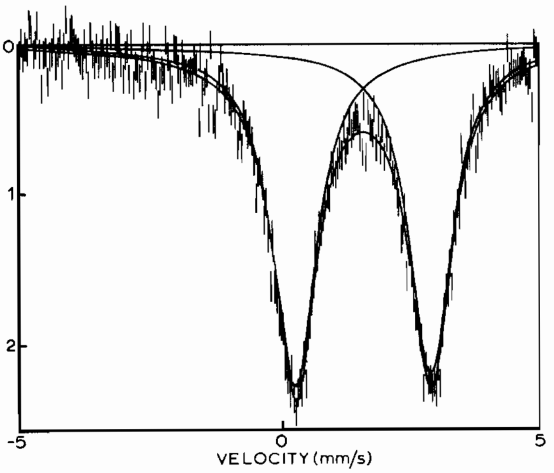

Figure. ^{119}Sn Mössbauer spectrum of $Ph_2ClSnFe(CO)_2cp$.

Discussion

^{57}Fe Spectra

^{57}Fe Mössbauer parameters are shown in Table I for the $Ph_{3-n}Cl_nFe(CO)_2cp$ and $Ph_{3-n}Cl_nFe(CO)cp$ PPh_3 compounds, as well as for the $Cl_3SnFe(CO)cpL$ ($L = PPh_3, PEt_3, P(OPh)_3$ and $P(OEt)_3$) compounds and $Cl_3SnFecp[P(OPh)_3]_2$. The results for $Ph_3SnFe(CO)cp$ PPh_3 and $Cl_3SnFe(CO)cpPPh_3$ are in good agreement with those published previously[6] when the centre shifts are corrected for the normal temperature shift between 78K and 298K.[12] Thus our room temperature centre shifts are ~0.07 mm s^{-1} lower than those reported previously at liquid nitrogen temperature.

In the $Ph_{3-n}Cl_nFe(CO)_2cp$ and $Ph_{3-n}Cl_nFe(CO)cp$ PPh_3 compounds (1–4 and 5–8, Table I), the ^{57}Fe centre shifts are remarkably insensitive to the different substituents on the Sn, while the CO stretching frequencies and τ_{Cp} change substantially. The latter two variations indicate that there is a substantial build up of charge on the Fe atom from the Cl_3Sn compound to the Ph_3Sn compound, as expected from an increase in σ donor ability in this direction. Thus, CO becomes a better π acceptor from Cl_3Sn to Ph_3Sn, and the concomitant increase in τ_{Cp} indicates an increased shielding of the C_5H_5 protons. Such an inverse correlation between ν_{CO} and τ_{Cp} has been well documented.[13] The constant ^{57}Fe centre shift is one more indication of the high *s* character of the Sn–Fe bond – in this case the high Fe 4*s* character of the bond. Although Ph_3Sn is a better σ donor than Cl_3Sn, the Fe 4*s* character in the Fe–Sn bond in the Ph_3Sn compound is substantially smaller than in the Cl_3Sn compound such that the 4*s* electron density and the *s* electron density at the Fe nucleus is very similar for both. The Fe *s* character thus parallels the change in Sn *s* character of the Fe–Sn bond.[1,2]

However in the CO substituted compounds (5–12, Table I), the ^{57}Fe C.S. changes in a way which is entirely consistent with that expected from Fe(II) low spin compounds[12]. Thus for PPh_3, a constant increase in C.S. of about 0.10 mm s^{-1} is obtained on substituting CO for PPh_3 (compounds 5–8). This is very close to the difference in partial centre shift values (0.08 mm s^{-1}) assigned to these two ligands in the Fe(II) work[12], and indicates that PPh_3 is an appreciably poorer ($\sigma + \pi$) ligand than CO[12,14]. Similarly for compounds 8–11, it is apparent that ($\sigma + \pi$) increases in the order PPh_3

TABLE I. ^{57}Fe Mössbauer, Infrared and NMR Data for the Compounds $Ph_{3-n}Cl_nSnFe(CO)_{2-x}(cp)L_x$ at 298°K.

