Derivatives of Divalent Germanium, Tin, and Lead. Part V.[1] Bis(pentane-2,4-dionato)-, Bis(1,1,1-trifluoropentane-2,4-dionato)-, and Bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)-tin(II)

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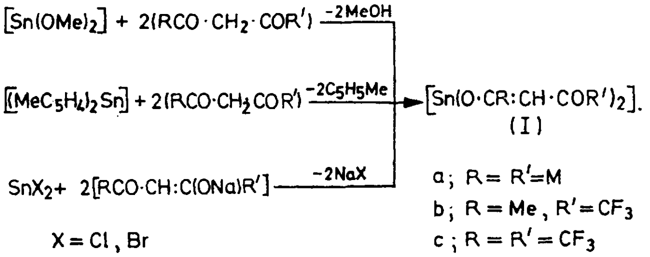
The tin(II) β-diketonato-derivatives, bis(pentane-2,4-dionato)tin(II) [Sn(acac)$_2$], bis(1,1,1-trifluoropentane-2,4-dionato)tin(II) [Sn(tfac)$_2$], and bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)tin(II) [Sn(hfac)$_2$], have been synthesised by the reaction of the appropriate β-diketone with tin(II) dimethoxide or bis(methylcyclopentadienyl)-tin(II), or from tin(II) chloride or bromide and the sodium salt of the β-diketone. The derivatives are monomeric in both benzene solution and the gas phase, and exhibit high volatility and solubility in both polar and non-polar organic solvents. The perfluorinated derivatives are Lewis acids and form 1 : 1 complexes with 2,2'-bipyridyl and 1,10-phenanthroline. [Sn(hfac)$_2$] Also undergoes ready ligand exchange with tin(II) chloride forming [Sn(hfac)Cl]. I.r., ^{1}H and ^{19}F n.m.r., tin-119 Mössbauer, and mass spectra have been recorded and structural information inferred therefrom.

THE structure of metal–pentane-2,4-dionato-derivatives has aroused much interest in recent years. Studies of tin derivatives have largely been confined to the elucidation of the stereochemistry of diorganotin(IV) bis(pentane-2,4-dionato)-derivatives, which are readily available by reaction of the corresponding diorganotin(IV) oxide and the pentane-2,4-dionate or by the substitution of the organotin(IV) halide using pentane-2,4-dionatothallium(I).[2] Physicochemical studies including dipole moment, i.r., Raman, u.v., and n.m.r. data suggest a six-co-ordinate structure with *trans*-organic groups and bidentate pentane-2,4-dionato-ligands for this type of compound,[2,3] a hypothesis recently corroborated by *X*-ray analysis for [Me$_2$Sn(acac)$_2$].[4] In spite of the numerous data available for organotin(IV) derivatives, none is available for analogous derivatives of divalent tin. Here we report our studies on bis(pentane-2,4-dionato)tin(II) [Sn(acac)$_2$], and the perfluorine analogues, bis(trifluoropentane-2,4-dionato)tin(II) [Sn(tfac)$_2$], and bis(hexafluoropentane-2,4-dionato)tin(II) [Sn(hfac)$_2$]. While this work was in progress, Noltes *et al.* have reported the synthesis and some properties of [Sn(acac)$_2$] as well as bis(pivaloylacetonato)tin(II) [Sn(pac)$_2$] and bis(dipivaloylmethanato)tin(II) [Sn(dpm)$_2$].[5]

RESULTS AND DISCUSSION

The synthesis of bis(pentane-2,4-dionato)tin(II) derivatives (I) is readily obtained by the reaction of tin(II) dimethoxide or bis(methylcyclopentadienyl)tin(II) with the β-diketone, or by the substitution of tin(II) chloride or bromide using the corresponding sodium salt:



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[1] Part IV, S. Borkett, J. Doe, and P. G. Harrison, *J. Organometallic Chem.*, 1973, **52**, 343.

[2] C. Z. Moore and W. H. Nelson, *Inorg. Chem.*, 1969, **8**, 138, 143; and refs. therein.

[3] H. Serpone and K. A. Hersh, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 115.

[4] G. A. Miller and E. O. Schlemper, *Inorg. Chem.*, 1973, **12**, 677.

[5] K. D. Bos, H. A. Budding, E. J. Bulten, and J. G. Noltes, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 961.

