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Synthesis and spectroscopic and X-ray structural characterisation of some *para*-substituted triaryltin(pentacarbonyl)manganese(I) complexes

Dharamdat Christendat, Ivor Wharf *, Anne-Marie Lebuis, Ian S. Butler *, Denis F.R. Gilson *

Department of Chemistry, McGill University, 801, Sherbrooke Street, W. Montreal, Quebec, Canada H3A 2K6

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Abstract

A series of *para*-substituted triaryltin(pentacarbonyl)manganese(I) compounds $[(p-XC_6H_4)_3SnMn(CO)_5$: II, $X = CH_3$; III, $X = CH_3$; II, $X = CH_3$; IV, $X = CH_3$; V, X = F; VI, X = C; VII, $X = CH_3S(O_2)$] is reported for comparison with the known phenyl analogue I. IR data $[\nu(CO)]$ as well as complete ¹¹⁹Sn/⁵⁵Mn/¹³C solution NMR results are given for I–VII. Chemical shifts, ¹¹⁹Sn versus ⁵⁵Mn, except I, correlate well, but have differing single parameter (SP) correlations, ¹¹⁹Sn versus σ_1 and ⁵⁵Mn versus σ_p° . These results are compared with previous SP studies of the ¹¹⁹Sn solution NMR spectra of the series, $(p-XC_6H_4)_4$ Sn and $(p-XC_6H_4)_3$ SnY (Y = Cl, Br, I). Full crystal structures are reported for compounds II–VI. All are similar to that of I, with the Mn(CO)₅ moiety being a distorted tetragonal pyramid, and having a quasi-mirror plane through the central C₄Mn–SnC₃ skeleton. The Ar₃Sn are distorted trigonal propellers with ring torsion angles in the range 30–80°, the exception being IV with one torsion angle of 22°. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Triaryltin(pentacarbonyl)manganese(I) compounds; Crystal structures; IR spectra; ¹¹⁹Sn/⁵⁵Mn/¹³C NMR

1. Introduction

Substituent effects in the ¹¹⁹Sn and ¹³C NMR spectra of aryltins have been reported recently for various Ar₄Sn and Ar₃SnX (Ar = Aryl; X = Cl, Br, I, NCS) compounds [1,2] as well as earlier for ArSn(CH₃)₃ [3]. We have extended these studies to the bimetallic system, Ar₃SnMn(CO)₅, by observing for the first time the solid-state ¹¹⁹Sn NMR spectra for a series of these compounds containing a range of *para*-substituents [4]. In this work, use was made of *para*-substituents having varying σ - and π -interactions with the phenyl rings to probe differences in the various NMR parameters that can be obtained in this type of study.

Solid-state (CP-MAS) NMR spectra of a ¹¹⁹Sn nu-

cleus (I = 1/2) bound to one or more nuclei **X** (I > 1/2) provide much more information [5–7] than do the corresponding solution spectra where only the ¹¹⁹Sn chemical shift of the solution species is obtained. However, for the complete analysis of solid-state NMR data, a precise value of $r_{\text{Sn-X}}$ must be known. Thus as part of our solid-state study of Ar₃SnMn(CO)₅ derivatives, crystal structures of all but one of the compounds examined were obtained and compared with that of (Ph₃Sn)Mn(CO)₅ [8]. Some aspects of the crystal structures determined have already been given [4]. Full details of these structures are now reported here.

Comprehensive solution NMR data (¹¹⁹Sn, ⁵⁵Mn, and ¹³C) have also been obtained for the various *para*-substituted (Ar₃Sn)Mn(CO)₅ derivatives, enabling a study of electronic substituent effects in this system, independent of structural factors, to be realised. In addition, a comparison with an earlier study [1] of *para*-substituent effects in the ¹¹⁹Sn and ¹³C NMR spectra of Ar₄Sn and Ar₃SnX (X = Cl, Br, I) enables the bonding characteristics of Mn(CO)₅ versus halogen

^{*} Corresponding authors. Tel.: +1-514-398 6931; fax: +1-514-398 3797.

E-mail addresses: ivor.wharf@mcgill.ca (I. Wharf), ian.butler@mcgill.ca (I.S. Butler), denis.gilson@mcgill.ca (D.F.R. Gilson).

as a substituent on tin in Ar₃SnX complexes to be assessed. Although ⁵⁵Mn NMR solution data for R₃SnMn(CO)₅ derivatives, including Ph₃SnMn(CO)₅, have been known for some time [9–13], only one ¹¹⁹Sn study, of Ph₃SnMn(CO)₅, is available [14] at this time.

2. Experimental

All experimental procedures, including the synthesis of triaryltin chlorides, and the solution (CDCl₃) NMR (¹¹⁹Sn and ¹³C) measurements were as given earlier [1,15,16]. Microanalyses were performed by the Microanalysis Service of the University of Montreal. All syntheses and manipulations were done under dry nitrogen. NMR (⁵⁵Mn) spectra of THF-d₈ solutions were obtained using a Varian XL-300 spectrometer and referenced against external KMnO₄ in D₂O. Mid-IR spectra of powders were acquired using a Bruker IFS-48 instrument equipped with a A-590 microscope. Raman spectra of powders in the standard sample cup were recorded in a Bruker IFS-88 FT-IR spectrometer fitted with a FRA-106 Raman module, using the CaF₂ beamsplitter.

