Derivatives of Bivalent Germanium, Tin, and Lead. Part XI.[1] The Interaction of Tin(II) Halides and Bis(β-ketoenolates) with Di-iron Enneacarbonyl

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Tin(II) halides and bis(β-ketoenolates) react with di-iron enneacarbonyl to give high yields of complexes $[(X_2Sn)\text{-}Fe(CO)_4]$ (X = Cl, Br, pd, tbd, bpd, pbd, or dpd). In chloroform solution (osmometry), the pentane-2,4-dionate (pd) is dimeric but the remainder are only partially associated. Nujol mull i.r. spectra of the halide derivatives are consistent with a dimeric structure, but some dissociation is apparent for the β-ketoenolates being essentially complete for the bulky 4-phenylbutane-2,4- and 1,3-diphenylpropane-1,3-dionate ligands. In pyridine solution all the complexes are completely dissociated into pyridine-stabilised monomeric $[(X_2Sn)Fe(CO)_4]\cdot py$ species. Varying degrees of dissociation occur in less nucleophilic solvents such as tetrahydrofuran and acetonitrile. Iron-57 Mössbauer spectra of all the solid complexes demonstrate complete association into dimers at 77 K, but in frozen pyridine solution rehybridisation at iron to give trigonal-bipyramidal geometry occurs. The very low values of the tin-119 isomer shifts in the base-stabilised monomer complexes indicate substantial synergic tin→iron σ and iron→tin (*d*→*d*) π bonding.

THE interaction of bivalent tin compounds with transition-metal derivatives to yield tin–metal bonds has aroused much interest over the last few years.[2-9] Two general modes of reaction may be identified: (*i*) formal insertion into M–X or M–M bonds (oxidative addition to the tin lone-pair), (*ii*) co-ordination of the stannylene species to the transition-metal centre. Reaction (*i*) has

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[1] Part X, P. F. R. Ewings and P. G. Harrison, preceding paper.

[2] A. B. Cornwell and P. G. Harrison, *J.C.S. Dalton*, 1975, 1486.

[3] (*a*) F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 179; (*b*) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 1405; (*c*) S. R. A. Bird, J. D. Donaldson, A. F. Le C. Holding, B. J. Senior, and M. J. Tricker, *J. Chem. Soc.* (*A*), 1971, 1616; (*d*) P. Hackett and A. R. Manning, *J. Chem. Soc.* (*A*), 1971, *ibid.*, p. 1487; (*e*) P. F. Barrett and W. J. Jacobs, *Canad. J. Chem.*, 1972, **50**, 972; (*f*) B. J. Cole, J. D. Cole, and D. McWilliam, *J. Organometallic Chem.*, 1974, **64**, 223; (*g*) P. Hackett and A. R. Manning, *J. Organometallic Chem.*, 1974, **66**, C17; (*h*) P. Hackett and A. R. Manning, *J.C.S. Dalton*, 1974, 227; (*i*) J. D. Cotton P. J. Davison, D. E. Goldberg, M. F. Lappert, and K. M. Thomas, *J.C.S. Chem. Comm.*, 1974, 893.

[4] D. Uhlig, H. Behrens, and E. Lindner, *Z. anorg. Chem.*, 1973, **401**, 233.

[5] T. Kruck, F. J. Becker, H. Breuer, K. Ehlert, and W. Rother, *Z. anorg. Chem.*, 1974, **405**, 95.

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[7] P. J. Davison and M. F. Lappert, *J.C.S. Chem. Comm.*, 1973, 317.

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[9] M. D. Brice and F. A. Cotton, *J. Amer. Chem. Soc.*, 1973, **95**, 4529.

been studied extensively for several systems,[3] but the donor properties are relatively little explored. Complexes of tin(II) halides,[4] trihalogenostannate(II) anions,[4-6] tin(II) bis(ketoenolates),[2] bis(trimethylsilylmethyl)tin(II),[3i,7] and dialkylstannylenes (stabilised by base) [8] with Group 6 metal pentacarbonyl moieties have all been synthesised quite recently by photolytic or reductive methods, and in two cases [3i,9] the presence of a (co-ordinate) tin(II)–transition-metal bond has been confirmed crystallographically.

