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Synthesis, characterisation, Mössbauer spectra, and structures of some trinuclear iron–tin clusters

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Reactions of $[Fe_3(CO)_{12}]$ with diaryltin species SnR_2 (R^1 = 2,4,6-triisopropylphenyl, R^2 = 2,6-diethylphenyl, R^3 = pentamethylphenyl) and with $Sn[CH(PPh_2)_2]_2$ have been investigated. The tin reagents SnR_2 ($R = R^1$ or R^2) reacted under mild conditions to give in moderate yields the trinuclear species $[Fe_2(CO)_8(\mu\text{-}SnR^1{}_2)]$ **1** or $[Fe_2(CO)_8(\mu\text{-}SnR^2{}_2)]$ **2**, as orange-red crystalline solids, which decompose in air on prolonged exposure. The compound $[Fe_2(CO)_8(\mu\text{-}SnR^4{}_2)]$ **3** (R^4 = 2,4,6-triphenylphenyl) can be similarly obtained. Prolonged treatment of the carbonyl with the novel tin reagent $SnR^3{}_2$, by contrast, afforded the known compound *spiro*-$[(OC)_8Fe_2SnFe_2(CO)_8]$ **4** for which data are briefly reported. Reactions with tin or lead reagents $M[CH(PPh_2)_2]_2$ (M = Sn or Pb) afforded $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)]$ [dppm = 1,2-bis(diphenylphosphino)methane] rapidly and almost quantitatively. Full crystal and molecular structural data are reported for $[Fe_2(CO)_8(\mu\text{-}SnR^1{}_2)]$ and $[Fe_2(CO)_8(\mu\text{-}SnR^2{}_2)]$. Mössbauer data are also presented for compounds **1**–**3**, and interpreted in terms of the structural data for these and other systems.

We have recently reported on a series of cluster species derived from divalent tin,[1,2] and also on the use of such reagents in the synthesis of mixed heterometallic cluster systems[3–5] which can have core nuclearities of up to ten metal atoms. With ruthenium and osmium dodecacarbonyls we have shown that cluster expansion can occur with organo-tin(II)[6] or -lead(II)[7] reagents, as is also the case for tetrairidium dodecacarbonyl.[8] Nuclearities of Ru_3Sn_2, Ru_3Sn_3, Os_3Sn_3, Ir_4Sn and Ir_4Sn_5 and many others have been characterised. Initially these results were obtained with the tin(II) dialkyl SnR_2 [$R = CH(SiMe_3)_2$], but more recently a variety of other tin(II) species has become available. We now report on the reactions of the iron carbonyl $[Fe_3(CO)_{12}]$ with diaryltin(II) compounds and with $M[CH(PPh_2)_2]_2$ (M = Sn or Pb). The diaryltin species SnR_2 (R^1 = 2,4,6-triisopropylphenyl, R^2 = 2,6-diethylphenyl) are accessible from tin(II) chloride and the appropriate lithium reagent.[9] These species exist in solution as oligomers, but have been shown to be the sources of SnR_2 units in cluster synthesis.[10] The species $M[CH(PPh_2)_2]_2$ (M = Sn or Pb) are monomers with three-co-ordinate tin atoms, and have P_2C ligation at the metal atom (see below). The Mössbauer spectra of heterometallic clusters with two or more active nuclei have previously been studied, and shown to provide useful information on the bonding in such molecules when used in conjunction with crystallographic data.[11–16] In the present work, both tin and iron were available as probes, and spectra for both are reported.

Results and Discussion

(*a*) Synthesis of iron–tin clusters

Bis(2,4,6-triisopropylphenyl)tin(II) has been shown to exist in solution as a trimer.[17] However, on warming or irradiation, solutions of this orange material turn deep red. Such solutions have reactivity towards clusters paralleling that of bis[bis(trimethylsilyl)methyl]tin(II)[6,18] (also deep red), known from cryoscopic and other measurements[19,20] to exist as a mixture of monomers and dimers in solution. On refluxing a mixture of $(SnR^1{}_2)_3$ and $[Fe_3(CO)_{12}]$ in hexane the deep green of the iron compound is slowly discharged, and orange crystals of $[Fe_2(CO)_8(\mu\text{-}SnR^1{}_2)]$ **1** may be isolated after chromatography. The reaction also affords a blue species, but this decomposes on the silica column. By contrast, if the diaryltin reagent is used immediately after synthesis (at *ca.* −80 °C) as the deep red solution prior to trimerisation,[9a] there is no reaction with the dodecacarbonyl, as is also the case for the dialkyltin species $Sn[CH(SiMe_3)_2]_2$ under these conditions.

Compound **1** is a moderately air-stable, diamagnetic material, which shows no bridging carbonyl frequencies in the IR spectrum. The ^1H NMR spectrum reveals the presence of the triisopropylphenyl ligand, and microanalytical data indicate a Sn:Fe ratio of 1:2. A single-crystal structure analysis revealed the structure shown in Fig. 1, having an iron–iron bond, bridged by a single SnR_2 group. The detailed description of the structure is given below, in conjunction with those for $[Fe_2(CO)_8(\mu\text{-}SnR^2{}_2)]$ **2** and $[Fe_2(CO)_8(\mu\text{-}SnR^4{}_2)]$ **3**.