2.1. Synthesis

All the *para*-substituted triaryltin(pentacarbonyl)manganese(I) compounds, with the exception of that given below, were obtained using the procedure reported earlier for the triphenyltin compound [17]. Thus dimanganese decacarbonyl (7.5 mmol) in dry THF (35 ml) was stirred with sodium amalgam (0.95 g Na/10 ml Hg) for 35 min at room temperature (r.t.) and the amalgam was then separated. Triaryltin chloride (15.5 mmol) was added to the THF solution of NaMn(CO)₅, the mixture stirred for 40 min and then poured on 100 g crushed ice. Extracting the pale green solid obtained, using boiling hexane, followed by evaporation of the filtrate and cooling gave the triaryltin(pentacarbonyl)manganese(I) compound in 65–85% yield. Recrystallisation gave crystals suitable for X-ray analysis. Further details of the (Ar₃Sn)Mn(CO)₅ I–VI prepared in this work are given in Tables 1–3.

2.1.1. Tris(p-methylsulphonylphenyl)tin(pentacarbonyl)manganese(I) (VII)

A slurry of *m*-chloroperbenzoic acid (15.5 g; 85%) in dichloromethane (CH₂Cl₂) (50 ml) was added slowly to a well-stirred solution of IV (6.95 g) over 2 h at -10 °C. Further CH₂Cl₂ (60 ml) was added and the stirred mixture was allowed to warm up slowly to r.t. The white suspension was separated, redissolved in (1:1) CH₂Cl₂/ether (150 ml), and then addition of ether (125 ml) to the filtrate precipitated the off-white product. This product was then dissolved in the least amount of CH₂Cl₂ and reprecipitated by slow addition of benzene: yield, 73%; m.p. (dec) 260-264 °C. Anal. Calc. for C₂₆H₂₁MnO₁₁S₃Sn: C, 40.07; H, 2.72; S, 12.43. Found: C, 40.33; H, 2.56; S, 12.25%. NMR (ppm): δ ⁽¹¹⁹Sn) (CDCl₃): 6.63(0.05), (solid) - 6.63 (0.2); δ ⁽⁵⁵Mn) [$v_{1/2}$ (Hz)] (THF): -2435 [8642]. Vibrational [IR/Raman] and ¹³C NMR data are reported in Tables 2 and 3, respectively.

2.2. Crystal structure determinations

For compounds II–VI a suitable crystal was selected from those available (Table 1) and X-ray data were collected [T = 293(2) K] on a Rigaku AFC6S diffractometer using Mo K α ($\lambda = 0.70930$ Å) radiation. Cell measurements were by standard methods and during each data collection, intensities of three standard reflections checked after every 200 reflections, showed essen-

Table 1

Synthesis and characterisation details for triaryltin(pentacarbonyl)manganese(I) complexes ([(p-XC₆H₄)₃SnMn(CO)₅])

Complex	X	Solvent	Yield (%)	m.p. (°C)	Colour	$\delta(^{119}\text{Sn})$ (ppm)		$\delta(^{55}Mn)$ (ppm)	
						CDCl ₃	Solid ^a	THF	$(\Delta v_{1/2})^{b}$
I	Н	hexane	85	150–152 (148–150) °	white	-11.93	-13.6 (×2), 2.8, 5.7	-2502 (-2530) ^d	4470 (3000) ^d
П	CH ₃	CH ₂ Cl ₂ /hexane	67	137–138	white	-10.37	-16.6	-2526	5662
Ш	OCH ₃	hexane	75	146-148	white	-6.33	11.4	-2524	5736
IV	SCH ₃	CH ₂ Cl ₂ /hexane	74	126-128	pale-yellow	-4.84	12.0	-2498	9089
V	F	benzene/heptane	70	128-130	white	-0.19	6.6, 16.0	-2493	5588
VI	Cl	CH_2Cl_2 /butanol	73	143–145	white	1.13	-32.1	-2479	6407

^a Ref. [7].

^b Peak width at half-height.

° Ref. [17].

^d Ref. [13].

Table 2			
Vibrational data	$[v(CO)] (cm^{-1})$	for $[(p-\mathbf{X}\mathbf{C}_{6}\mathbf{H}_{4})_{3}\mathbf{S}\mathbf{n}]$	Mn(CO) ₅]

Complex	Assignment	$a_1^{(2)}$	b_1			$\{e + a_1^{(1)}\}$	
I	IR	2092	2029	2012	1998	1983	1975
	Raman	2093	2024	2013		1991	1975
II	IR	2090	2030	2009		1992	1981
	Raman	2091	2026	2006		1991	1986
III	IR	2095	2033	2014		1998	1983
	Raman	2093	2023	2014		2001	1988
IV	IR	2095	2034			2001	1979
	Raman	2093	2023	2008			1991
V	IR	2096	2031	2012		1999	1991
	Raman	2095	2031	2012		2002	1991
VI	IR	2096	2035	2012		1998	1983
	Raman	2096	2033	2022		2001	1994
VII	IR	2106	2051	2027	2009	1989	1980
	Raman	2107	2051	2029	2015	1991	1981

Table 3 ¹³C NMR data [δ (ppm); "J(¹¹⁹Sn-¹³C)] for [(*p*-XC₆H₄)₃SnMn(CO)₅]

Complex	$\delta(C_i) {}^1 J(SnC)$	$\delta(C_o)^2 J(SnC)$	$\delta(C_m) {}^{3}J(SnC)$	$\delta(\mathbf{C}_p)$	$\delta(\mathrm{CO}_{\mathrm{eq}})$	$\delta(\mathrm{CO}_{\mathrm{ax}})$	$\delta(\mathrm{CH}_3)$
I	141.2 (382.3)	136.7 (37.6)	128.5 (46.6)	128.6	213.4	211.6	
П	137.4 (393.5)	136.6 (38.3)	129.3 (48.6)	138.3	213.4	211.7	21.4
Ш	131.7 (405.2)	137.7 (43.4)	114.4 (51.8)	160.1	213.6	211.7	54.9
IV	137.0 (388.9)	136.7 (38.5)	126.1 (47.5)	139.4	212.9	211.2	15.1
V ^a	135.7 (383.5)	138.0 (43.8)	115.7 (51.1)	163.5	212.6	210.8	
VI	137.4 (372.8)	137.7 (41.3)	128.9 (47.1)	135.5	212.3	210.6	
VII	148.5 (336.2)	137.6 (38.3)	127.1 (43.8)	141.7	211.8	210.2	44.5