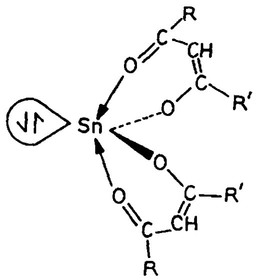
The reactions generally occur readily at room temperature, except for those involving tin(II) dimethoxide, an insoluble polymeric material, which was heated if necessary until complete dissolution was achieved. No satisfactory results were obtained using tin(II) iodide. Yields of crude material were essentially quantitative; those of purified material are reported in Table 3.

Compound (Ia) is a volatile oil whilst (Ib) and (Ic) are highly crystalline solids with sharp melting points which are easily sublimed *in vacuo*. All are monomeric in both benzene solution (osmometry) and in the vapour state (mass spectrometry). Unlike most other divalent tin compounds, the derivatives (Ia—c) exhibit a remarkable range of solubility, being freely soluble without decomposition in polar and non-polar (oxygen-free) organic solvents including methanol, dichloromethane, benzene, and pentane. Exposure to air results in rapid oxidative hydrolysis in all cases.

The perfluorinated derivatives, (Ib) and (Ic), but not (Ia), function as fairly strong Lewis acids, readily forming 1 : 1 adducts with 2,2′-bipyridyl and 1,10-phenanthroline. Ready ligand redistribution between [Sn(hfac)$_2$] and tin(II) chloride occurs in solution forming [Sn(hfac)Cl]. Unlike the analogous compounds [Sn(acac)Cl] and [Sn(pac)Cl], which sublime unchanged at 100—115 °C under high vacuum,[5] [Sn(hfac)Cl] reverts to its precursors under the same conditions.

The ease of solubility and volatility of the compounds (Ia—c) suggest that the monomeric character observed in solution and the vapour state is preserved in the solid phase, in contrast to other tin(II)–oxygen derivatives which often possess polymeric bridged lattices in the crystal.[6,7] Crystals of (Ib) and (Ic) are highly susceptible to multiple twinning; nevertheless an *X*-ray analysis of (Ib) is underway in this laboratory. In the absence of unequivocal structural data, inferences concerning structure and electronic distribution may be made from spectroscopic data.

The i.r. spectra for (Ia—c) are listed in Supplementary Publication SUP 21211 (4 pp.).* Vibrational assignments are assisted by the known spectra of hexafluoropentane-2,4-dionatolithium tetramethylethylenediamine,[8] [M^{II}(hfac)$_2$] (M^{II} = Ni, Zn, Mn, Fe, or Cu), [M^{III}(hfac)$_3$] (M^{III} = Rh, Cr, Fe, Al, or Nd), and [M^{IV}(hfac)$_4$] (M^{IV} = Th or Zn).[9] As observed previously with these compounds, considerable mixing of fundamentals in the compounds (Ia—c) takes place, principally between the C=O and C=C stretching vibrations. In all three compounds, two clearly resolved components are observed for the two mixed vibrations $\nu(\mathrm{C}\overset{...}{-}\mathrm{O}) + [\nu(\mathrm{C}\overset{...}{-}\mathrm{C})]$ and $\nu(\mathrm{C}\overset{...}{-}\mathrm{C}) + [\nu(\mathrm{C}\overset{...}{-}\mathrm{O})]$ (except for [Sn(acac)$_2$] which exhibits a very broad band for the latter vibration), indicating inequivalence of the two pentane-2,4-dionato-groups attached to tin. Divalent tin compounds are generally accepted to achieve co-ordination saturation at co-ordination number three,[10] as in tin(II) sulphate[6] or potassium tris(formato)stannate(II)[11] which have pyramidal three-co-ordinate tin. On this basis, in order to satisfy three-co-ordination for tin in the present case, one β-diketonate ligand must function as a bidentate ligand, the second being unidentate with the carbonyl group essentially remote from the tin atom. However, more recent structural investigations on tin(II)–oxygen compounds show that simple trigonal-pyramidal geometry for tin(II) is by no means exclusive and that co-ordination numbers at tin(II) can increase beyond three. Indeed, co-ordination numbers of six at tin(II) have been observed for [Sn(O$_2$C·C$_6$H$_4$·NO$_2$-*o*)$_4$O]·THF[7] and dihydrogen ethylenediaminetetra-acetatostannate(II)[12] albeit with different geometries (pentagonal pyramidal and trigonal prismatic, respectively). In all metal complexes of β-diketonates for which structural data are available[13] the β-diketonate functions as an intramolecularly co-ordinating bidentate ligand. Since there is no reason to expect different behaviour in the present case, the tin atom in the compounds (Ia—c) is expected to be four-co-ordinate. Hence the most probable structure for these compounds is likely to be similar to that of bis(diethyldithiocarbamato)tin(II)[14] in which the tin lone-pair exhibits stereochemical activity, occupying an equatorial position of a distorted trigonal bipyramid at tin, *viz.*:



Proton and fluorine n.m.r. data at ambient temperatures are presented in Table 1. All three compounds exhibit a single sharp methine resonance which becomes progressively deshielded on increasing perfluorination. In addition, the spectra show single

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* For details of the Supplementary publications scheme see *J.C.S. Dalton*, 1974, Index issue, Notice to Authors No. 7.

[6] J. D. Donaldson and D. C. Puxley, *Acta Cryst.*, 1972, **B28**, 864.

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[10] J. D. Donaldson, *Progr. Inorg. Chem.*, 1967, **8**, 235.

[11] A. Jelen and O. Lindquist, *Acta Chem. Scand.*, 1969, **23**, 3071.

[12] K. G. Shields, R. C. Seccombe, and C. H. L. Kennard, *J.C.S. Dalton*, 1973, 741.

[13] For example A. N. Knyazeva, E. A. Shugam, and L. M. Shkol'nikova, *J. Struct. Chim.*, 1970, **11**, 875; M. V. Veidis, G. H. Schreiber, T. E. Gough, and G. J. Palenik, *J. Amer. Chem. Soc.*, 1969, **91**, 1859.

[14] J. Potenza and D. Mastropaolo, *Acta Cryst.*, 1973, **B29**, 1830.

methyl and/or trifluoromethyl resonances, which for (Ia) (Me) and (Ib) (Me and CF_3) remain sharp at −40 °C. However, the single CF_3 resonance observed at ambient temperatures for (Ic) gradually broadens on decreasing temperature, and at −40 °C is resolved into four components of equal intensity, consistent with four inequivalent trifluoromethyl groups of two inequivalent hexafluoropentanedionato-groups attached to tin, and thus lending support to the similar conclusion derived from the i.r. spectra. At higher temperatures the compound is stereochemically non-rigid, and a single time-averaged resonance is observed.

TABLE 1

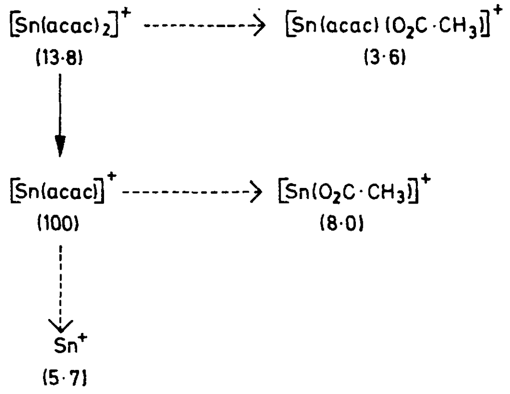
Tin-119*m* Mössbauer and n.m.r. data for tin(II) pentane-2,4-dionates and their derivatives

	Sn^{119m} Mössbauer data		^1H N.m.r. data (in Hz)		^{19}F N.m.r. data
Compound	I.S./ mm s^{-1}	Q.S./ mm s^{-1}	(C*H*)	(*Me*)	C*F*$_3$
[Sn(OMe)$_2$]	2·92	1·89			
[Sn(acac)$_2$]	3·10	2·02	4·87	8·28	
	3·12 [a,b]	1·89 [b]			
[Sn(tfac)$_2$]	3·40	1·87	4·22	7·88	7205
[Sn(hfac)$_2$]	3·60	1·66	4·02		7295
[Sn(tfac)$_2$]·phen	3·47	1·44			
[Sn(hfac)$_2$]·phen	3·55	1·34			
[Sn(tfac)$_2$]·bipy	3·05	1·02			
[Sn(hfac)$_2$]·bipy	3·15	0·90			
[Sn(hfac)Cl]	3·56	1·71			
[Sn(dpm)$_2$] [b]	3·22 [a]	1·90			
[Sn(pac)$_2$] [b]	3·10 [a]	2·21			
[Sn(acac)Cl] [b]	3·36 [a]	1·86			
[Sn(dpm)Cl] [b]	3·44 [a]	2·03			