2,6-Diethylphenyllithium was obtained from the aryl bromide and butyllithium. Reaction of this reagent with tin(II) chloride afforded bis(2,6-diethylphenyl)tin(II),[9b] whereas when 2,6-diethylphenyl bromide was treated with lithium powder, and the product added to tin(II) chloride, a tetracyclostannane was obtained quantitatively.[2] Addition of $SnR^2{}_2$ to iron dodecacarbonyl in refluxing toluene yielded compound **2** in poor to moderate yield. Compound **2** is also a moderately air-stable, diamagnetic material. It shows no bridging carbonyl frequencies in the IR spectrum, and the ^1H NMR spectrum reveals the presence of the aryl ligand. The structure of a single molecule of **2** is shown, together with selected bond lengths and angles, in Fig. 2. The compound $[Fe_2(CO)_8(\mu\text{-}SnR^4{}_2)]$ (R^4 = 2,4,6-triphenylphenyl) was similarly prepared.[5c]

The reaction of tin(II) chloride with lithiopentamethylbenzene yields a new tin species **5**. This is an orange crystalline material, with infrared and NMR spectra as expected for $(SnR^3{}_2)_n$ ($R^3 = C_6Me_5$) showing for example the required three aliphatic and

Table 1 Selected bond lengths (Å) and angles (°) for compounds **1**–**3** and related species

Compound	Fe–Fe	Fe–Sn	Sn–C	C–Sn–C	Sn–Fe–Fe	Fe–Sn–Fe	Dihedral(twist) angle[a]
1	2.788(2)	2.603(2)	2.220(6)	101.3(3)	57.9(1)	64.6(1)	77.3
		2.614(2)	2.212(6)		57.5(1)		
	2.797(3)	2.608(2)	2.221(8)	102.7(3)	57.6(1)	64.8(1)	76.1
		2.608(2)	2.202(5)		57.6(1)		
2	2.797(2)	2.606(1)	2.197(6)	106.8(1)	58.0(1)	64.9(1)	74.2
3	2.794(4)	2.616(2)	2.18(1)	102.3(1)	57.7(1)	64.6(1)	73.8
6 $[Fe_2(CO)_6(\mu\text{-}SnR_2)_2]$	2.806(4)	2.600(2)	2.190(15)	111.4(7)	59.7(4)	64.0(4)	
		2.696(2)	2.188(20)		56.4(4)		
$[Fe_2(CO)_8(\mu\text{-}SnMe_2)_2]$	4.139(15)	2.631(11)	2.20(7)	105(14)		103.7(4)	
4[13]	2.87(±0.01)	2.55(±0.01)			55.7(±0.2)	68.9(±0.2)	
	2.87(±0.01)	2.53(±0.01)			56.0(±0.2)	68.9(±0.2)	
		2.53(±0.01)			55.7(±0.2)		
		2.55(±0.01)			55.3(±0.2)		
4[b]	2.890(4)	2.559(4)			55.7(1)	68.9(1)	
	2.890(5)	2.546(3)			55.3(1)		
		2.546(4)			55.6(1)	69.0(1)	
		2.555(4)			55.4(1)		
$[SnPh_2\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$[23]	*c*	2.579	2.156	100.8	*c*	118.6	
		2.586	2.156				
$[Sn(C_5H_5)_2\{Fe(C_5H_5)(CO)_2\}_2]$[25]	*c*	2.569	2.184	95.3	*c*	115.9	
		2.579	2.177				
$[SnMe_2\{Fe(C_5H_5)(CO)_2\}_2]$[24]	*c*	2.603	2.174	103.3	*c*	123.4	
		2.601	2.184				
$[SnCl_2\{Fe(C_5H_5)(CO)_2\}_2]$[22]	*c*	2.498			*c*	128.7	
		2.498					

[a] The dihedral angle between the Fe–Sn metal plane and the tin ligand plane. [b] Data derived from our observations. [c] Non-bonding or absent parameter.

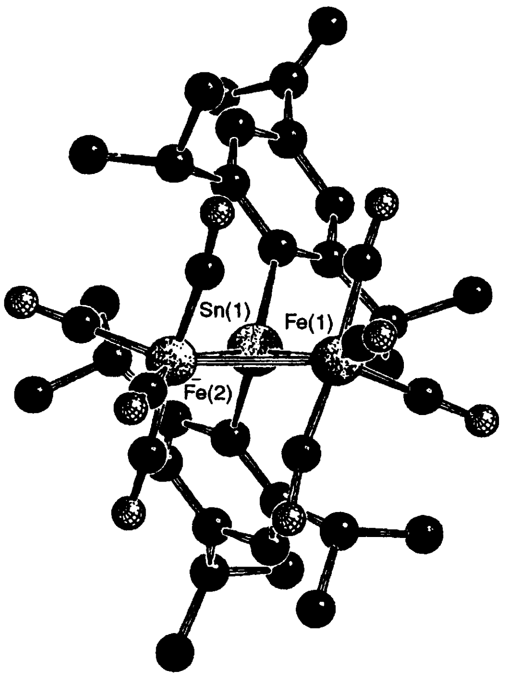

Fig. 1 A single molecule of $[Fe_2(CO)_8(\mu\text{-}SnR^1{}_2)]$ **1** showing the typical twist of the R^1 ligands on Sn with respect to the Fe_2Sn plane. Selected bond lengths and angles: Sn(1)–Fe(1) 2.603(2), Sn(1)–Fe(2) 2.614(2), Fe(1)–Fe(2) 2.788(2), Sn(1)–C(1) 2.220(6) and Sn(1)–C(16) 2.212(6) Å; Fe(2)–Sn(1)–Fe(1) 64.6(1), C(1)–Sn(1)–C(16) 101.3(3), Fe(1)–Fe(2)–Sn(1) 57.5(1) and Fe(2)–Fe(1)–Sn(1) 57.9(1)°. All values relate to molecule 1 in the asymmetric unit

four aromatic ^{13}C NMR signals. The extent of association of **5** was not established either in the condensed or gaseous phases, but mass spectrometry using an electron impact (EI) source showed the presence of an ion at *m*/*z* 681, corresponding to the fragment $[Sn_2R^3{}_3]^+$ and lower fragments of $(SnR^3{}_2)_n$. The material was employed as a potential source of the diaryltin species $SnR^3{}_2$. Reaction of **5** in refluxing toluene (16 h) with $[Fe_3(CO)_{12}]$ yielded, after work-up, crystals of $[Sn\{Fe_2(CO)_8\}_2]$ **4**, in rather poor yield. This compound had been previously obtained from tributyltin chloride and iron pentacarbonyl,[21] and structurally characterised by photographic methods by Lindley and Woodward.[13] We have redetermined the structure (using a CAD-4 diffractometer) in order to make detailed comparisons with our other tin–iron clusters, and it is a tribute to the earlier work that the two sets of data are so close (Table 1 and Fig. 4).