^{a 1}*J*(¹⁹F-¹³C), 247.9 Hz; ²*J*(¹⁹F-¹³C), 19.5 Hz; ³*J*(¹⁹F-¹³C), 6.5 Hz; ⁴*J*(¹⁹F-¹³C), 3.9 Hz.

tially no decomposition over the data collection period. Full crystal parameters and data collection information are listed in Table 4.

The structures were solved by direct methods with SHELXS-86 [18] and refined on F^2 using SHELXL-93 [19]. Atom scattering factors and anomalous scattering terms were from the usual sources [20]. For all structures, all non-hydrogen atoms in the structure were refined anisotropically with the hydrogen atoms calculated at idealised positions, d(C-H) = 0.93-0.98 Å. More details of the refinement are given in Table 4. Pertinent geometric parameters for Ar₃Sn and Mn(CO)₅ units of molecules II–VI are given in Table 5. An ORTEP [21] view of the molecule of IV (Fig. 1) provides the general numbering scheme used and that in Fig. 2 shows the numbering scheme for the second molecule in the asymmetric unit of V.

3. Results and discussion

3.1. Syntheses

The new *para*-substituted triaryltin(pentacarbonyl)manganese(I) compounds II-VI were obtained from the corresponding $(p-XC_6H_4)_3SnCl$, as white or pale-yellow solids (Table 1) using the standard procedure first used for I, Ph₃SnMn(CO)₅ [17]. The products are relatively stable crystalline solids but do react slowly over 2-3 months in air to give discoloured materials presumably containing MnO₂ as well as other decomposition products. However, VII where p-X = $CH_3S(O_2)$, could not be made directly from the Ar₃SnCl precursor [22] possibly due to the strong electron-withdrawing ability of $p-H_3S(O_2)$ - causing the Sn-Cl bond to be less polar. This would then hinder the displacement of chloride by the nucleophile, $[Mn(CO)_5]^-$. Instead, the sulphone complex was prepared by an alternate route, viz. mild oxidation of IV using *m*-chloroperbenzoic acid [15] with the temperature at -10 °C or below, to avoid formation of MnO₂.

3.2. IR and Raman spectra

Both IR and Raman solid-state data for the carbonyl stretching region for compounds I-VII are given in Table 2. An idealised Mn(CO)₅ moiety has local C_{4v} symmetry giving rise to four v(CO) peaks, $a_1^{(2)}$ (IR, R) (eq), b_1 (R), E (IR, R), and $a_1^{(1)}$ (IR, R) (ax) [23]. In fact

the R₃SnMn(CO)₅ molecules have no symmetry but in solution with free rotation about the Sn–Mn bond, they behave as symmetric-tops ($C_{\infty v}$) with the v(CO) stretching modes assigned as $3a_1$ and e modes, all IR and Raman active [24]. However, since the mode equivalent to b_1 is weaker in the IR and stronger in the Raman, v(CO) solution data have usually been assigned as $a_1^{(2)}$, b_1 , e, and $a_1^{(1)}$, in that order, although the latter pair can overlap or interchange [25]. Thus, for Ph₃SnMn(CO)₅, v(CO) IR-data (cm⁻¹) in hexane are 2095 m ($a_1^{(2)}$), 2029 w ($b_{(1)}$), and 2004 s (e, and $a_1^{(1)}$).

In the solid state, all symmetry is lost and five v(CO) peaks are expected, both IR and Raman active. The results for II–VI (Table 2) agree with this analysis while the mutual exclusion for IR and Raman data, particularly for *e*, and $a_1^{(1)}$ modes, is consistent with the inversion centres present in the unit cells. However, the peak assigned to b_1 is still weaker in the IR and more prominent in the Raman spectrum. The results for IV are consistent with a more symmetric solid-state structure, which is not borne out by the X-ray data. In this case, we propose that one of the components into

which e is split is strongly IR active while the other is only observed in the Raman spectrum.

The spectra of I and VII are more complex. For I, this is expected since there are four independent molecules in the cell [8]. However, there are several pseudo-symmetry elements in the cell which cause pairs of molecules to be effectively equivalent, giving a situation like that for V where IR and Raman data also do not distinguish between molecules differing only slightly in their conformations. For VII there are six modes observed in both the IR and Raman spectra with some evidence of mutual exclusion. Thus, the packing of the asymmetric $R_3SnMn(CO)_5$ units of VII in the crystal may well differ from that found for I–IV. However, to-date, crystals of VII suitable for X-ray study have not been available.