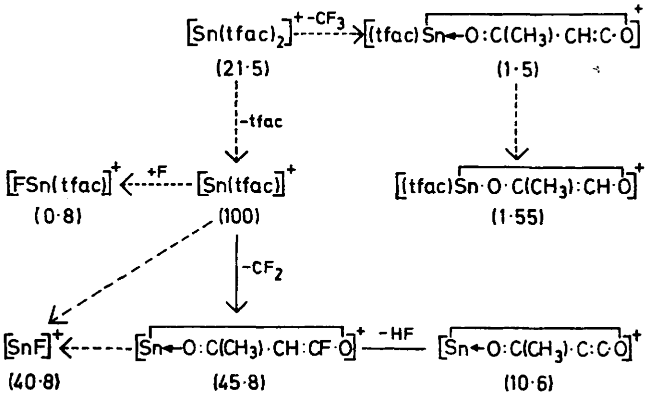
[a] Corrected by $\delta(SnO_2) = \delta(\alpha\text{-}Sn) + 2{\cdot}1$ mm s^{-1}. [b] Ref. 6.

Also in Table 1 are presented tin-119*m* Mössbauer data for (Ia—c) and their derivatives. Progressive replacement of methyl by trifluoromethyl groups causes an increase in isomer shift accompanied by a corresponding decrease in the quadrupole splitting. An increase in tin-119*m* isomer shift corresponds to an increase in 5*s* electron density at the tin nucleus. Increasing ligand electronegativity would be expected generally to remove electron density from tin and lower the isomer shift. The observed trends may, however, be rationalised on the basis of Bent's isovalent hybridisation theory,[15] according to which tin would use hybrid orbitals of greater 5*p* character in bonding to the more electronegative ligands, thus allowing the tin lone-pair of electrons to become concentrated in an orbital of increased 5*s* character. Alternatively, in valence-bond terms, the contribution of the canonical form $[Sn^{2+}2(L)^-]$ increases with increasing ligand electronegativity. The decreasing value of the quadrupole splitting is also consistent with this hypothesis, since the electronic arrangement at tin would become less distorted from spherical symmetry, thus reducing the electric field gradient and the quadrupole splitting. Complex formation with bipyridyl or phenanthroline, which presumably increases the co-ordination number at tin to five or six, has only a slight effect on the isomer shift, but lowers the quadrupole splitting significantly. None of the compounds exhibited a Mössbauer effect at ambient temperatures suggestive of non-polymeric lattices.*

Polyisotopic parent ions are the features of highest mass observed in the mass spectra of [Sn(acac)$_2$] (Scheme 1) and [Sn(tfac)$_2$] (Scheme 2), but in the spectrum of [Sn(hfac)$_2$] (Scheme 3) low-intensity fragments corresponding to $(P + F)^+$ and $(P + 2F)^+$ are observed above the parent ion, presumably due to the high affinity of tin for fluorine. This also accounts for the formation of SnF^+ in large quantities, and probably the low intensity fragments $[FSn(tfac)]^+$ and $[FSn(hfac)]^+$. In addition to the expected progressive loss of intact pentane-2,4-dionato-residues from the metal, the spectrum of [Sn(acac)$_2$] exhibits less abundant features at $m/e = 277$ and 178 corresponding to acetatotin



SCHEME 1 Fragmentation for [Sn(acac)$_2$] [a,b]



SCHEME 2 Fragmentation pattern for [Sn(tfac)$_2$] [a,b]