We have also studied the reaction of the three-co-ordinate species $M[CH(PPh_2)_2]_2$ (M = Sn or Pb)[26] with iron dodecacarbonyl. For both reagents we isolated no tin–iron clusters, but observed a rapid formation of the known species $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)]$ (dppm = $Ph_2PCH_2PPh_2$).[27] In the case of the tin reagent the iron complex was obtained essentially quantitatively, and it is interesting that under the same conditions the diphosphine dppm does not react with the dodecacarbonyl. This behaviour is similar to that found previously for these Group 14 reagents with the heavier Group 8 carbonyls.[6] As in those cases, the tin or lead reagents behave as rapid transfer sources of the fragment $CH(PPh_2)_2$, and subsequent work-up using conventional chromatographic methods affords the bis(phosphine) adducts.

(*b*) Crystal structures

Structural data have not been reported for any system of the type $[Fe_2(CO)_8(\mu\text{-}MR_2)]$, where M is a Group 14 element, though they are available for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}GeMe_2)]$,[28] but $[Fe_2(CO)_8\{\mu\text{-}Sn[CH(SiMe_3)_2]_2\}]$ has been described without structural characterisation[29] and $[Fe_2(CO)_6(\mu\text{-}GeMe_2)_3]$ has been crystallographically studied.[30] It was therefore of interest to determine the structures of **1**–**3**, particularly since it was known from other work[2,9] that the chemistry of tin(II) reagents bearing different aryl ligands is distinct. A comparison of significant geometrical parameters is presented in Table 1. The figures show the geometries of the

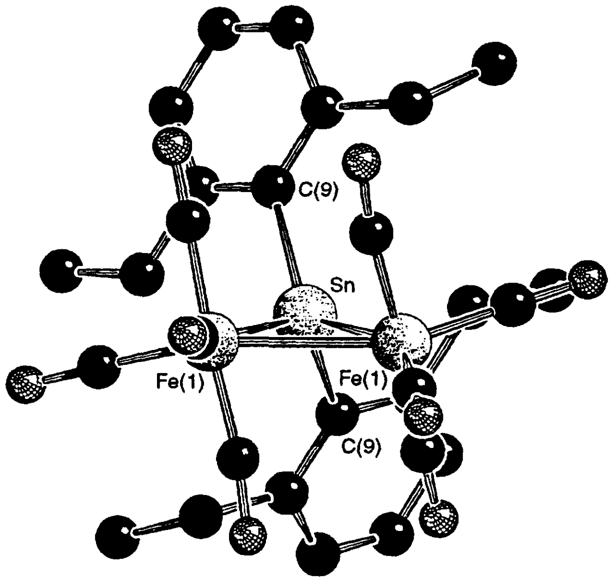

Fig. 2 A single molecule of $[Fe_2(CO)_8(\mu\text{-}SnR^2{}_2)]$ **2** showing the characteristic twist angle of the R^2 ligands with respect to the Fe_2Sn plane. Selected bond lengths and angles: Sn–Fe(1) 2.606(1), Fe(1)–Fe(1) 2.797(2) and Sn–C(9) 2.197(6) Å; Fe(1)–Sn–Fe(1) 64.9(1)°

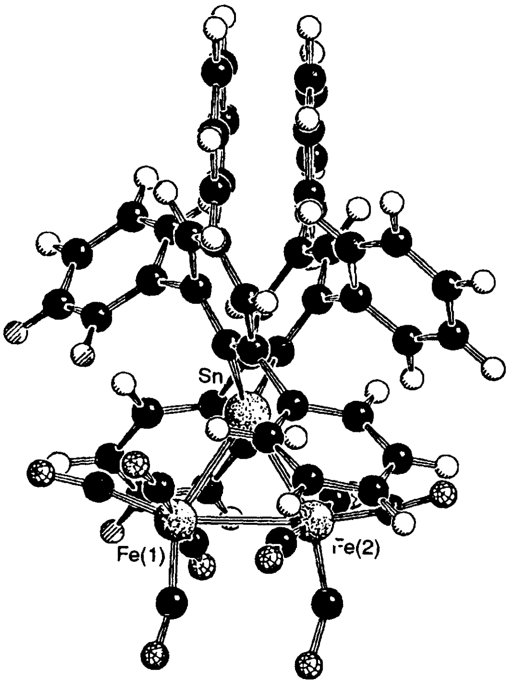

Fig. 3 A single molecule of $[Fe_2(CO)_8(\mu\text{-}SnR^4{}_2)]$ **3** showing the characteristic twist exhibited by compounds **1** and **2**. Selected bond lengths and angles: Sn–Fe(1) 2.616(2), Fe(1)–Fe(1) 2.794(4) and Sn–C(5) 2.18(1) Å; Fe(1)–Sn–Fe(1) 64.6(1)°

isostructural molecules, and reveal that differences between the metal triangles are small.

Noteworthy features of these structures are (*i*) the C–Sn–C angles and (*ii*) the twist angles at tin (the dihedral angles between the C–Sn–C plane and the Fe–Sn–Fe plane in each case). The C–Sn–C angle is largest in the least sterically hindered compound (**2**, the diethylphenyl derivative) showing that this angle is not primarily determined by steric effects. It also shows an inverse correlation with the twist angle as defined above, so that the twist angle is smallest (that is, shows the greatest deviation from orthogonality) for the bulkiest ligand, the order being **1** > **2** > **3**. The electronic basis of the twist angle has been investigated by carrying out Fenske–Hall calculations on the molecule $[Fe_2(CO)_8(\mu\text{-}SnMe_2)]$ with twist angles of 90 and 78° (representing a typical value from a range of structural determinations on these and related penta- and hexa-nuclear clusters). The overall overlap populations between the SnR_2 moiety and the Fe_2 units do not change significantly on introducing the twist (though contributions from individual orbitals do) so there is no simple correlation with electronic factors. At present therefore we cannot be certain of the origin of the twist, which is a feature of all the cluster molecules with bridging SnR_2 groups which we have studied [and also of $(SnR^1{}_2)_3$],[9a] and we are continuing to study this phenomenon. Distortions at the tin centre can therefore be measured in terms of these two parameters: the twist angle (measuring the deviation from the orthogonality of planes in a regular tetrahedral environment) and the C–Sn–C angle (measuring changes from the regular tetrahedral angle of 109° 28′). Compound **3**, which has the largest tin substituents (molecular volumes for the diethylphenyl-, triisopropylphenyl- and triphenylphenyl-substituted compounds are 729, 1031 and 1150 $Å^3$ respectively) accordingly has the greatest deviation from orthogonality of the planes, and a C–Sn–C angle less than that of **2**, and at least comparable with the angles found in the two molecules of **1** in the crystal.