3.3. Solution NMR data

All NMR data sets have been examined for correlation with various substituent parameters (SP) [26]. As shown earlier for several series of *para*-disubstituted

Table 4

Crystal data and structure refinement parameters for [(p-XC₆H₄)₃SnMn(CO)₅]

Compound	II	III	IV	V	VI
Empirical formula	C26H21MnO5Sn	C26H21MnO8Sn	C26H21MnO5S3Sn	C23H12F3MnO5Sn	C23H12Cl3MnO5Sn
Formula mass	587.06	635.06	683.24	589.96	648.31
Crystal system	triclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P\overline{1}$	$P2_{1}/c$	$P2_1/n$	$P\overline{1}$	$P2_{1}/c$
Unit cell dimensions					
a (Å)	8.815(2)	14.096(2)	10.966(1)	10.636(5)	9.918(2)
b (Å)	11.160(3)	11.161(2)	21.229(2)	11.450(3)	22.940(4)
<i>c</i> (Å)	13.689(2)	17.000(10)	12.297(3)	21.992(7)	11.718(2)
α (°)	98.28(2)	90	90	83.20(3)	90
β (°)	91.11(2)	91.71(2)	101.22(1)	78.30(4)	109.78(1)
γ (°)	106.31(2)	90	90	63.03(2)	90
$V(Å^3)$	1276.5(5)	2673(2)	2808.0(8)	2336(2)	2508.8(8)
Z; Z'	2; 1	4; 1	4; 1	4; 2	4; 1
$D_{\text{calc}} (\text{g cm}^{-1})$	1.527	1.578	1.616	1.703	1.716
Crystal size (mm)	$0.36 \times 0.18 \times 0.13$	$0.35 \times 0.22 \times 0.12$	$0.45 \times 0.25 \times 0.22$	$0.52 \times 0.35 \times 0.12$	$0.51 \times 0.49 \times 0.09$
$\mu ({\rm mm}^{-1})$	1.505	1.452	1.596	1.664	1.849
$T_{\rm max}, T_{\rm min}$	0.71; 0.67	0.76; 0.64	0.66; 0.57	0.66; 0.45	0.62; 0.33
Data collection method	ω scans	ω –2 θ scans	ω –2 θ scans	ω scans	ω scans
Absorption correction	Ψ method				
$\theta_{\min}; \theta_{\max}$ (°)	2.25; 24.96	2.18; 24.98	2.12; 24.99	2.18; 25.00	2.04; 24.97
Index ranges	$-10 \le h \le 10$,	$-17 \le h \le 17$,	$-13 \le h \le 12$,	$-11 \le h \le 12$,	$-11 \le h \le 11$,
	$-13 \le k \le 13,$	$0 \le k \le 13,$	$0 \leq k \leq 25,$	$0 \le k \le 13$,	$0 \le k \le 27,$
	$-16 \le l \le 16$	$-20 \le l \le 20$	$0 \le l \le 14$	$-25 \le l \le 26$	$0 \le l \le 13$
F(000)	584	1264	1360	1168	1264
Number of reflections measured	9016	9414	9864	16 582	8805
Number of unique reflections (R_{int})	4508 (0.025)	4716 (0.083)	4961 (0.077)	8291 (0.079)	4412 (0.062)
Number of observed reflections $[I \ge 2\sigma(I)]$	3314	2891	3188	5383	3381
R_1 observed (total)	0.0400 (0.0680)	0.0546 (0.1121)	0.0544 (0.1073)	0.0518 (0.0988)	0.0474 (0.0748)
wR_2 observed (total)	0.0723 (0.0788)	0.0918 (0.1033)	0.1079 (0.1240)	0.0997 (0.1108)	0.1192 (0.1264)
Goodness-of-fit (S)	1.044	1.023	1.037	1.101	1.068

 $R_{1} = \Sigma(||F_{o}| - |F_{c}||)/\Sigma|F_{o}|. wR^{2} = [\Sigma[w(F_{o}^{2} - F_{c}^{2})^{2}/\Sigma(wF_{o}^{2})^{2}]^{1/2}. S = [\Sigma[w(F_{o}^{2} - F_{c}^{2})^{2}/(number of reflections - number of parameters)]^{1/2}.$ Function minimised, $\Sigma[w(F_{o}^{2} - F_{c}^{2})].$