Compound	C.S.[a,b]	Δ C.S.[a,c]	Q.S.[a]	Γ_1[a]	Γ_2[a]	ν(CO)cm^{-1} [d]		τ_{cp}[f]
1. $Ph_3SnFe(CO)_2cp$	0.28		1.75	0.27	0.26	1997	1950	5.29 s
2. $Ph_2ClSnFe(CO)_2cp$	0.30		1.71	0.25	0.28	2014	1966	5.12 s
3. $PhCl_2SnFe(CO)_2cp$	0.30		1.68	0.25	0.27	2030	1986	4.96 s
4. $Cl_3SnFe(CO)_2cp$	0.32		1.82	0.27	0.26	2050	2010	4.94 s
5. $Ph_3SnFe(CO)(cp)PPh_3$	0.39	0.11	1.79	0.23	0.25	1913	1924 sh[e]	5.67 d
6. $Ph_2ClSnFe(CO)(cp)PPh_3$	0.39	0.09	1.73	0.24	0.24	1932		5.48 d
7. $PhCl_2SnFe(CO)(cp)PPh_3$	0.40	0.10	1.73	0.24	0.24	1949		5.32 d
8. $Cl_3SnFe(CO)(cp)PPh_3$	0.41	0.09	1.80	0.24	0.25	1973[e]		5.28 d
9. $Cl_3SnFe(CO)(cp)PEt_3$	0.40	0.08	1.84	0.30	0.31	1968		5.22 d
10. $Cl_3SnFe(CO)(cp)P(OPh)_3$	0.36	0.04	1.77	0.25	0.26	1996		5.54 d
11. $Cl_3SnFe(CO)(cp)P(OEt)_3$	0.35	0.03	1.79	0.30	0.26	1985		5.61 d
12. $Cl_3SnFe(cp)[P(OPh)_3]_2$	0.44	0.12	1.80	0.25	0.26	–		5.55 t

[a] All units are in mm s^{-1} and errors are ± 0.01 mm s^{-1} for C.S. and Q.S. and ± 0.02 mm s^{-1} for Δ C.S. [b] Relative to sodium nitroprusside. [c] Δ C.S. = C.S. $[Ph_{3-n}Cl_nSnFe(CO)_{2-x}cpL_x]$–C.S. $[Ph_{3-n}Cl_nSnFe(CO)_2cp]$. [d] In $CHCl_3$ solution, errors are ± 4 cm^{-1}. [e] From reference 6, values for $Ph_3SnFe(CO)(cp)PPh_3$ are 1911 and 1923 cm^{-1}, and 1969 cm^{-1} for $Cl_3SnFe(CO)(cp)PPh_3$ both in cyclohexane solution. [f] In $CDCl_3$ solution: s, singlet; d, doublet; t, triplet, errors are ± 0.01.

E<PEt_3<$P(OPh)_3$<$P(OEt)_3$<CO in agreement with the order established from the Fe(II) low spin compounds. Once again, ΔC.S. is within error equal to the differences in pcs values (Δpcs) established in the Fe(II) study (Δpcs for PPh_3, $P(OPh)_3$ and $P(OEt)_3$ are 0.07, 0.06 and 0.05 mm s^{-1} respectively compared to ΔC.S. in Table I of 0.08, 0.04 and 0.03 mm s^{-1} respectively).

As for the Fe(II) carbonyl compounds reported earlier[12], the phosphite compounds have substantially larger ν_{CO} frequencies than the phosphines indicating that the phosphites are substantially better π acceptors than the phosphines. Also, the CO doublet in the infrared for $Ph_3SnFe(CO)cpPPh_3$ is consistent with the existence of two rotamers, as noticed previously[6].