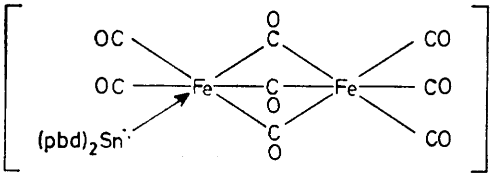
Attempts to prepare dialkylstannylene complexes of iron carbonyl moieties by the reduction of dialkyltin dichlorides by the tetracarbonylferrate anion yielded dimeric $[\{R_2SnFe(CO)_4\}_2]$ species [10] containing the Sn_2Fe_2 four-membered ring system.[11] Monomeric species (albeit stabilised by co-ordinated pyridine, tetrahydrofuran, or dimethyl sulphoxide) could, however, be obtained by dissolution of the tetranuclear dimer molecules in the appropriate donor solvent.[10] In this paper we report investigations concerning the interaction of tin(II) halides and bis(β-ketoenolates) with di-iron enneacarbonyl.

RESULTS AND DISCUSSION

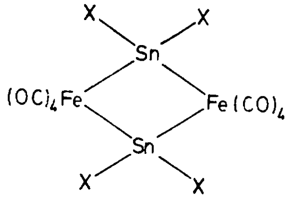
Tin(II) chloride, bromide, and bis(β-ketoenolates) reacted with di-iron enneacarbonyl in benzene or tetrahydrofuran (thf) to afford complexes of composition $[(X_2Sn)Fe(CO)_4]$ (X = Cl, Br, pd, tbd, bpd, pbd, or dpd) * as reddish or purple solids. The halogen derivatives are insoluble in non-basic organic solvents and decompose without melting at high temperatures. The β-ketoenolate derivatives, on the other hand, exhibit good solubility in common organic solvents except aliphatic hydrocarbons and melt sharply without decomposition. Molecular-weight determinations by osmometry in chloroform solution indicated a dimeric nature for the pd derivative, but substantial dissociation for the remainder. All the derivatives dissolve in nucleophilic solvents usually with a lightening in colour.

Reaction of $Fe_2(CO)_9$ with $Sn(pbd)_2$ yielded a small quantity of a second product of composition $[\{(pbd)_2Sn\}Fe_2(CO)_8]$. The i.r. spectrum of this complex exhibited bands at 2 030s, 1 995s,br, and 1 925s,vbr cm^{-1} and also a band at 1 800m cm^{-1}, indicating the presence of bridging carbonyl groups, and suggests that the complex is formed by displacement of CO by $Sn(pbd)_2$ and has structure (I) similar to that of $Fe_2(CO)_9$ itself.

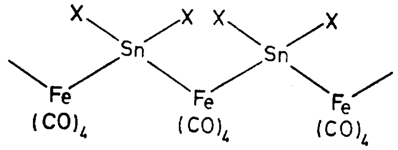
Tetracarbonyliron derivatives of tin have been prepared previously by various methods.[10,12-15] No structural data are available for simple binuclear complexes of the type $[(L_nSn)Fe(CO)_4]$, but both $[\{(Me_2Sn)Fe(CO)_4\}_2]$ [11] and $[\{(H_5C_5)_2SnFe(CO)_4\}_2]$ [16] have been shown to contain a Fe_2Sn_2 four-membered ring in the solid. The heavy-atom framework of these diorganotin derivatives is preserved in non-co-ordinating solvents, but nucleophilic solvents promote dissociation to base-stabilised monomeric units.[10] It has been shown previously that, to a first approximation, only the 'local' symmetry of the iron atoms in these types of complexes need be considered to account for the number of carbonyl-stretching bands observed in the i.r. spectra.[13] Complexes $[\{(R_2Sn)Fe(CO)_4\}_2]$ generally exhibit three bands at *ca.* 2 050s, *ca.* 2 000s, and 1 990vs cm^{-1}.[10,14] Base-stabilised monomers $[(R_2Sn)Fe(CO)_4]\cdot L$ [10] and anions of the type $[(X_3Sn)Fe(CO)_4]^-$ [15] exhibit bands shifted to lower energy at *ca.* 2 020s, *ca.* 1 950wm, and



(I)



(II)



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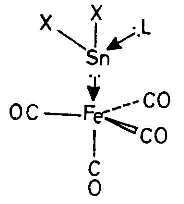

(IV)

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* pd = Pentane-2,4-dionate, tbd = 4-trifluoromethylbutane-2,4-dionate, bpd = 1,3-bis(trifluoromethyl)propane-1,3-dionate, pbd = 4-phenylbutane-2,4-dionate, and dpd = 1,3-diphenylpropane-1,3-dionate.