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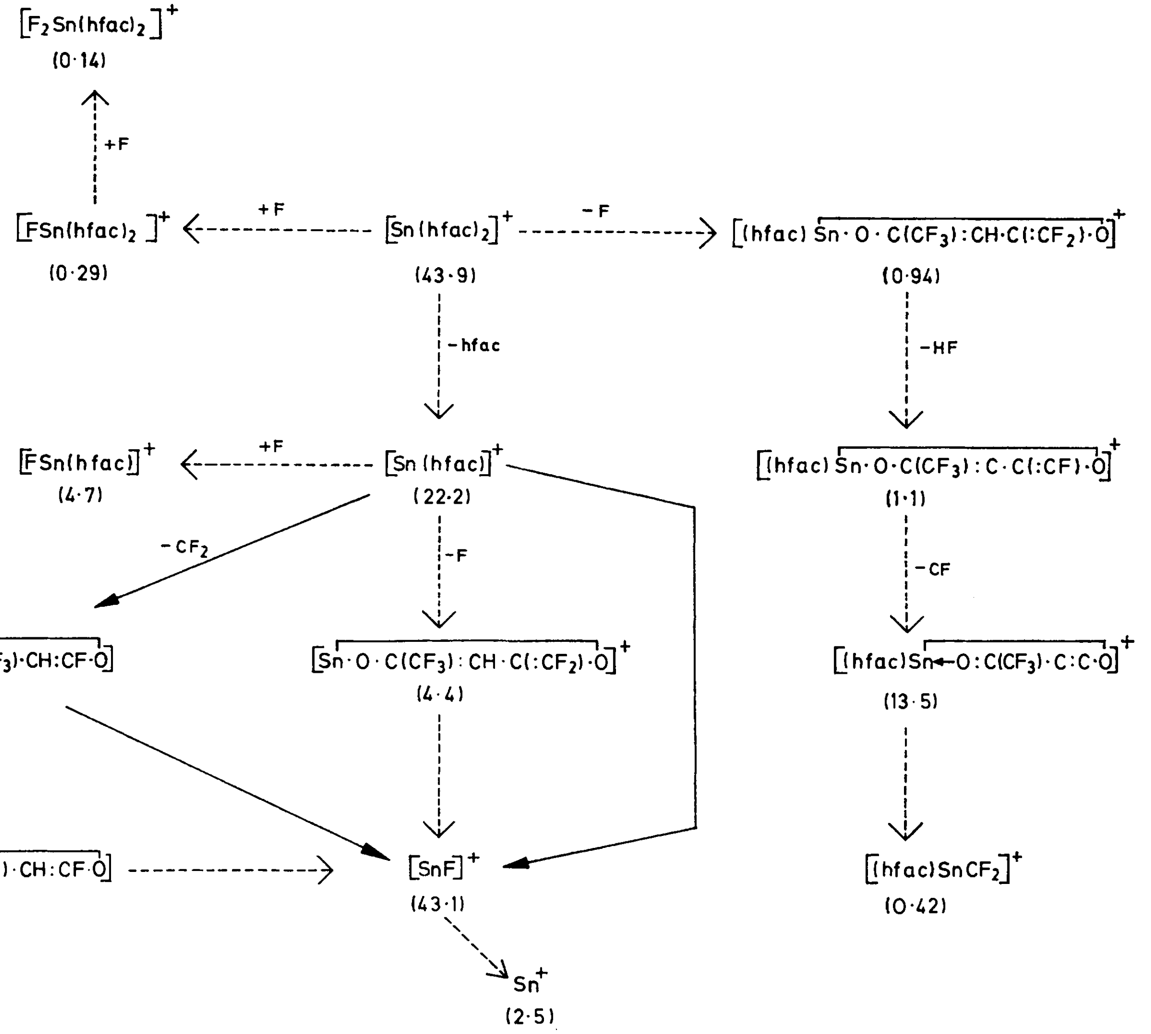
* *cf.* $[Sn_2(O_2C{\cdot}C_6H_4{\cdot}NO_2\text{-}o)_4O]{\cdot}THF$, which has a three-dimensional polymeric lattice,[7] and also exhibits a strong room-temperature resonance.[16]

[15] H. Bent, *Chem. Rev.*, **1961**, **61**, 275.

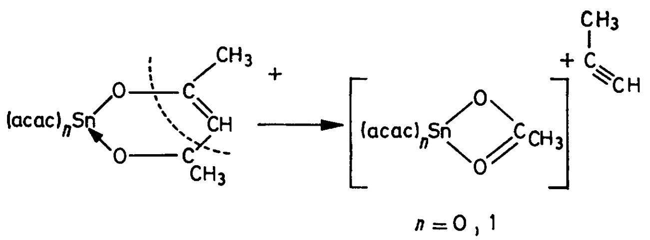
[16] P. F. R. Ewings and P. G. Harrison, to be published.