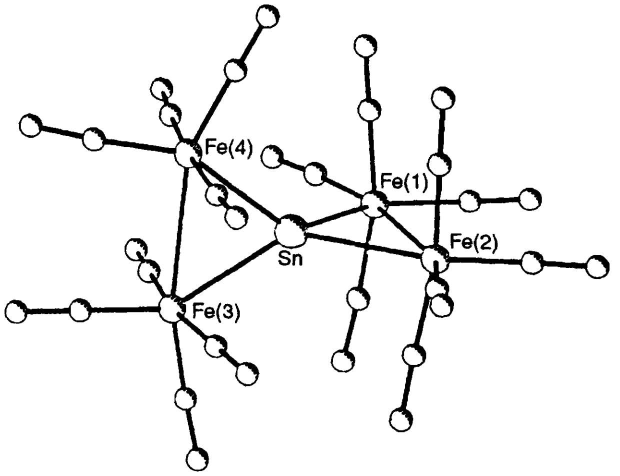

Fig. 4 A single molecule of $[Sn\{Fe_2(CO)_8\}_2]$ **4**. Selected bond lengths and angles: Sn(1)–Fe(1) 2.559(4), Sn(1)–Fe(2) 2.546(4), Sn–Fe(3) 2.546(3), Sn–Fe(4) 2.555(4), Fe(1)–Fe(2) 2.890(4) and Fe(3)–Fe(4) 2.890(5) Å; Fe(1)–Sn–Fe(2) 68.9(1) Fe(3)–Sn–Fe(4) 69.0(1), Sn–Fe(2)–Fe(3) 55.4(1) and Sn–Fe(1)–Fe(2) 55.3(1)°

The structures of $[SnPh_2\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$, $[SnMe_2\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$ and $[SnCl_2\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$ are known. The Fe–Sn–Fe angles in these compounds where there is no constraining Fe–Fe bond are very much larger than those of **1**–**3**, and the different ligands on the tin cause only small effects on this angle. The values are 128.7° in $[SnCl_2\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$,[22] 118.6° in $[SnPh_2\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$[23] and 123.4° in $[SnMe_2\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$.[24] The Fe–Sn bond lengths are much shorter where no Fe–Fe bonding occurs. For the case where the Fe–Fe vector is bridged by a third iron atom as in $[Fe_3(CO)_{12}]$ the relevant Fe–Fe distance is 2.558 Å, which is substantially less than those of **1**–**3**.

Data were also collected for compound **4**, and the structure solved, some of our data being presented in Fig. 4. It is interesting that the Fe–Fe distances in this molecule are significantly larger than in **1** or **2**, despite the shorter Sn–Fe distances; presumably the Fe atoms are using more electron density in bonding to the tin atoms, and less in Fe–Fe bonding. Also noteworthy is the remarkable agreement between our CAD-4 data and those obtained earlier.[13]

(*c*) Mössbauer spectra

The Mössbauer spectroscopic data for compounds **1**–**3** are presented in Table 2 along with relevant literature values for

Table 2 Iron-57 and ^{119}Sn Mössbauer spectroscopic data (mm s^{-1}) for compounds studied in this work and relevant literature values

		^{119}Sn			^{57}Fe			
Compound[a]	T/K	δ	Δ	Γ	δ	Δ	Γ*[b]	Ref.
1	78	1.79(1)	1.97(1)	0.44(1)	−0.03(2)	0.84(2)	0.16(1)	This work
2	78	1.72(2)	2.01(2)	0.46(2)	0.00(1)	0.94(1)	0.12(1)	This work
	298				−0.06(1)	0.91(1)	0.15(1)	This work
3	78	1.73(1)	1.86(1)	0.42(2)	0.00(1)	0.93(1)	0.16(1)	This work
6	80	1.73(1)	1.53(5)					11
7	80	1.83(6)	1.16(12)					12
8	295				[c] 0.012	−0.197	0.31	31
					[d] 0.022	+0.944	0.13	31
9	298				0.08(6)	1.088(10)	0.144(8)	15
10	4.2				[e] 0.01	−0.96		16

[a] **6** $[\{Fe(CO)_3\}_2Sn\{CH(SiMe_3)_2\}_2]$, **7** $[\{Fe(CO)_4(SnBu^t_2)\}_2]$, **8** $[Fe_3(CO)_{12}]$, **9** $[Fe_2(\mu\text{-}S)_2(CO)_6]$, **10** $[Ph_3Sb(OC)_3PhFePh_2SbFe(CO)_4]$. [b] Half width at half height. [c] Unique iron atom site A of triangle. [d] Carbonyl-bridged iron atoms B. [e] Iron bound to three CO.

comparison. It was previously suggested that the ^{119}Sn isomer shift (i.s.) and quadrupole splitting (q.s.) for $[Fe_2(CO)_8(\mu\text{-}SnR_2)]$ [R = $CH(SiMe_3)_2$] clearly rule out a stannylene formulation and were consistent with a triangulated structure.[11] The i.s. value[11] [1.73(1) mm s^{-1}] compared closely to that of $[\{Fe(CO)_4(SnBu^t_2)\}_2]$ [1.83(6) mm s^{-1}][12] which has a four-membered Sn_2Fe_2 ring, but the q.s. was slightly higher (1.53 *versus* 1.16 mm s^{-1}). It was further suggested that the higher value may be associated with the greater distortion from a tetrahedral geometry expected in a three-membered ring system.[11] A comparison was made with the Fe–Sn–Fe bond angle of 69° in *spiro*-$[(OC)_8Fe_2SnFe_2(CO)_8]$[13] and that of 103° in $[\{Fe_2(CO)_4(SnMe_2)\}_2]$.[14]