[10] T. J. Marks and A. R. Newman, *J. Amer. Chem. Soc.*, 1973, **95**, 769.

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[12] R. M. Sweet, C. J. Fritchie, and R. A. Schunn, *Inorg. Chem.*, 1967, **6**, 749.

[13] J. D. Cotton, S. A. R. Knox, I. Paul, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1967, 264 and refs. therein.

[14] C. D. Garner and R. G. Senior, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 609.

[15] W. M. Butler, W. A. McAllister, and W. M. Risen, *Inorg. Chem.*, 1974, **13**, 1702.

[16] A. B. Cornwell, P. G. Harrison, and J. A. Richards, *Abs. 1st Symp. Org. Chem. Germanium, Tin, and Lead*, Marseille, October 1974.

1 920vs cm^{-1}, the lowest-energy band usually being quite broad, as predicted for either ' local ' or overall C_{3v} symmetry at iron. In the present case Nujol mulls of the dihalogenotin derivatives exhibited three bands at *ca.* 2 090m—s, *ca.* 2 045s—vs,br, and *ca.* 1 990w—m (sh) cm^{-1}. Dissolution in pyridine drastically changed the spectra, and bands were observed at 2 040s, *ca.* 1 990m—s, and *ca.* 1 930vs,vbr cm^{-1}. The former set of bands may be associated with octahedrally co-ordinated iron in dimeric (II) [or polymeric (III)] structures, whilst the latter set are characteristic of the trigonal-bipyramidal species (IV). In weakly co-ordinating solvents such as thf or acetonitrile, both monomer and dimer (or oligomer) species are present.

It might be expected that, since a molecule of base appears to be necessary for stabilisation of the monomeric species, intramolecular co-ordination to tin by chelating ligands such as β-ketoenolato-groups provides sufficient stabilisation for the monomer. Such a tendency is indeed borne out by the molecular-weight data (Table 4) and the i.r. spectra for the bis(β-ketoenolato)tin complexes (Table 1) which all show bands diagnostic of both monomer and dimer even in Nujol mulls as well as dichloromethane solutions. In pyridine solution, only monomeric species are present. The position of the carbonyl-stretching frequency of the β-ketoenolate residue confirms that these groups still chelate the tin following the formation of iron–tin bonds, although some unidentate β-ketoenolate groups are observed in pyridine solution.[2]