Table 5 Bond lengths (Å) and bond angles (°) for $[(p-XC_6H_4)_3SnMn(CO)_5]$

(a) Compounds II and	I VI	
	II $(\mathbf{X} = \mathbf{CH}_3)$	VI $(\mathbf{X} = \mathrm{Cl})$
Sn-Mn	2.693(1)	2.6814(12)
Mn-C(1)	1.829(5)	1.821(10)
Mn-C(2)	1.847(5)	1.841(8)
Mn-C(3)	1.839(6)	1.836(9)
Mn-C(4)	1.845(5)	1.824(9)
Mn-C(5)	1.812(7)	1.821(10)
Sn-C(11)	2.150(4)	2.142(6)
Sn-C(21)	2.159(4)	2.143(6)
Sn–C(31)	2.145(4)	2.151(7)
C(1)=O(1)	1 141(5)	1 153(10)
C(2) = O(2)	1 138(5)	1 130(9)
C(3) - O(3)	1.137(6)	1.152(10)
C(4) - O(4)	1.137(5)	1.141(9)
C(5) - O(5)	1.143(6)	1.130(10)
	106.00	100.000
C(11) - Sn - C(21)	106.0(2)	108.3(2)
C(11) - Sn - C(31)	107.7(2)	109.5(3)
C(21) - Sn - C(31)	108.2(2)	105.9(3)
C(11)-Sn-Mn	112.63(12)	105.2(2)
C(21)-Sn-Mn	110.34(11)	114.5(2)
C(31)-Sn-Mn	111.66(11)	113.2(2)
C(1)–Mn–Sn	84.2(2)	85.6(3)
C(2)–Mn–Sn	84.3(2)	82.5(3)
C(3)–Mn–Sn	86.2(2)	89.3(3)
C(4)-Mn-Sn	87.7(2)	86.6(3)
C(5)–Mn–Sn	179.0(2)	177.5(3)
C(12)C(11)Sn Mn	56 4(4)	0(5)
C(12)C(11)SnMn C(22)C(21)SnMn	30.4(4)	-96.2(3)
C(22)C(21)SnMn C(22)C(21)SnMn	-121.0(3)	30.0(0) 116.0(6)
C(32)C(31)SIIWIII	-109.3(4)	-110.9(0)
C(4)MnSnC(11)	121.6(2)	123.9(3)
C(4)MnSnC(21)	3.4(2)	5.0(4)
C(4)MnSnC(31)	-117.0(2)	-116.6(4)
(b) Compounds III an	d IV	
(b) Compounds III an	ш	$\mathbf{IV} (\mathbf{X} = \mathbf{SCH}_{*})$
	$(\mathbf{X} = \mathbf{OCH}_{*})$	iv (ir beilig)
Sn-Mn	2669(2)	2 6596(12)
Mn-C(1)	1 854(9)	1 827(8)
Mn = C(2)	1 849(8)	1 849(9)
Mn-C(3)	1 837(8)	1 867(8)
Mn-C(4)	1 824(8)	1 856(9)
Mn-C(5)	1.808(9)	1.832(9)
Sn-C(11)	2.144(6)	2.156(7)
Sn-C(21)	2.153(4)	2.145(7)
Sn-C(31)	2.163(6)	2.171(7)
	1.122(0)	1.1.52(0)
C(1) = O(1)	1.129(8)	1.153(9)
C(2)–O(2)	1.140(8)	1.133(9)
C(3) = O(3)	1.136(8)	1.125(8)
C(4) - O(4)	1.144(8)	1.133(8)
C(5) = O(5)	1.129(8)	1.133(9)
C(11)-Sn-C(21)	109.5(2)	103.6(3)
C(11)-Sn-C(31)	103.0(2)	100.9(3)
C(21)-Sn-C(31)	103.5(2)	108.4(3)
C(11)–Sn–Mn	113.0(2)	114.8(2)
C(21)-Sn-Mn	112.15(12)	112.8(2)
C(31)-Sn-Mn	115.0(2)	115.1(2)
C(1) Mr. S.	0(7(2)	92 5(2)
C(1)-Mn-Sn C(2) Mn Sn	85.7(3)	83.3(2) 84.0(2)
C(2)-Mn-Sn C(2) Mn S-	83.3(2)	84.9(2)
C(3)-IMIN-SIN	ð3.ð(2)	ðð.3(2)

C(4)-Mn-Sn C(5)-Mn-Sn	85.9(2) 177.4(3)	88.9(2) 174.4(3)	
C(12)C(11)SnMn C(22)C(21)SnMn C(32)C(31)SnMn	-101.3(5) 54.64(10) 31.3(6)	48.3(7)) -116.3(6) -22.0(7)	
C(4)MnSnC(11) C(4)MnSnC(21) C(4)MnSnC(31)	-116.2(3) 8.1(3) 125.9(3)	124.6(3) 6.3(3) -118.8(3)	
C(15)C(14)Z ^a (1x) C(17)	7.4(11)	-5.4	
C(25)C(24)Z ^a (2x) C(27)	176.6(7)	168.5(6)	
$C(35)C(34)Z^{a}(3x)$ C(37)	1.3(12)	33.2(8)	
(c) Compound V (X = Molecule A	= F)	Molecule B	
Sn(1) - Mn(1)	2 656(2)	Sn(2) = Mn(2)	2.664(2)
$M_{n}(1) C(1)$	1.848(0)	$M_{n}(2) C(6)$	1.847(0)
Mn(1) - C(1) Mn(1) - C(2)	1.040(9)	Mn(2) = C(0) Mn(2) = C(7)	1.047(9) 1.026(9)
Mn(1) = C(2) Mn(1) = C(2)	1.823(9)	Mn(2) = C(7) Mn(2) = C(8)	1.020(0)
Mn(1) - C(3)	1.842(9)	Mn(2) = C(8)	1.854(9)
Mn(1)-C(4)	1.838(9)	Mn(2) - C(9)	1.852(10)
Mn(1) - C(5)	1.820(8)	Mn(2) - C(10)	1.841(9)
Sn(1)-C(11)	2.147(6)	Sn(2)-C(41)	2.145(7)
Sn(1)-C(21)	2.143(7)	Sn(2)-C(51)	2.153(7)
Sn(1)–C(31)	2.151(7)	Sn(2)-C(61)	2.155(7)
C(1)=O(1)	1 120(9)	C(6) = O(6)	1 1 3 4 (8)
C(2) = O(2)	1.120(9) 1.150(9)	C(7) = O(7)	1.134(0) 1.126(8)
C(2) O(2) C(3) O(3)	1.136(9)	C(8) O(8)	1.120(0) 1.131(0)
C(3) = O(3) C(4) = O(4)	1.120(9) 1.151(9)	C(0) = O(0) C(0) = O(0)	1.131(9) 1.131(0)
C(4) = O(4) C(5) = O(5)	1.131(9) 1.122(8)	C(3) = O(3) C(10) = O(10)	1.131(9) 1.120(0)
C(3)=O(3)	1.155(8)	C(10)=O(10)	1.120(9)
C(11)-Sn(1)-C(21)	104.8(3)	C(41)-Sn(2)-C(51)	107.8(3)
C(11)-Sn(1)-C(31)	104.0(2)	C(41)-Sn(2)-C(61)	104.6(3)
C(21)-Sn(1)-C(31)	107.8(3)	C(51)-Sn(2)-C(61)	104.0(3)
C(11)-Sn(1)-Mn(1)	114.8(2)	C(41)-Sn(2)-Mn(2)	113.8(2)
C(21)-Sn(1)-Mn(1)	114.1(2)	C(51)-Sn(2)-Mn(2)	110.5(2)
C(31)-Sn(1)-Mn(1)	110.5(2)	C(61)-Sn(2)-Mn(2)	115.3(2)
C(1)-Mn(1)-Sn(1)	83.6(3)	C(6)-Mn(2)-Sn(2)	85.6(2)
C(2)-Mn(1)-Sn(1)	84 5(3)	C(7) - Mn(2) - Sn(2)	86 5(3)
C(3)-Mn(1)-Sn(1)	87.6(2)	C(8) - Mn(2) - Sn(2)	83 5(3)
C(4) - Mn(1) - Sn(1)	86.0(2)	C(0) - Mn(2) - Sn(2)	87.9(3)
C(5)-Mn(1)-Sn(1)	1784(2)	C(10) - Mn(2) - Sn(2)	178 9(3)
	1,011(2)		1,015(0)
C(12)C(11)Sn(1)Mn(1)) - 141.3(5)	C(42)C(41)Sn(2)Mn(2)	111.7(6)
C(22)C(21)Sn(1)Mn(1)) 59.6(6)	C(52)C(51)Sn(2)Mn(2)	-54.0(6)
C(32)C(31)Sn(1)Mn(1)) 66.0(6)	C(62)C(61)Sn(2)Mn(2)	131.0(6)
C(4)Mn(1)Sn(1)C(11)	122 3(3)	C(9)Mn(2)Sn(2)C(41)	115 2(4)
C(4)Mn(1)Sn(1)C(21)	1 2(3)	C(9)Mn(2)Sn(2)C(51)	-63(4)
C(4)Mn(1)Sn(1)C(21)	-1204(3)	C(9)Mn(2)Sn(2)C(51)	-123.9(4)
C(+)MII(1)SII(1)C(51)	120.4(3)	C())MII(2)SI(2)C(01)	125.7(4)