In fact the crystal structures and ^{119}Sn Mössbauer parameters for compounds **1**–**3** reported here confirm the previous suggestions: the ^{119}Sn i.s. values are very similar to that for the $CH(SiMe_3)_2$ complex, though the q.s. values are larger. We would expect from our previous findings[11] that the larger q.s. would be associated with the most distorted geometry around tin. Of the four ligands in these compounds, the overall crystallographic bulk order is 2,6-diethylphenyl < $CH(SiMe_3)_2$ < 2,4,6-triisopropylphenyl < 2,4,6-triphenylphenyl, however the *effective* bulk (estimated from a cone angle subtended by the ligand at the tin atom) would follow the order 2,6-diethylphenyl < 2,4,6-triisopropylphenyl < 2,4,6-triphenylphenyl < $CH(SiMe_3)_2$, which is consistent with the ^{119}Sn Mössbauer q.s. values. In fact the angles around the tin atoms in compounds **1** and **2** are not very different; it must, however, be remembered that the q.s. splitting measures imbalance in the electron density around the tin atoms and this is not necessarily reflected in the atomic positions. Indeed in compound **3**, which has a tin atom in a geometric environment close to that in **2**, the q.s. is only 1.86(1) mm s^{-1} showing that the electronic environment at tin is more symmetrical than those in compounds **1** and **2**. A novel way of looking at this may be to assume that relatively small asymmetries of the environment may be electronically compensated by the tin. Also the actual difference in the q.s. values of **1** and **2** is very small. Compound **3** has a smaller q.s. than those of **1** and **2**, and is expected to contain a less-distorted tetrahedral tin geometry.

The values of the ^{119}Sn i.s. and q.s., taken together, for these triangular metal clusters are quite different from other ^{119}Sn Mössbauer parameters.[11] [For a wide range of compounds, including tin(II) alkyls and cyclopentadienyls, organotin(II) halides, tin-borane compounds, complexes of tin(II) ligands (and their base adducts) attached to a variety of single transition-metal atoms, organotin(IV) halides and related tin-iron carbonyl(cyclopentadienyl) species.] An i.s. value in the range 1.72–1.79 mm s^{-1} with a q.s. value greater than 1.4 mm s^{-1} for such a formulation we take therefore as a clear sign of the presence of an $SnFe_2$ triangular cluster.

The ^{57}Fe Mössbauer parameters at 78 K for compounds **1**–**3** are similar to those of the carbonyl-bridged Fe–Fe atoms in $[Fe_3(CO)_{12}]$ at 295 K. The iron sites in **1**–**3** can be considered as distorted octahedra and as such may be expected to be more similar in geometry to the unique site in $[Fe_3(CO)_{12}]$, yet the Mössbauer parameters show that they are much more similar to the carbonyl-bridged sites. This finding suggests that the electronic environment experienced by the iron atoms in **1**–**3** is more similar to that of the bridged sites of the parent carbonyl, again reflecting the fact that the electronic environment may be more or less symmetrical than the crystallographic one. In the case of $[Fe_3(CO)_{12}]$[32] the Fe–Fe distance is 2.558(1) Å, compared with 2.788(2) in **1**, 2.797(2) in **2** and 2.794(4) Å in **3**. The Fe(B)–Fe(B)–Fe(A) bond angles are 61.37(4) and 61.63(4)° in $[Fe_3(CO)_{12}]$ compared with Fe–Fe–Sn angles of 57.9(1) in **1** and 57.6(1) in **2**. An Fe–Fe distance of 2.55 Å is found in $[Fe_2(\mu\text{-}S)_2(CO)_6]$[33] which also has Mössbauer data[15] similar to those reported here (see Table 2). The magnitude of the q.s. for the octahedral iron site in $[(Ph_3Sb)(OC)_3PhFePh_2SbFe(CO)_4]$ is also very similar to those of compounds **2** and **3**, but in this case the sign of the field gradient is negative. The sign for the bridged iron atoms in $[Fe_3(CO)_{12}]$ is positive, and is very likely to be the same in compounds **1**–**3**.

Experimental

All manipulations were conducted under an inert atmosphere using Schlenk tubes. Solvents were dried, degassed, and distilled immediately before use.

Reactions

$[Fe_3(CO)_{12}]$ and bis(2,4,6-triisopropylphenyl)tin(II). *In refluxing hexane.* The carbonyl (0.18 g, 0.36 mmol) and the tin reagent (0.06 g, 0.36 mmol of trimer) were mixed in hexane 30 cm^3). The solution was heated to gentle reflux (1 h). After cooling to room temperature a small aliquot was removed for TLC [hexane–dichloromethane (40:60), on silica] which showed two products (orange, R_f 0.88; blue, R_f 0.3) and no unreacted tin reagent. The solution was concentrated under vacuum to *ca.* 10 cm^3, and chromatographed under nitrogen on a silica column using the 'flash' technique. The blue compound decomposed on the column, and the orange fraction was recovered, concentrated, and on cooling (−20 °C) yielded an orange microcrystalline solid **1** (0.1 g) (Found: C, 52.2; H, 4.90. Calc. for $C_{38}H_{46}Fe_2O_8Sn$: C, 53.0; H, 5.30%). IR (CsI disc): ν(CO) 2084s, 2040s, 2023s, 2014s, 2005m, 1985m and 1973s cm^{-1}; the unexpectedly large number of absorptions is presumably associated with the existence of two molecules in the unit cell, the spectra having been recorded in the solid state. ^{1}H NMR (80 MHz, SiMe$_4$, CDCl$_3$): δ 6.92 (s, 2 H), 3.33 (m), 2.79 (spt), 1.18 (d), 1.01 (m) (together 21 H). M.p. (decomp.) 135 °C. Recrystallisation from octane slowly yielded (*ca.* 2 y) large needles suitable for X-ray study.