TABLE 1

I.r. data (cm^{-1}) for the complexes

Complex	ν(M–C=O)	ν(C=O)	δ(M–CO)	ν(SnCl)
[{$(Cl_2Sn)Fe(CO)_4$}$_2$]				
Nujol mull	2 090s, 2 040vs, br, 1 987m (sh)		595s, 585s	310w
thf Solution	2 095s, 2 040vs, 2 010m (sh), 1 938vs, vbr		628s, 604m	
Pyridine solution	2 040s, 1 995m, 1 928vs, vbr		625s, 610m (sh)	
MeCN Solution	2 100mw, 2 045vs, 2 020mw, 1 965ms (sh), 1 940vs		630vs, 608m	
[{$(Br_2Sn)Fe(CO)_4$}$_2$]				
Nujol mull	2 095m, 2 048s, br, 1 995w (sh)		599ms, 586ms	
thf Solution	2 082mw, 2 040vs, 2 018s, 1 935vs, br		625s	
Pyridine solution	2 040s, 1 990s, 1 930vs, vbr		630s	
[{[(pd)$_2$Sn]$Fe(CO)_4$}$_2$]				
Nujol mull	2 080m, 2 038s, 2 010s, 1 960s (sh), 1 920s, vbr	1 620s, br, 156s, br	625s, 601ms	
Pyridine solution	2 030ms, 1 940s	1 700m, 1 600ms, 1 580ms, 1 620s, br	635m	
[{[(tbd)$_2$Sn]$Fe(CO)_4$}$_2$]				
Nujol mull	2 108mw, 2 063—2 010vs, 1 990vs, 1 960m (sh) br, 1 930m, br	1 615vs, br	605s, 593s	
CH_2Cl_2 Solution	2 102w, 2 090w, 2 045s, 2 035s, 1 945vs, br	1 612vs, br	629s, 608ms	
Pyridine solution	2 040ms, 1 925vs, br	1 610ms, 1 570ms	630ms	
[{[(bpd)$_2$Sn]$Fe(CO)_4$}$_2$]				
Nujol mull	2 082m, 2 034vs, 2 000s, 1 945m (sh)	1 645s, 1 620s, 1 560s, 1 540s	600m	
CH_2Cl_2 Solution	2 060ms, 2 010m, 1 940vs, br	1 640m, 1 630m, 1 620m	628ms, 600s	
Pyridine solution	2 040m, 1 933vs, br	1 712m, 1 682m, 1 610mw, 1 550mw, 1 530mw	628s	
[{[(pbd)$_2$Sn]$Fe(CO)_4$}$_2$]				
Nujol mull	2 040s, 2 000m, 1 925vs, vbr	1 515vs, br, 1 520vs, br	630m	
CH_2Cl_2 Solution	2 045ms, 2 004mw 1 935vs, br	1 548s, br, 1 520s, br	630m	
Pyridine solution	2 035m, 1 924vs, br	1 550vs, br, 1 520vs, br	630m	
[{[(dpd)$_2$Sn]$Fe(CO)_4$}$_2$]				
Nujol mull	2 040ms, 1 995ms, 1 925s, vbr	1 630s, br	625m	
Pyridine solution	2 040m, 1 930s	1 720m, 1 590ms, 1 520s, br	630m	
[{$(Me_2Sn)Fe(CO)_4$}$_2$] [a]				
Hydrocarbon solution	2 050s, 2 000s, 1 990vs			
Pyridine solution	2 010s, 1 928m (sh), 1 903vs, 1 895s			
[{$(Bu^tSn)Fe(CO)_4$}$_2$] [a]				
Hydrocarbon solution	2 045s, 1 994s, 1 984vs			
Pyridine solution	2 005s, 1 896vs			
[Ph_4As][$(Cl_3Sn)Fe(CO)_4$] [b]	2 036, 1 954mw, 1 937vs		622s	**335, 315**
[Ph_4As][$(Br_3Sn)Fe(CO)_4$] [b]	2 033s, 1 951mw, 1 935vs		623s	

[a] Ref. 10. [b] M. W. Butler, W. A. McAllister, and W. M. Risen, *Inorg. Chem.*, 1974, **13**, 1702.

Mössbauer spectroscopy yields data concerning electronic distribution and, by inference, molecular geometry about both tin and iron. The ^{119}Sn and ^{57}Fe Mössbauer spectral data for the complexes as neat solids and also as frozen pyridine solutions are in Table 2, together with pertinent data for related compounds. ^{119}Sn Spectra for all the complexes in the solid and solution consist of two fairly sharp resonances [Γ(solid) fell in the range 0.84—1.14, Γ(solution) in the range 0.89—1.40 mm s^{-1}]. In contrast, the ^{57}Fe spectra of the solid complexes consisted of a single rather broad line [Γ(solid) in the range 0.51—0.96 mm s^{-1}], whilst in pyridine solution two sharp [Γ(solution) in the range 0.36—0.54 mm s^{-1}] lines were observed. The change on dissolution is, however, expected for a dimer $\rightleftharpoons$ monomer dissociation. The dimeric species (II) [and also the polymer (III)] contain iron atoms which are octahedrally co-ordinated by four carbonyl groups and two tin atoms, ligands of similar electronegativity. Hence, only a very small quadrupole splitting resulting from small electronegativity differences and slight deviations from octahedral geometry are expected, and only a broadening of the resonance is actually observed. In solution, rehybridisation takes place and the iron atoms now enjoy trigonal-bipyramidal co-ordination resulting in formation of a large electric-field gradient at the metal nucleus, and the observed high magnitude of the quadrupole splitting (1.86—2.62 mm s^{-1}) is of the same order as other compounds with this geometry such as $Fe(CO)_5$ (2.57), $[(Ph_3P)Fe(CO)_4]$ (2.54), and $[\{(EtO)_3P\}Fe(CO)_4]$ (2.31 mm s^{-1}).[17] Surprisingly, whereas the i.r. spectra of the bis(β-ketoenolato)tin complexes indicate the presence of both monomer and dimer in Nujol mulls at the spectrometer beam temperature, the Mössbauer spectra indicate the presence of the dimer only in the solid at 77 K. It appears, therefore, that in these complexes there is a finely balanced monomer $\rightleftharpoons$ dimer equilibrium.