SCHEME 3 Fragmentation pattern for $[\mathrm{Sn(hfac)_2}]$ [a,b]

[a] Relative fragment abundances are given in parentheses. [b] Solid lines represent pathways confirmed by the observation of metastable ions.

fragments formed by the elimination of methylacetylene from the tin-containing heterocycle, *viz.*:



We have previously observed analogous ring contraction processes involving the formal loss of O and PhN from the $\overline{\mathrm{O{\cdot}NR{\cdot}CO{\rightarrow}ML_n}}$ heterocyclic fragments in the mass spectra of triorgano-tin(IV) and -lead(IV) *N*-acylhydroxylamines.[17] No similar process is observed with either $[\mathrm{Sn(tfac)_2}]$ or $[\mathrm{Sn(hfac)_2}]$. However, the spectra of these compounds show a greater abundance of tin-containing fragments, primarily due to the fragmentation of the perfluorinated ligands attached to tin. As in $[\mathrm{Sn(acac)_2}]$, most of the ion current in $[\mathrm{Sn(tfac)_2}]$ is carried by the $\mathrm{LSn^+}$ ion, which readily eliminates $\mathrm{CF_2}$ to afford $[\overline{\mathrm{Sn{\leftarrow}O{:}C(CH_3){\cdot}CH{:}CF{\cdot}O}}]^+$ ions. In $[\mathrm{Sn(hfac)_2}]$, this process is readier and the $[\overline{\mathrm{Sn{\leftarrow}O{:}C(CF_3){\cdot}CH{:}CF{\cdot}O}}]^+$ ion is the major feature of the spectrum. Further degradation leads to the formation of $\mathrm{SnF^+}$ ions, which in $[\mathrm{Sn(hfac)_2}]$ can be formed directly from $[\mathrm{Sn(hfac)}]^+$ or from the intermediately formed $[\overline{\mathrm{Sn{\leftarrow}O{:}C(CF_3){\cdot}CH{:}CF{\cdot}O}}]^+$ ions. Other low-intensity features in the spectra of $[\mathrm{Sn(tfac)_2}]$ and $[\mathrm{Sn(hfac)_2}]$ correspond largely to the loss of HF or F from the ligand. Most of the important processes have been corroborated by the observation of metastable ions (Table 2).

EXPERIMENTAL

All manipulations involving divalent tin compounds were performed under an atmosphere of dry oxygen-free

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[17] P. G. Harrison, *Inorg. Chem.*, 1973, **12**, 1545.

nitrogen or argon. Bis(methylcyclopentadienyl)tin(II) was prepared from tin(II) chloride and lithium methylcyclopentadienide in THF. Tin(II) dimethoxide was prepared by the addition of triethylamine to tin(II) chloride in dry methanol. All solvents were dried and freed from dissolved oxygen by standard procedures, and distilled immediately before use.

I.r. spectra were recorded using a Perkin-Elmer 521 instrument calibrated against water vapour and ammonia. Proton and fluorine n.m.r. spectra were obtained using a Varian HA-100 spectrometer using TMS (^1H) and $CFCl_3$ (^{19}F) as internal lock signals. Tin-119*m* Mössbauer spectra were obtained at 77 K using a Harwell spectrometer against a $Ba^{119m}SnO_3$ source. Mass spectra were recorded using an AEI MS-902 mass spectrometer. Molecular weights were determined by osmometry in benzene solution.

TABLE 2

Observed metastable transitions in the mass spectra of $[Sn(acac)_2]$, $[Sn(tfac)_2]$, and $[Sn(hfac)_2]$

Process	m_{calc} *	m_{obs} *
(i) $[Sn(acac)_2]$		
$[Sn(acac)_2]^+ \longrightarrow [Sn(acac)]^+ + [acac]$	147·2—150·8	147—151
(ii) $[Sn(tfac)_2]$		
$[Sn(tfac)]^+ \longrightarrow [Sn \leftarrow O{:}C(Me){\cdot}CH{:}CF{\cdot}O]^+ + [CF_2]$	178·3—182·2	178—185
$[Sn \leftarrow O{\cdot}C(Me){\cdot}CH{:}CF{\cdot}O]^+ \longrightarrow [Sn{\cdot}O{\cdot}C{:}C{\cdot}C(Me){:}O] + [HF]$	181·6—184·8	
(iii) $[Sn(hfac)_2]$		
$[Sn(hfac)]^+ \longrightarrow [Sn \leftarrow O{:}C(CF_3){\cdot}CH{:}CF{\cdot}O]^+ + [CF_2]$	231—235	231—236
$[Sn(hfac)]^+ \longrightarrow [SnF]^+ + [O_2C_5HF_5]$	Sn^{120} : 59·0 Sn^{118} : 57·8 Sn^{116} : 56·4	59·0 57·7 56·3
$[Sn \leftarrow O{:}C(CF_3){\cdot}CH{:}CF{\cdot}O]^+ \longrightarrow [SnF]^+ + [O_2C_4HF_4]$	Sn^{120} : 69·7 Sn^{118} : 68·2 Sn^{116} : 66·7	69·7 68·2 66·7