As noted in previous papers[6,15], the quadrupole splittings are all ~1.8 ± 0.1 mm s^{-1} and there are no discernable trends. These constant values are due to the compensating bonding nature of CO and Cp, and the changes in η which can mask changes in the Q.S. due to bonding variations.[15]

^{119}*Sn spectra*

As shown in our previous work[1,2,3], the centre shift for the $R_{3-n}Cl_nSnM$ compounds [M = $Fe(CO)_2cp$, $Mn(CO)_5$] increases as x increases, and a parallel trend is seen in Table II for the substituted compounds. This trend is largely due[2,3] to the concentration of Sn 5*s* electron density in the Sn–M bond, and the high *p* character in the Sn–X bonds. It is immediately apparent in the substituted compounds that the Sn C.S. increases from the parent compound and that the phosphites generally show smaller increases in the Sn C.S. than the phosphines–as for the Fe C.S. results. Thus the *s* electron density at the Sn nucleus increases in the order CO < $P(OR)_3$ < PR_3. It is interesting that the change in ^{119}Sn C.S. is at least as large as the changes in ^{57}Fe

TABLE II. ^{119}Sn Mössbauer Data for the compounds $Ph_{3-n}Cl_nSnFe(CO)_{2-x}(cp)L_x$ at 80°K.

Compound	C.S.[a,b,g]	Δ C.S.[c,g]	Q.S.[a,g]	Δ Q.S.[c,g]	Γ_1[a]	Γ_2[a]
$Ph_3SnFe(CO)_2cp$[d]	1.39		0.32 ± 0.10		1.06	1.06
[e]	1.41		0		0.96	
$Ph_2ClSnFe(CO)_2cp$[d]	1.57		2.54		1.31	1.16
$PhCl_2SnFe(CO)_2cp$[d]	1.70		2.84		1.15	1.12
$Cl_3SnFe(CO)_2cp$[d]	1.75		1.83		1.18	1.12
[e]	1.77		1.80		0.99	0.99
$Ph_3SnFe(CO)(cp)PPh_3$	1.53	0.14	0.66 ± 0.10	0.34 ± 0.15	1.22	0.95
[e]	1.48		0.69		0.83	0.83
$Ph_2ClSnFe(CO)(cp)PPh_3$	1.63	0.11	2.74	0.20	1.07	1.07
$PhCl_2SnFe(CO)(cp)PPh_3$	1.80	0.10	3.00	0.16	1.04	1.05
$Cl_3SnFe(CO)(cp)PPh_3$	1.86	0.11	1.89	0.06	1.10	1.04
[e]	1.88		1.88		0.82	0.80
$Ph_3SnFe(CO)(cp)PEt_3$	1.51	0.12	0.76 ± 0.10	0.44 ± 0.15	1.03	1.00
$Ph_2ClSnFe(CO)(cp)PEt_3$	1.63	0.11	2.59	0.05	1.27	1.08
$PhCl_2SnFe(CO)(cp)PEt_3$	1.83	0.13	3.03	0.19	1.23	1.11
$Cl_3SnFe(CO)(cp)PEt_3$	1.95	0.20	1.91	0.08	1.15	1.07
$Ph_3SnFe(CO)(cp)P(OPh)_3$[f]	1.48	0.09	0.53 ± 0.10	0.21 ± 0.15	0.97	0.97
	1.39	0	0	0	1.29	
$Ph_2ClSnFe(CO)(cp)P(OPh)_3$	1.57	0.05	2.69	0.15	1.29	1.13
$PhCl_2SnFe(CO)(cp)P(OPh)_3$	1.77	0.07	2.83	–0.01	1.13	0.98
$Cl_3SnFe(CO)(cp)P(OPh)_3$	1.79	0.04	1.82	–0.01	1.14	0.96
$Ph_3SnFe(cp)[P(OPh)_3]_2$	1.49	0.10	0.78 ± 0.10	0.46 ± 0.15	1.05	0.93
$Ph_2ClSnFe(cp)[P(OPh)_3]_2$	1.65	0.13	2.71	0.17	1.07	1.03
$PhCl_2SnFe(cp)[P(OPh)_3]_2$	1.75	0.05	2.90	0.06	1.07	1.04
$Cl_3SnFe(cp)[P(OPh)_3]_2$	1.88	0.13	1.92	0.09	1.17	0.97
$Cl_3SnFe(CO)(cp)P(OEt)_3$	1.77	0.02	1.85	0.02	1.12	1.04