TABLE 2

Tin-119*m* and iron-57 Mössbauer data (mm s^{-1})

Complex	Nuclide	Solid I.s.	Solid Q.s.	Solid Γ_1	Solid Γ_2	Frozen pyridine solution I.s.	Frozen pyridine solution Q.s.	Frozen pyridine solution Γ_1	Frozen pyridine solution Γ_2
$[\{(Cl_2Sn)Fe(CO)_4\}_2]$	^{119}Sn	2.01	2.09	0.90	1.01	1.53	1.98	1.19	1.27
	^{57}Fe	−0.17	0	0.51		−0.24	2.45	0.41	0.44
$[\{(Br_2Sn)Fe(CO)_4\}_2]$	^{119}Sn	2.40	2.23	0.93	0.99	1.40	2.25	1.21	1.36
	^{57}Fe	0.06	0	0.64		−0.20	2.62	0.51	0.54
$[\{[(pd)_2Sn]Fe(CO)_4\}_2]$	^{119}Sn	1.46	1.85	0.92	1.14	1.42	2.02	0.98	0.96
	^{57}Fe	0.11	0	0.65		−0.39	2.09	0.39	0.41
$[\{[(tbd)_2Sn]Fe(CO)_4\}_2]$	^{119}Sn	1.47	1.49	0.84	0.87	1.30	2.03	1.27	1.38
	^{57}Fe	−0.04	0	0.72		−0.31	2.03	0.36	0.37
$[\{[(bpd)_2Sn]Fe(CO)_4\}_2]$	^{119}Sn	1.37	2.03	0.91	1.10	1.20	1.95	1.25	1.40
	^{57}Fe	−0.18	0	0.80		−0.36	1.86	0.40	0.39
$[\{[(pbd)_2Sn]Fe(CO)_4\}_2]$	^{119}Sn	1.45	1.91	0.96	1.10	1.27	2.01	0.89	1.00
	^{57}Fe	0.08	0	0.96		−0.15	1.99	0.41	0.48
$[\{[(dpd)_2Sn]Fe(CO)_4\}_2]$	^{119}Sn	1.38	1.73	0.90	1.05	1.29	1.81	0.92	1.01
	^{57}Fe	0.03	0	0.74		0.28	2.06	0.43	0.51
$[\{(Me_2Sn)Fe(CO)_4\}_2]$ [a]	^{119}Sn	1.47	1.22						
	^{57}Fe	−0.11	0.15						
$[\{(Bu^n{}_2Sn)Fe(CO)_4\}_2]$ [a]	^{119}Sn	1.70	1.26						
	^{57}Fe	0.02	0.2						
$[\{(Me_2\mathit{Sn})[Fe(CO)_4]_2\}_2Sn]$ [a]	^{119}Sn	1.45	1.24						
	^{57}Fe	−0.10	0.30						
$Fe(CO)_5$ [b]	^{57}Fe	−0.09	2.57						
$[(Ph_3P)Fe(CO)_4]$ [b]	^{57}Fe	−0.09	2.54						
$[\{(EtO)_3P\}Fe(CO)_4$ [b]	^{57}Fe	−0.12	2.31						
$[(Bu^t{}_2Sn)Fe(CO)_4]\cdot py$ [c]	^{119}Sn	1.82	3.06						
$[\{(\eta\text{-}H_5C_5)Fe(CO)_2\}_2(SnCl_2)]$ [d]	^{119}Sn	1.90	2.40						
$[\{(\eta\text{-}H_5C_5)Fe(CO)_2\}_2(SnBr_2)]$ [d]	^{119}Sn	1.99	2.42						
$[\{\eta\text{-}H_5C_5)Fe(CO)_2\}_2\{Sn(O_2CH)_2\}]$ [d]	^{119}Sn	1.61	2.19						
$[\{(\eta\text{-}H_5C_5)Fe(CO)_2\}_2\{Sn(O_2CMe)_2\}]$ [d]	^{119}Sn	1.63	2.60						

[a] Ref. 12. [b] Ref. 17. [c] G. W. Grynkewich, B. Y. K. Ho, T. J. Marks, D. L. Tomaja, and J. J. Zuckerman, *Inorg. Chem.*, 1973, **12**, 2522. [d] Ref. 3*c*.