^a $\mathbf{Z} = \mathbf{O}$, $\mathbf{x} = 4$, or $\mathbf{Z} = \mathbf{S}$, No x.

benzenes [27] and for Ar₄Sn and Ar₃SnX [8], ¹³C chemical shift data (Table 3) correlate well with $\sigma_{\rm R}^{\circ}$ (Fig. 3(a)). In contrast, ¹J(¹¹⁹Sn-¹³C) values are *less* than those for the corresponding Ar₄Sn and Ar₃SnX derivatives, and correlate with $\sigma_{\rm p}$ [Fig. 3(b)] or $\sigma_{\rm p}^{\circ}$ (r = -0.970) rather than $\sigma_{\rm R}$, as was found for Ar₄Sn and Ar₃SnX. Both ¹¹⁹Sn and ⁵⁵Mn chemical shifts show the same trend with *para*-substituent (Fig. 4), especially if the phenyl data point is omitted. This requirement would suggest that the ¹¹⁹Sn and ⁵⁵Mn chemical shifts have different SP behaviour. Thus, $\delta(^{119}Sn)$ depends on $\sigma_{\rm I}$ (Fig. 5(a)) while $\delta(^{55}{\rm Mn})$ varies almost equally with σ_p° [Fig. 5(b)] or σ_p (r = 0.9909). The same correlation of δ (⁵⁵Mn) with Hammett constant values was reported earlier for the series $CH_{3-n}F_nMn(CO)_5$ [9] as well as $RMn(CO)_5$, $RMn(PPh_3)(CO)_4$, for the and $RCOMn(PPh_3)(CO)_4$ (R = $XC_6H_4CH_2$) series [28]. By comparison, inverse correlations are found with δ ⁽¹¹⁹Sn) data for Ar₄Sn ($\sigma_{\rm R}$ or $\sigma_{\rm R}^{\circ}$) and for Ar₃SnI ($\sigma_{\rm p}$ or σ_p° [1]. There are even substituent effects in $\delta^{(13}CO_{ax}) [\sigma_{p}^{\circ}; r = -0.935] \text{ and } \delta^{(13}CO_{eq}) [\sigma_{p}^{\circ}; r = -0.935]$ 0.945] although the variation in chemical shifts is small in these cases. Dual substituent parameter (DSP) analyses for I-VII (Table 6) confirm the strong dependence of δ ⁽¹¹⁹Sn) on the inductive parameter while compara-



Fig. 1. ORTEP view of the molecule of IV showing the general numbering scheme adopted for II-VI. Ellipsoids are drawn at 40% probability level.



Fig. 2. ORTEP view of the second molecule of V showing the numbering scheme adopted. Ellipsoids are drawn at 40% probability level.



Fig. 3. Correlation of ¹³C NMR data for I–VII with substituent parameters: (a) $\delta(C_{ipso})$ vs. σ_{R}° (r = 0.9668; n = 7). (b) ¹J(¹¹⁹Sn–¹³C) vs. σ_{p} (r = 0.9903; n = 7).



Fig. 4. Plot of δ^{55} Mn vs. δ^{119} Sn for the series **II–VII**; omitting the data point for **I** gives r = 0.9533 (n = 6).

ble resonance and inductive parameters for δ (⁵⁵Mn) are also consistent with the SP behaviour.