[a] All units are in mm s^{-1}. [b] C.S. values are relative to barium stannate at room temperature. [c] Δ C.S. (Q.S.) = C.S. (Q.S.) $[Ph_{3-n}Cl_nSnFe(CO)_{2-x}cpL_x]$–C.S. (Q.S.) $[Ph_{3-n}Cl_nSnFe(CO)_2cp]$. [d] Reference 2. [e] Reference 6. [f] Constrained fit; line widths held equal at 0.97 mm s^{-1}. [g] Errors in C.S. and Q.S. are ±0.02 mm s^{-1}, and ±0.04 mm s^{-1} for Δ C.S. and Δ Q.S. except where noted.

C.S. for the same compound indicating a fairly free flow of electrons across the Fe–Sn bond.

The increase in C.S. cannot be rationalized by a π bonding argument as pointed out recently[6,16] because the expected strongest π acceptor $Fe(CO)_2cp$ gives the smallest Sn C.S. Thus the increase in Sn C.S. can only be due to an increase in σ donor power in the order $L = CO < P(OR)_3 < PR_3$ and/or that there is an increase in the Sn *s* character of the Sn–Fe bond in the above direction. As we will show below, the quadrupole splittings indicate that the *s* character of the Sn–Fe bond increases in the opposite order to that given above, *i.e.* $PR_3 \leq P(OR)_3 < CO$. It thus appears that the donor properties of the ligands are most important in determining the ^{119}Sn C.S. in these compounds.

We assume that all Ph_3Sn compounds have negative quadrupole splittings as shown for $Bu_3SnFe(CO)_2cp$,[17] and that the Cl_3Sn compounds have positive Q.S. as shown for $Cl_3SnMn(CO)_5$ and $Cl_3SnFe(CO)_2cp$[17]. It is immediately apparent from Table II that for the Sn–Fe compounds, the substituted $Ph_3SnFe(CO)cpL$ compounds have Q.S. values that become *larger* (more negative) than the parent $Ph_3SnFe(CO)_2cp$. In contrast, the corresponding Q.S. for the $Ph_3SnCo(CO)_3L$ compounds become *smaller* than their parent $Ph_3SnCo(CO)_4$ (Table III). These results indicate that the pqs values for the Fe(CO)cpL species becomes *less* negative than that for $Fe(CO)_2cp$, while those for the $Co(CO)_3L$ species become *more* negative than for $Co(CO)_4$. Specifically, the derived pqs value for $Fe(CO)cpPPh_3$ is -0.93 mm s^{-1} compared to -1.08 mm s^{-1} for $Fe(CO)_2cp$, while that for $Co(CO)_3PPh_3$ is $\gtrsim -0.9$ mm s^{-1} compared to -0.7 mm s^{-1} for $Co(CO)_4$. Using the pqs treatment, the $SnCl_3$ compounds should show equal and opposite changes in Q.S. between the parent and substituted compounds. This is in fact observed for the $Co(CO)_4$ and $Co(CO)_3PBu_3$ compounds, but is not observed for the $Fe(CO)_2cp$ compounds (Tables II and III). The predicted values for $Cl_3SnCo(CO)_4$, $Cl_3SnCo(CO)_3PBu_3$ and $Cl_3SnFe(CO)cpPPh_3$ (and other L ligands) are in substantial agreement with those observed, while the predicted value for $Cl_3SnFe(CO)_2cp$ differs from the observed by over 0.4 mm s^{-1}. Predicted (and observed) values in mm s^{-1} are respectively; 1.42(1.20), ~1.8(1.67), 1.86(1.89) and 2.16(1.83).

TABLE III. ^{119}Sn Mössbauer Quadrupole Splittings for Substituted $R_{3-n}Cl_nCo(CO)_4$ Compounds.