At this point it is appropriate to comment on Marks' conclusions concerning base-promoted dissociation of the Fe_2Sn_2 ring system. He concluded,[10] on the basis of low electrical-conductivity data, that homolytic [equation (1)] rather than heterolytic Fe–Sn bond fission occurred [equation (2)]. Since, however, process (2) does not give rise to ionic species, no increase in conductivity is expected {*cf.* the high conductivity measured for $[(Ph_3Sn)Co(CO)_4]$ in *NN*-dimethylformamide [18]} and there is no reason for a homolytic process to be preferred.

The mode of synthesis of the dihalogeno-, bis(cyclopentadienyl)-, and bis(β-ketoenolato)-tin complexes directly from the Sn^{II} compound and $Fe_2(CO)_9$ suggests that the monomeric species $[(X_2Sn)Fe(CO)_4]$ are formed initially and subsequently dimerise because of the highly Lewis acidic tin and basic iron centres. Addition of base B: initiates a competition between B: and the iron for the Lewis acidic tin centre, thus giving rise to the monomer–dimer equilibrium (2). Strong bases such as pyridine are not easily displaced from tin and can effectively stabilise the monomeric species. Weak donors such as thf, acetonitrile, or the carbonyl group of the β-ketoenolate residue are more easily displaced and both monomer and dimer are observed at room temperature. Cooling to 77 K forces the equilibrium to the apparently more thermodynamically favoured dimer. That the equilibrium is dynamic for the bis(β-ketoenolato)tin complexes is apparent from the ^1H

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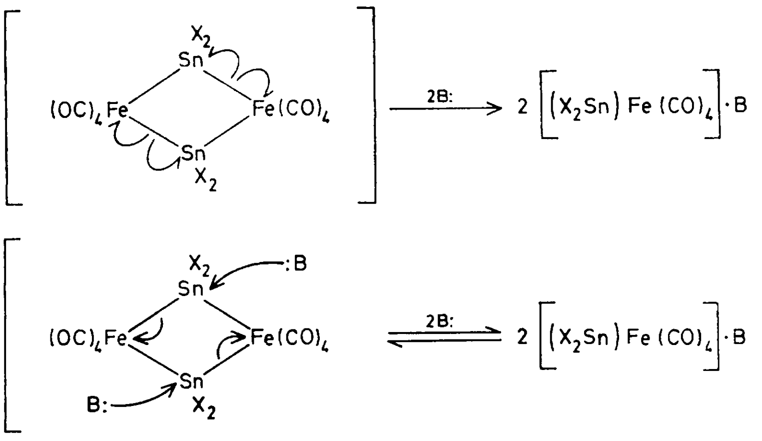
[17] 'Mössbauer Spectroscopy,' eds. N. N. Greenwood and T. C. Gibb, Chapman and Hall, London, 1971.

[18] J. M. Burlitch, *J. Amer. Chem. Soc.*, 1969, **91**, 4562, 4563.

n.m.r. spectra (Table 3) which exhibited a single set of resonances for each complex. Although the equilibrium is expected to be affected by a number of variable parameters such as the electronic and steric nature of the groups attached to tin (electron-withdrawing and bulky groups favouring dissociation), nature of the solvent, temperature, *etc.*, the Mössbauer spectra show that at 77 K only the dimeric species are present in the neat solids and only the base-stabilised monomers in the frozen pyridine solutions. It should be noted, however, that no information is available as to the *degree* of solvation except that this is expected to be small. In this light the Mössbauer parameters may be examined in further detail.



(1)

(2)

TABLE 3

^{1}H and ^{19}F N.m.r. data

Compound	τ(CF_3)	τ(CH)	τ(CH_3)	τ(C_6H_5)
$Sn(pd)_2$ [a]		4.87	8.28	
$[\{[(pd)_2Sn]Fe(CO)_4\}_2]$		4.54 (1 H)	7.93 (6 H)	
$Sn(tbd)_2$ [a]	72.05	4.22	7.88	
$[\{[(tbd)_2Sn]Fe(CO)_4\}_2]$	77.45	4.07 (1 H)	7.73 (3 H)	
$Sn(bpd)_2$ [a]	72.95	4.02		
$[\{[(bpd)_2Sn]Fe(CO)_4\}_2]$	76.40	3.78		
$Sn(pbd)_2$ [b]		3.99	7.81	2.20 (2 H), 2.68 (3H) [c]
$[\{[(pbd)_2Sn]Fe(CO)_4\}_2]$		3.85 (1 H)	7.74 (3 H)	2.12 (2 H), 2.61 (3H) [c]
$Sn(dpd)_2$ [b]		3.38		2.20 (2 H), 2.68 (3 H) [c]
$[\{[(dpd)_2Sn]Fe(CO)_4\}_2]$		3.30 (1 H)		2.12 (2 H), 2.61 (3 H) [c]

[a] P. F. R. Ewings, P. G. Harrison, and D. E. Fenton, *J.C.S. Dalton*, 1975, 821. [b] Ref. 2. [c] Centre of multiplet.