In diethyl ether below ambient temperature. A deep red solution of (SnR$^1_2$)$_n$ (where we believe $n < 3$, see Discussion) was obtained from reaction of the lithium aryl with tin(II) chloride (Et$_2$O, −80 °C).[9a] An excess of this solution, at −80 °C, was added dropwise to a solution of the carbonyl (0.2 g, 0.39 mmol) in diethyl ether (30 cm^3) at −40 °C. The solution was stirred (1 h) and allowed to warm to room temperature, and the products monitored by TLC [hexane–dichloromethane (60:40), silica gel] revealing unreacted carbonyl and a single orange product, subsequently characterised as the trimeric tin species.

[Fe$_3$(CO)$_{12}$] and bis(2,6-diethylphenyl)tin(II). Bis(2,6-diethylphenyl)tin(II) (0.5 g, 0.17 mmol of trimer) was added in hexane (30 cm^3) to a solution of the carbonyl (0.87 g, 0.17 mmol) in toluene (100 cm^3), and the mixture was refluxed (1.5 h). After cooling to room temperature a small aliquot was removed for TLC (hexane, on silica) revealing three materials (green, R_f 0.75, unreacted carbonyl; orange, R_f 0.6; and pink, R_f 0.4). The solution was concentrated under vacuum to *ca.* 10 cm^3, and chromatographed under nitrogen on a silica column using the 'flash' technique. The pink product decomposed on the column, and the orange fraction was collected, concentrated, and cooled to −25 °C. Red crystals (0.131 g) of the product **2** m.p. 122 °C (decomp.), were filtered off. IR (CsI disc): ν(CO) 2083, 2029, 2006, 1994 and 1964 cm^{-1}. ^{1}H NMR (80 MHz, SiMe$_4$, CDCl$_3$): δ 7.10 (m, 3 H), 2.97 (q, 3 H), 1.11 (t, 2 H). Crystals grown in this way were suitable for X-ray analysis.

Tin(II) chloride and pentamethylphenyllithium. The pentamethylphenyl group was lithiated (at −20 °C, in diethyl ether, 2 h) using its bromide and 1 mol equivalent butyllithium. After separation of the precipitated lithium bromide, the reagent was assayed. Two molar equivalents of this solution were added at low temperature (−90 °C) to a suspension of SnCl$_2$ in tetrahydrofuran (thf). On slow warming to room temperature the initially deep red mixture precipitated lithium choride, and afforded the product **5** as a yellow solid, soluble in toluene, and