Compound	Q.S.	Δ Q.S.	Ref.
$Cl_3SnCo(CO)_4$	(+) 1.20		3, 16
$Cl_3SnCo(CO)_3PBu_3$	(+) 1.67	0.47	16
$Ph_3SnCo(CO)_4$	(−) 1.14		3, 16
$Ph_3SnCo(CO)_3PBu_3$	<0.6	>0.5	16
$Cl_2Sn[Co(CO)_4]_2$	1.43		3, 16
$Cl_2Sn[Co(CO)_3PBu_3]_2$	1.96	0.53	16
$Ph_2Sn[Co(CO)_4]_2$	1.22		3, 16
$Ph_2Sn[Co(CO)_3PBu_3]_2$	<0.6	>0.6	16

The above trends can be rationalized considering the relative *s* characters of the Sn–M bonds. We have shown previously[2,3] that the Sn–Fe bond in the $Fe(CO)_2cp$ compounds has a larger and more variable Sn 5*s* character than the Sn–Co bonds in the $Co(CO)_4$ compounds. For convenience, the pqs can be represented by:

$$\text{pqs} \propto -\sigma(1-s) \qquad (1)$$

where σ = donor capacity of the ligand L, s = Sn 5*s* character in the Sn–L bond. Thus the pqs value becomes more negative as σ increases and more positive as the *s* character increases. The increased negative pqs value for $Co(CO)_3PBu_3$ compared to $Co(CO)_4$ is readily rationalized if $Co(CO)_3PBu_3$ is a better donor than $Co(CO)_4$, as expected. The acceptable agreement between predicted and observed quadrupole splittings for both $Co(CO)_4$ and $Co(CO)_3PBu_3$ compounds indicates that the pqs value (and thus the *s* character of the Sn–Co bond) is not changing substantially. The *s* character in the Sn–Co bond in the Cl_3SnCo compounds is known to be slightly larger than the *s* character in the Sn–Co bond in the Ph_3SnCo compounds. This increase results in a slightly smaller measured Q.S. than predicted for the Cl_3SnCo compounds. In addition, the *s* character in the Sn–Co bond does not appear to vary measurably between $Co(CO)_4$ and $Co(CO)_3PBu_3$, and the expected differences in the Ph_3Sn, Ph_2Sn, Cl_3Sn and Cl_2Sn compounds are observed (Table III).

However, for the Fe(CO)cpL species, the *s* character in the Sn–Fe bond varies markedly, both between the Ph_3SnFe compound and the Cl_3SnFe compounds, but also as CO is replaced by phosphines and phosphites. In the $Fe(CO)_2cp$ compounds, the s character in the Sn–Fe bond increases markedly on going from the Ph_3Sn compound to the Cl_3Sn compound[2], such that the "effective" pqs value for $Fe(CO)_2cp$ varies from -1.08 mm s^{-1} to -0.93 mm s^{-1} respectively. This decrease in pqs is as expected if *s* is dominant in eq. 1. When CO is replaced by phosphines or phosphites, the pqs value for the Fe(CO)cpL moiety becomes less negative despite the expected increase in σ. The decrease in pqs value can then be attributed to a smaller Sn *s* character in the Sn–Fe bond in Fe(CO)cpL than in $Fe(CO)_2cp$, and we obtain good agreement between predicted and observed Q.S. for the $Cl_3SnFe(CO)cpL$ compounds. Like in the Co compounds, the smaller *s* character is accompanied by a smaller variation in *s* character between Ph_3SnM and Cl_3SnM compounds. At the present time, we prefer not to derive pqs values for the substituted ligands Fe(CO)cpL because of the relatively large error in the magnitudes of the Ph_3Sn Q.S. values.

It is apparent, then, that pqs values should be derived from the least distorted compounds in which the *s* characters of the Sn ligand bonds are similar. Discrepancies between predicted and observed quadrupole splittings will occur when there are large changes in Sn *s* character in a Sn–L bond from one compound to another. For small changes in *s* character, compensating changes in pqs values of the other ligands will result in good agreement between predicted and observed Q.S. values.

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