The geometry at the tin atoms in the two halogeno-derivatives is expected to be similar to that in $[\{(\eta\text{-}H_5C_5)Fe(CO)_2\}_2(SnCl_2)]$ which is known from crystallographic data to possess a distorted tetrahedral disposition of chlorine and iron atoms about tin.[19] Attempts to relate observed quadrupole-splitting values with those calculated using the point-charge method are pointless in the absence of structural data since even small variations in molecular geometry produce significant changes in the calculated values.[3c] However, the values observed for $[\{(X_2Sn)Fe(CO)_4\}_2]$ (X = Cl or Br) are only slightly lower than those for the corresponding $[\{(\eta\text{-}H_5C_5)Fe(CO)_2\}_2(SnX_2)]$ complexes.[3c] The isomer shifts for the two halogenotin complexes are in the order expected on ligand electronegativity grounds (Br > Cl), but this order is reversed in the pyridine-solvated monomers although the quadrupole splittings remain fairly constant. Thus, it is apparent that factors other than simple ligand electronegativity influence the isomer-shift values.

The ^{119}Sn Mössbauer isomer shifts for the bis(β-ketoenolato)tin complexes in the solid all fell in the narrow range 1.37—1.47 mm s^{-1}, decreasing progressively as more electronegative CF_3 or Ph groups replaced Me groups on the β-ketoenolate residue. The low values of the quadrupole splitting for these complexes (1.49—2.03 mm s^{-1}) confirm the *cis*-Fe_2SnO_4 geometry at the octahedrally co-ordinated tin atoms. ^{57}Fe Isomer shifts for all the complexes fell in the range -0.18 to $+0.11$ mm s^{-1}, again decreasing monotonically on CF_3 or Ph substitution. Dissolution in pyridine further decreased both the ^{57}Fe (corresponding to an effective increase in *s*-electron density) and the ^{119}Sn isomer shifts (an effective decrease in *s*-electron density).

The pyridine-solvated monomers are especially interesting since they are formally stannylene complexes, analogous to Group 6 pentacarbonyls previously examined.[2] In the latter complexes the spectroscopic data indicated substantial synergic $(d\rightarrow d)\pi$ multiple bonding between the transition metal and tin. In the present case there are three principal contributions to the drastic decrease (*ca.* 2 mm s^{-1}) in ^{119}Sn isomer shift on going from the free tin(II) bis(β-ketoenolates) to the iron tetracarbonyl complexes: (*i*) co-ordination of the stereochemically active lone pair of the tin(II) bis(β-ketoenolate) to iron (removal of *s*-electron density from tin to iron), (*ii*) co-ordination of pyridine to tin (lowering of the effective *s*-electron density by shielding), and (*iii*) $(d\rightarrow d)\pi$ multiple bonding along the Fe–Sn bond which would place electron density in vacant tin *d* orbitals and lower the effective 5*s*-electron density again by shielding. Mechanism (*ii*) is known to decrease the isomer shift of tin(II) bis(β-ketoenolates) only to a small degree,[2] and it is likely that mechanisms (*i*) and (*iii*) acting synergically

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[19] J. E. O'Connor and E. R. Corey, *Inorg. Chem.*, 1967, **5**, 968

are dominant in the reduction in effective 5*s*-electron density at tin. Evidence of substantial electron transfer from tin to iron is available from the ^{57}Fe isomer-shift values of the monomer complexes (−0.15 to −0.39 mm s^{-1}) which are significantly less than those of $Fe(CO)_5$, $[(Ph_3P)Fe(CO)_4]$, or $[\{(EtO)_3P\}Fe(CO)_4]$ (−0.09 to −0.12 mm s^{-1}),[17] thus illustrating that these stannylene species are appreciably better σ donors than either carbon monoxide or phosphines.