Table 3 Fractional atomic coordinates for compound **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sn(1)	0.154 78(2)	0.110 87(6)	0.377 93(2)	Sn(2)	0.370 61(2)	0.185 96(6)	0.362 42(2)
Fe(1)	0.178 19(4)	0.105 32(15)	0.328 82(5)	Fe(3)	0.329 37(5)	0.019 36(15)	0.356 47(5)
Fe(2)	0.201 31(4)	0.269 75(15)	0.396 02(5)	Fe(4)	0.313 37(5)	0.184 98(18)	0.291 07(5)
O(1)	0.111 8(2)	0.192 9(9)	0.265 5(3)	O(9)	0.330 1(3)	−0.125 4(9)	0.290 8(3)
O(2)	0.245 3(3)	0.022 0(11)	0.392 6(3)	O(10)	0.327 1(3)	0.166 8(9)	0.420 2(3)
O(3)	0.161 7(3)	−0.143 1(10)	0.298 4(3)	O(11)	0.377 3(3)	−0.142 2(9)	0.422 7(3)
O(4)	0.204 1(2)	0.197 9(9)	0.278 3(3)	O(12)	0.264 7(3)	−0.088 1(13)	0.328 5(4)
O(5)	0.240 2(2)	0.116 4(8)	0.471 8(3)	O(13)	0.312 6(3)	0.431 7(11)	0.262 3(3)
O(6)	0.261 3(3)	0.370 1(13)	0.403 9(4)	O(14)	0.275 5(2)	0.271 3(11)	0.327 1(3)
O(7)	0.162 6(2)	0.417 0(8)	0.319 9(3)	O(15)	0.254 1(4)	0.070 8(17)	0.221 8(5)
O(8)	0.189 3(3)	0.440 4(8)	0.446 2(3)	O(16)	0.352 5(3)	0.104 5(10)	0.255 1(3)
C(101)	0.136 3(4)	0.160 9(11)	0.290 6(4)	C(109)	0.330 3(4)	−0.064 7(13)	0.315 1(5)
C(102)	0.218 6(4)	0.061 8(12)	0.369 9(4)	C(110)	0.327 3(3)	0.119 6(12)	0.394 1(4)
C(103)	0.167 4(3)	−0.044 8(12)	0.311 0(4)	C(111)	0.359 4(4)	−0.078 4(12)	0.397 4(5)
C(104)	0.194 0(3)	0.168 5(13)	0.297 9(4)	C(112)	0.289 8(4)	−0.043 1(16)	0.338 8(5)
C(105)	0.225 5(3)	0.172 9(12)	0.441 6(4)	C(113)	0.313 1(4)	0.337 6(15)	0.273 6(4)
C(106)	0.237 9(4)	0.329 1(15)	0.400 4(5)	C(114)	0.291 2(4)	0.231 6(16)	0.315 5(4)
C(107)	0.177 1(3)	0.353 7(13)	0.347 9(4)	C(115)	0.277 4(5)	0.115 2(20)	0.249 1(5)
C(108)	0.193 0(3)	0.371 9(13)	0.426 4(3)	C(116)	0.339 3(4)	0.131 6(12)	0.270 9(4)
C(7)	0.105 0(3)	0.376 4(11)	0.350 9(3)	C(37)	0.412 5(3)	0.399 9(9)	0.348 7(3)
C(8)	0.107 8(3)	0.452 5(12)	0.387 3(4)	C(38)	0.400 8(3)	0.455 1(12)	0.303 9(4)
C(9)	0.089 1(3)	0.447 3(13)	0.309 7(4)	C(39)	0.436 0(3)	0.482 7(10)	0.385 1(3)
C(10)	−0.000 3(5)	0.166 4(19)	0.318 6(6)	C(40)	0.502 0(4)	0.162 5(14)	0.351 0(4)
C(11)	0.001 6(5)	0.184 3(19)	0.358 2(7)	C(41)	0.529 6(4)	0.098 1(17)	0.386 7(5)
C(12)	−0.020 9(6)	0.181 4(28)	0.282 3(8)	C(42)	0.493 1(4)	0.124 4(15)	0.307 9(5)
C(13)	0.093 7(3)	−0.090 1(10)	0.335 7(3)	C(43)	0.415 6(3)	−0.067 7(11)	0.360 7(3)
C(14)	0.088 8(3)	−0.182 0(11)	0.362 6(4)	C(44)	0.439 2(4)	−0.137 4(13)	0.402 1(4)
C(15)	0.077 9(4)	−0.130 2(14)	0.289 1(4)	C(45)	0.406 5(4)	−0.150 5(13)	0.322 0(4)
C(1)	0.100 8(1)	0.141 6(6)	0.346 9(2)	C(31)	0.414 0(1)	0.165 8(6)	0.356 2(2)
C(2)	0.087 1(1)	0.255 9(6)	0.344 7(2)	C(32)	0.427 3(1)	0.274 7(6)	0.352 2(2)
C(3)	0.054 5(1)	0.264 8(6)	0.334 3(2)	C(33)	0.455 6(1)	0.272 8(6)	0.350 3(2)
C(4)	0.035 6(1)	0.159 5(6)	0.326 0(2)	C(34)	0.470 8(1)	0.161 8(6)	0.352 3(2)
C(5)	0.049 3(1)	0.045 2(6)	0.328 1(2)	C(35)	0.457 5(1)	0.052 9(6)	0.356 3(2)
C(6)	0.081 9(1)	0.036 3(6)	0.338 6(2)	C(36)	0.429 2(1)	0.054 8(6)	0.358 2(2)
C(22)	0.190 3(3)	−0.184 4(10)	0.408 1(3)	C(52)	0.433 0(3)	0.151 2(10)	0.462 5(3)
C(23)	0.171 0(3)	−0.295 9(10)	0.379 6(4)	C(53)	0.429 3(3)	0.085 6(13)	0.495 7(4)
C(24)	0.225 9(3)	−0.215 3(13)	0.436 9(4)	C(54)	0.468 3(4)	0.149 6(14)	0.472 9(5)
C(25)	0.157 4(3)	−0.273 1(10)	0.512 8(3)	C(55)	0.443 6(4)	0.572 8(14)	0.516 3(4)
C(26)	0.135 2(4)	−0.375 6(13)	0.488 2(4)	C(56)	0.462 6(5)	0.651 7(18)	0.507 7(6)
C(27)	0.190 3(4)	−0.309 4(14)	0.549 9(4)	C(57)	0.448 5(8)	0.556 0(32)	0.550 1(9)
C(28)	0.145 4(3)	0.155 7(10)	0.457 9(3)	C(58)	0.344 9(2)	0.472 5(9)	0.376 2(3)
C(29)	0.173 5(3)	0.212 2(12)	0.498 3(4)	C(59)	0.348 1(3)	0.586 0(10)	0.354 5(4)
C(30)	0.113 2(3)	0.177 5(13)	0.455 6(4)	C(60)	0.320 4(3)	0.495 7(12)	0.390 5(4)
C(16)	0.164 6(2)	0.015 3(5)	0.429 7(2)	C(46)	0.389 0(1)	0.311 3(5)	0.416 7(2)
C(17)	0.174 6(2)	−0.136 2(5)	0.432 2(2)	C(47)	0.418 6(1)	0.276 6(5)	0.453 2(2)
C(18)	0.173 3(2)	−0.217 2(5)	0.460 2(2)	C(48)	0.436 1(1)	0.360 2(5)	0.486 1(2)
C(19)	0.161 9(2)	−0.177 3(5)	0.485 7(2)	C(49)	0.424 0(1)	0.478 4(5)	0.482 5(2)
C(20)	0.151 9(2)	−0.056 5(5)	0.483 3(2)	C(50)	0.394 4(1)	0.513 1(5)	0.445 9(2)
C(21)	0.153 2(2)	0.024 5(5)	0.455 3(2)	C(51)	0.376 9(1)	0.429 5(5)	0.413 0(2)

Table 4 Fractional atomic coordinates for compound **2**

Atom	*x*	*y*	*z*
Sn	0.0	0.275 09(3)	0.25
Fe(1)	0.040 15(6)	0.155 88(5)	0.384 44(9)
O(1)	0.220 3(4)	0.199 9(3)	0.376 5(6)
O(2)	0.084 8(4)	0.000 3(3)	0.402 2(6)
O(3)	0.068 2(4)	0.204 2(4)	0.656 9(7)
O(4)	−0.142 4(4)	0.120 1(3)	0.389 9(6)
C(1)	0.150 3(6)	0.183 5(4)	0.377 2(7)
C(2)	0.067 5(5)	0.059 5(5)	0.394 1(7)
C(3)	0.057 3(5)	0.186 0(4)	0.548 5(10)
C(4)	−0.072 5(6)	0.135 7(4)	0.379 9(6)
C(5)	0.081 6(5)	0.391 8(4)	0.474 0(7)
C(6)	0.109 0(7)	0.439 9(5)	0.588 4(9)
C(7)	0.140 4(5)	0.302 7(4)	0.036 9(8)
C(8)	0.132 8(6)	0.345 1(4)	−0.089 3(8)
C(9)	0.114 0(4)	0.346 1(3)	0.258 3(8)
C(10)	0.136 5(5)	0.390 0(4)	0.367 7(7)
C(11)	0.209 4(5)	0.434 8(4)	0.383 0(8)
C(12)	0.260 3(6)	0.432 4(5)	0.289 6(10)
C(13)	0.239 4(5)	0.390 4(5)	0.184 0(9)
C(14)	0.163 9(5)	0.347 0(3)	0.163 0(8)

slightly soluble in hexane. The extent of association of this highly reactive material was not established.