The electronic environment around the tin atom in Ar_3SnX systems may be simply considered in terms of the resonance structures A-C below. With X = Ar, **B** is



Fig. 5. Correlation of δ^{119} Sn and δ^{55} Mn data for I–VII with substituent parameters: (a) δ^{119} Sn vs. σ_{I} (r = 0.9726; n = 7). (b) δ^{55} Mn vs. σ_{p}° (r = 0.9914; n = 7).

the principal contributor but as Ar is replaced by I, Br, and then Cl, A becomes more significant.

$$Ar_{3}Sn^{+}X^{-} \leftrightarrow Ar_{3}Sn^{-}X \leftrightarrow Ar_{3}Sn^{-}X^{+}$$

Table 6

Chemical shifts regression analysis parameters for compounds I–VII (n = 7)

In contrast with Ar₃SnMn(CO)₅, ${}^{1}J({}^{119}Sn-{}^{13}C)$ values are less than for a given Ar₄Sn, implying that the Sn-Mn bond has more tin-5s character than Sn-Ar in Ar₄Sn due to the lower effective electronegativity of Mn(CO)₅ compared with an aryl group [14], and that C is now an important contributor to the overall structure. This result is seemingly contradicted by the trend in δ ⁽¹¹⁹Sn) data for the same series which suggest that tin in Ar₃SnMn(CO)₅ is even less shielded than in the corresponding Ar₃SnCl. Shielding of heavy atom nuclei, including tin, is considered to be dominated by the paramagnetic term which is represented by the expression, $\sigma_{\rm p} = -A(\delta E)^{-1}[Q_{\rm p} + Q_{\rm d}]$, where A is a numerical constant, δE is the average excitation energy, and $Q_{\rm p}$ and $Q_{\rm d}$ depend on the size of and electron imbalance in the valence shell p- and d-orbitals, respectively [1,14]. For tin, it is usually assumed that δE is constant for a series of related molecules and participation of tin 5d orbitals in bonding is insignificant [1]. Thus, σ_p for Ar₃SnX varies mainly with Q_p consistent with the simple bonding picture given above.

With $X = Mn(CO)_5$, these two assumptions are no longer valid since $Mn(CO)_5$ is both a σ -acceptor and π -donor ligand. The latter behaviour involves interaction between filled 3d orbitals on manganese with empty orbitals (perhaps 5d or σ^*) on tin which results in a decrease in δE and a shift to high field for the tin resonance. The completely different substituent effects given by δ ⁽¹¹⁹Sn) data for Ar₃SnX (X = Cl, Br, I) and Ar₃SnMn(CO)₅ systems are also consistent with this picture. Thus, if the *para*-substituent is a strong π donor, e.g. CH₃O, the resulting increase in π -electron density at tin will be compensated by decrease in π back-donation from the manganese therefore nullifying any resonance effect. This then leaves only the throughbond inductive effect with increasing σ_{I} causing deshielding at tin, as is the case. In contrast, both resonance and inductive substituent effects contribute

	$ ho_{\mathrm{I}}$	$ ho_{ m R}$	С	r ^a	SD ^b	f^{c}
$\overline{\delta = \rho_{\rm I} \sigma_{\rm I} + \rho_{\rm P} \sigma_{\rm P} + C}$						
$\delta(^{119}\text{Sn})$	25.78	5.61	-10.73	0.991	0.800	0.138
$\delta(^{55}Mn)$	104.1	85.53	-2507	0.996	2.59	0.084
$\delta({}^{13}C_{inso})$	7.81	20.62	140.8	0.995	0.481	0.098
${}^{1}J({}^{119}\text{Sn}{-}^{13}\text{C})$	-60.54	-72.96	382.1	0.999	0.909	0.045
$\delta = \rho_{\rm I} \sigma_{\rm I} + \rho_{\rm R} \sigma_{\rm R}^{\circ} + C$						
$\delta(^{119}\text{Sn})$	25.54	6.52	-10.86	0.988	0.900	0.154
$\delta(^{55}Mn)$	100.7	103.13	-2508	0.990	3.96	0.129
$\delta(^{13}C_{inso})$	7.01	25.14	140.6	0.994	0.518	0.106
${}^{1}J({}^{119}\text{Sn}{-}^{13}\text{C})$	-57.67	-88.54	383.2	0.995	1.97	0.098

^a Multiple correlation coefficient.

^b Standard deviation of residuals.

^c Goodness-of-fit parameter, SD/RMS [29].

to δ (⁵⁵Mn) again with the more electron withdrawing groups, e.g. CH₃S(O₂), causing concommitant deshield-ing at manganese.