EXPERIMENTAL

All manipulations were made under an atmosphere of dry oxygen-free nitrogen or argon. Anhydrous tin(II) halides were commercial products used without further purification. The tin(II) bis(β-ketoenolates) were synthesised from tin(II) dimethoxide or bis(methylcyclopentadienyl)tin(II) and the appropriate β-diketone as described previously.[2] Di-iron enneacarbonyl was obtained by photolysis of iron pentacarbonyl. All solvents were dried and freed from dissolved oxygen by standard methods prior to use.

TABLE 4

Preparation and characterisation of the complexes

Complex	θ_c/°C (t/h)	Solvent	Yield (%)	Colour	M.p. (θ_c/°C)	Analysis(%) Found C	Found H	Found Hal.	Calc. C	Calc. H	Calc. Hal.	M[a]
$[\{(Cl_2Sn)Fe(CO)_4\}_2]$	20 (48)	Benzene	92	Vermilion orange	decomp. >170	13.65	0.30	19.55	13.45	0	19.85	*b*
$[\{(Br_2Sn)Fe(CO)_4\}_2]$	20 (24)	thf	74	Pale purple	decomp. 180	10.65	0.40	23.35	10.75	0	24.6	*b*
$[\{[(pd)_2Sn]Fe(CO)_4\}_2]$	20 (24)	thf	63	Dark red-brown	73—74	34.9	3.20		34.7	2.90		967 (969)
$[\{[(tbd)_2Sn]Fe(CO)_4\}_2]$	20 (24)	thf	60	Pale golden brown	85	28.15	1.45		28.25	1.70		1 018 (1 189)
$[\{[(bpd)_2Sn]Fe(CO)_4\}_2]$	20 (24)	thf	55	Dark purple-red	90	23.65	0.90		23.95	0.55		1 028 (1 405)
$[\{[(pbd)_2Sn]Fe(CO)_4\}_2]$	80 (8)	thf	62	Dark red-brown	115	47.0	3.35		47.3	3.00		782 (1 222)
$[\{[(dpd)_2Sn]Fe(CO)_4\}_2]$	80 (8)	thf	51	Dark red-brown	120	55.9	3.35		55.7	3.05		975 (1 467)

[a] By osmometry in chloroform; calculated values are given in parentheses. [b] Too insoluble for measurement.

I.r. spectra were recorded using Perkin-Elmer 457 or 521 spectrophotometers. ^{1}H and ^{19}F N.m.r. spectra were recorded in $CDCl_3$ solution using a Varian HA-100 spectrometer with $SiMe_4$ (^{1}H) and $CFCl_3$ (^{19}F) as internal lock signals. Mössbauer spectra were recorded at 77 K using a Harwell instrument equipped with a 256 channel analyser. ^{57}Fe and ^{119}Sn Spectra were obtained against ^{57}Co–Pd and $Ba[^{119m}SnO_3]$ sources, respectively. ^{57}Fe Isomer shifts are quoted with respect to iron metal (+0.165 mm s^{-1}) and ^{119}Sn shifts with respect to SnO_2. Data reduction to Lorentzian line shapes was effected by usual least-squares methods. Maximum estimated standard deviations for the parameters are ±0.05 (isomer shift) and ±0.10 mm s^{-1} (quadrupole splitting).

Syntheses.—The complexes were synthesised by stirring a suspension of $Fe_2(CO)_9$ (1.5 mmol) with tin(II) halide or bis(β-ketoenolate) (1.5 mmol) in benzene or thf (25 cm^3) at room temperature or under reflux. The progress of the reactions was monitored by the disappearance of the band at *ca.* 1 800 cm^{-1} in the i.r. spectrum of the enneacarbonyl. When the reaction was complete, the solution was filtered and the volume of solvent reduced. The complexes were crystallised as coloured *powders*. Pertinent synthetic details are in Table 4.

A small amount of a second product was isolated from the reaction with tin(II) bis(4-phenylbutane-2,4-dionate) which appeared to be $[\{(pbd)_2Sn\}Fe_2(CO)_8]$ (Found: C, 42.9; H, 2.90. $C_{28}H_{18}Fe_2O_8Sn$ requires C, 43.15; H, 2.60%), ν(C=O) at 2 030s, 1 995s,br, 1 925s,vbr, and 1 800m cm^{-1}.

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