Iron dodecacarbonyl with compound 5. The tin reagent **5** (0.26 g, 1 mmol based on monomeric unit) and the dodecacarbonyl (0.48 g, 1 mmol) were heated in refluxing toluene (16 h). The resulting brown solution was evaporated to dryness under vacuum, the residue was taken up into dry hexane, yielding an orange solution, from which crystals of compound **4** (0.075 g) were isolated. IR (solution in hexane): ν(CO) 2077m, 2052s, 2013m and 1989m cm^{-1}. Crystals were obtained from hexane for X-ray analysis.

Iron dodecacarbonyl with M[CH(PPh$_2$)$_2$]$_2$ (M = Sn or Pb). The tin and lead compounds were made according to literature methods.[26] In the tin case, the reagent (0.4 g, 0.4 mmol) in thf (30 cm^3) was added to [Fe$_3$(CO)$_{12}$] (0.15 g, 0.3 mmol) in thf (50 cm^3) at ambient temperature. The solution turned rapidly from dark green to red-brown just before the addition was completed, and was examined immediately thereafter by TLC [hexane–dichloromethane (60:40), silica gel)], revealing a single compound moving above the baseline, and no residual carbonyl. The solution was filtered, concentrated to low volume under vacuum, cooled (−20 °C), to yield orange-brown microcrystals of the product (0.19 g, 95%), m.p. 170–175 °C (Found: C, 56.15; H, 3.25; P, 8.10. Calc. for $C_{32}H_{22}Fe_2O_7P_2$: C, 55.65; H, 3.05; P, 8.95%). IR (KBr disc): ν(CO) 2050s, 2010s, 1994s, 1967s, 1950s, 1940s and 1770s cm^{-1}. ^{1}H NMR (80 MHz, CDCl$_3$): δ 7.34 (m, 20 H) and 3.60 (t, 2 H). The lead analogue reacted under similar conditions affording the same product athough in lower yield (47%).

Crystallography

Compound 1. *Crystal data.* $C_{38}H_{46}Fe_2O_8Sn$, M 861.162, monoclinic, space group $C2/c$ (no. 15), $Z = 16$, $D_c = 1.33$ g cm^{-3}, $a = 47.810(6)$, $b = 10.9525(8)$, $c = 37.227(5)$ Å, $\beta = 122.178(5)°$, $U = 16\,500(3)$ Å^3 (by least-squares refinement of the setting angles of 23 reflections, $14 \leqslant \theta \leqslant 16°$), $\lambda = 0.710\,73$ Å, $F(000) = 7039.69$, μ(Mo-Kα) = 13.31 cm^{-1}.

Data collection. 8777 Reflections were measured ($1 \leqslant \theta \leqslant 20°$) using two red-brown needle-shaped crystals (0.1 × 0.1 × 0.25 mm) (due to a break in the data collection the initial crystal was found to be too decayed to enable all the data to be collected) on an Enraf-Nonius CAD-4 diffractometer (Mo-Kα radiation, graphite monochromator, ω–2θ scans). The data sets were corrected individually for decay (0.5% per hour), and then merged (interlayer scale factors 0.8658 and 1.1549) to give 6634 unique reflections (merging $R = 0.0510$), of which 5245 had $|F_o| \geqslant 4\sigma|F_o|$.

Structure solution and refinement. The structure was solved by the Patterson routine of SHELXS 86[34] and refined by blocked full-matrix least-squares analysis to $R = 0.0676$ (541 variables). The metal atoms and carbonyls of the two molecules in the asymmetric unit were refined with anisotropic thermal parameters using the SHELX 76[35] program, and refining on F ($R' = 0.0766$). The geometry of the phenyl rings was constrained and all the hydrogens were placed geometrically, with common thermal parameters given to those in similar environments [phenyl CH, 0.16(2); ligand CH, 0.068(7); CH$_3$ of each ligand, 0.15(1), 0.14(1), 0.16(1), 0.22(1) Å^2]. The highest peaks in the final difference map were 0.86 e Å^{-3}, in the vicinity of the tin atoms. Final atomic coordinates are given in Table 3.

Compound 2. *Crystal data.* $C_{28}H_{26}Fe_2O_8Sn$, $M = 720.893$, monoclinic, space group $C2/c$ (no. 15), $Z = 4$, $D_c = 1.64$ g cm^{-3}, $a = 15.613(4)$, $b = 18.448(2)$, $c = 10.382(3)$ Å, $\beta = 102.71(1)°$, $U = 2917(1)$ Å^3 (by least-squares refinement of the setting angles of 25 reflections in the range $16 < \theta < 18)°$, $F(000) = 1439.22$, $\lambda = 0.710\,73$ Å, μ(Mo-Kα) = 18.74 cm^{-1}.

Data collection. 1851 Reflections were measured ($1 < \theta < 22°$) using a red single crystal of approximate dimensions 0.3 × 0.2 × 0.3 mm as for compound **1**. The data merged to give 1075 unique reflections (R_{merg} 0.034, no decay or absorption correction was applied), of which 997 had $|F_o| \geqslant 4\sigma(F_o)$.

Structure solution and refinement. The structure was solved by the direct method and confirmed by the Patterson method of SHELXS 86.[34] All non-hydrogen atoms were located by Fourier-difference synthesis and assigned anisotropic thermal parameters and the structure refined using the SHELX 76[35] program, and refining on F ($R = 0.0301$, $R' = 0.03$). The hydrogen atoms were positioned geometrically. The highest peak in the final difference map was 0.66 e Å^{-3}. Final atomic coordinates are given in Table 4.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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