3.4. X-ray diffraction results

The structures of II-VI closely resemble that of the archetype I, Ph₃SnMn(CO)₅, and the exhaustive description of I [8] is still relevant. All bond lengths and angles are within the same range of these parameters for I and where there are differences between I, and II-VI, these may be simply due to the lower precision of the earlier structure determination. The Mn(CO)₅ moiety in all cases is a distorted tetragonal pyramid with the equatorial CO groups inclined towards the tin. In fact, the principal structural differences between molecules, including the molecules A and B of V, lie in the phenyl ring torsion angles. The relevance of these to the solid-state ¹¹⁹Sn NMR parameters of these compounds has already been discussed [4]. It is likely this variation in phenyl ring torsion angles that may be the main determinant of the detailed electronic environment at tin and account for the lack of correlation of solid-state δ ⁽¹¹⁹Sn) data with substituent constants. In particular, the structure of IV shows the most deviation from the norm, with one aryl ring torsion angle being unusually small (-22°) while the p-CH₃S group attached to this ring is out-of-plane by 33° rather than the more usual value of $\sim 10^{\circ}$ [30]. The offset of the data point for IV from the linear relation between ${}^{1}J({}^{119}\text{Sn}-{}^{55}\text{Mn})$ and the quadrupole coupling constant, γ (⁵⁵Mn) generally observed for these systems was earlier ascribed to this errant conformation of the phenyl rings in IV. Both ${}^{1}J({}^{119}\text{Sn}-{}^{55}\text{Mn})$ and $\chi({}^{55}\text{Mn})$ values show reasonable correlation with σ_p° , r = 0.930 and r = -0.949, respectively. Thus as the *para*-substituent on the ring becomes more electron withdrawing, χ (⁵⁵Mn) decreases, finally reversing sign with CH₃S(O₂) as the ring para-substituent. This perhaps reflects the fact that since Ar₃Sn competes with (CO)_{ax} as a π -acceptor, when $CH_3S(O_2)$ - is the para-substituent, the Ar₃Sn may then be the stronger π -acceptor, causing a reversal of electric field gradient at the manganese atom. This is also consistent with form C contributing more to the $Ar_3SnMn(CO)_5$ structure as are average angles $CSnC = 106^{\circ}$ and $CSnMn = 113^{\circ}$. In contrast, Ar₃SnCl have average angles $CSnC = 113^{\circ}$ and $CSnCl = 106^{\circ}$ [2] showing A is now the significant ionic contributor to these structures. One more notable feature of these structures is the quasi-mirror plane of symmetry in the central C₄Mn-SnC₃ skeleton as described earlier [6]. For molecule A of V, with $C(4)Mn(1)Sn(1)C(21) = 1.2(3)^{\circ}$, this is nearly exactly the case and may account for the symmetric tensor values noted for one of the tin sites in the ¹¹⁹Sn solid-state NMR spectrum of V.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 163789–163793, for compounds V, VI, II, IV and III, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc. cam.ac.uk).

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References

- [1] I. Wharf, Inorg. Chim. Acta 159 (1989) 41.
- [2] I. Wharf, M.G. Simard, J. Organomet. Chem. 532 (1997) 1.
- [3] H.-J. Kroth, H. Schumann, H.G. Kuivala, C.D. Schaeffer Jr., J.J. Zuckerman, J. Am. Chem. Soc. 97 (1975) 1754.
- [4] D. Christendat, I. Wharf, F.G. Morin, I.S. Butler, D.F.R. Gilson, J. Magn. Reson. 131 (1998) 1.
- [5] R.K. Harris, J. Magn. Reson. 78 (1988) 389.
- [6] D.C. Apperley, B. Haiping, R.K. Harris, Mol. Phys. 68 (1989) 1277.
- [7] D.C. Apperley, N.A. Davies, R.K. Harris, A.K. Brimar, S. Eller, R. Fischer, Organometallics 9 (1990) 2672.
- [8] H.P. Weber, R.F. Bryan, Acta Crystallogr., Sect. A 22 (1967) 822.
- [9] F. Calderazzo, E.A.C. Lucken, D.F. Williams, J. Chem. Soc., Part A (1967) 154.
- [10] W.J. Miles, B.B. Garrett, R.J.H. Clark, Inorg. Chim. 8 (1969) 2817.
- [11] S. Onaka, Y. Sasaki, H. Sano, Bull. Chem. Soc. Jpn. 44 (1971) 726.
- [12] S. Onaka, T. Miyamoto, Y. Sasaki, Bull. Chem. Soc. Jpn. 44 (1971) 1851.
- [13] G.M. Bancroft, H.C. Clark, R.G. Kidd, A.T. Rake, H.G. Spinney, Inorg. Chim. 12 (1973) 728.
- [14] D.H. Harris, M.F. Lappert, J.S. Poland, W. McFarlane, J. Chem. Soc., Dalton Trans. (1975) 311.
- [15] I. Wharf, M.G. Simard, H. Lamparski, Can. J. Chem. 68 (1990) 1277.
- [16] I. Wharf, R. Wojtowski, C. Bowes, A.-M. Lebuis, M. Onyszchuk, Can. J. Chem. 76 (1998) 1827.
- [17] R.D. Gorsich, J. Am. Chem. Soc. 84 (1962) 2486.
- [18] G.M. Sheldrick, SHELXS-86: Program for the Solution of Crystal Structures, University of Göttingen, Göttingen, Germany, 1986.
- [19] G.M. Sheldrick, SHELXL-93: Program for Structure Analysis, University of Göttingen, Göttingen, Germany, 1993.
- [20] International Tables for Crystallography, vol. C, Kluwer, Dordrecht, Holland, 1992, Tables 4.2.6.
- [21] C.K. Johnson, ORTEPII, Rep. ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA, 1976.
- [22] I. Wharf, A.-M. Lebuis, H. Lamparski, Acta Crystallogr., Sect. C 52 (1996) 2477.
- [23] D.M. Adams, Metal-Ligand and Related Vibrations, Edward Arnold, London, 1967, p. 98.

- [24] S. Onaka, Bull. Chem. Soc. Jpn. 44 (1971) 2135.
- [25] (a) F.A. Cotton, A. Musco, G. Yagupsky, Inorg. Chem. 6 (1967) 1357;

(b) J. Dalton, I. Paul, J.G. Smith, F.G.A. Stone, J. Chem. Soc., Part A (1968) 1195.

- [26] C. Hansch, A. Leo, Substituent Constants for Correlation Analysis in Chemistry and Biology, Wiley, New York, 1979.
- [27] J. Bromilov, R.T.C. Brownlee, D.J. Craik, M. Sadek, R.W. Taft, J. Org. Chem. 45 (1980) 2429.
- [28] J.D. Cotton, R.D. Markwell, Inorg. Chim. Acta 175 (1990) 187.
- [29] S. Ehrenson, J. Org. Chem. 44 (1979) 1793.
- [30] I. Wharf, M.G. Simard, J. Organomet. Chem. 332 (1987) 85.