TABLE 3

Preparative and physical data for $[Sn(acac)_2]$, $[Sn(tfac)_2]$, and $[Sn(hfac)_2]$

	Reactants (mmol)	Solvent (ml)	Conditions (°C/h)	Yield (%)	B.p. (m.p.)/°C	Microanalysis (%) C Calc.	H Calc.	C Found	H Found	*M* (Calc.)
$[Sn(acac)_2]$:										
	$[Sn(OMe)_2]$; Hacac (10 mmol) (excess)	Hacac (10 ml)	140/2	67·3	90/10^{-3} mmHg [a]	37·90	4·45	38·2	4·6	301 (317)
	$[Sn(C_5H_4Me)_2]$: Hacac (12·5 mmol) (excess)	Hacac (10 ml)	140/0·25	62·1		37·90	4·45	37·65	4·8	
$[Sn(tfac)_2]$:										
	$[Sn(OMe)_2]$; Htfac (2·5 mmol) (5·0 mmol)	Benzene (10 ml)	77/0·25	85·2		28·27	1·89	27·9	1·8	
	$[Sn(C_5H_4Me)_2]$: Htfac (13·2 mmol) (26·4 mmol)	Benzene (20 ml)	Room temp.	80·1	Sublimes 60/0·01 mmHg (53)	28·27	1·89	28·3	1·95	435 (425)
	$SnCl_2$; Natfac (10 mmol) (20 mmol)	THF–Ether (20 ml)	Room temp.	75·3		28·27	1·89	27·85	1·85	
$[Sn(hfac)_2]$:										
	$[Sn(OMe)_2]$; Hhfac (6·1 mmol) (12·4 mmol)	Benzene (20 ml)	Room temp.	87·3	Sublimes 80/0·01 mmHg (70)	22·54	0·37	22·1	0·4	
	$[Sn(C_5H_4Me)_2]$; Hhfac (9·3 mmol) (excess)	Benzene (10 ml)	Room temp.	75·7		22·54	0·37	22·7	0·6	528 (533)
	$SnCl_2$; Nahfac (2·5 mmol) (5 mmol)	Benzene–THF (25/10 ml)	Room temp.	81·8		22·54	0·37	22·05	0·4	

[a] Lit.,[6] 102—105/0·5 mmHg.

TABLE 4

Microanalytical data for complexes

Complex	M.p. (*t*/°C)	Found (%) C	H	N	Calc. (%) C	H	N
$[Sn(tfac)_2]{\cdot}bipy$	*ca.* 150 (decomp.)	43·2	2·75	4·9	43·41	2·92	5·07
$[Sn(tfac)_2]{\cdot}phen$	135	43·5	2·7	4·6	43·60	2·66	4·62
$[Sn(hfac)_2]{\cdot}bipy$	*ca.* 200 (decomp.)	34·7	1·55	3·9	34·84	1·46	4·07
$[Sn(hfac)_2]{\cdot}phen$	119	36·8	1·6	3·65	37·00	1·41	3·92

Preparation of $[Sn(acac)_2]$, $[Sn(tfac)_2]$, *and* $[Sn(hfac)_2]$.—The syntheses of all three tin(II) pentane-2,4-dionates from bis(methylcyclopentadienide)tin(II), dimethoxide, and dihalide were all essentially similar for each particular reagent. Details are summarised in Table 3. Full experimental details are given for a few specific examples.

(i) *From tin*(II) *dimethoxide.* Tin(II) dimethoxide (2·0 g, 9·1 mmol) was treated with dry redistilled acetylacetone (*ca.* 10 g, excess), and the mixture refluxed (140 °C) for 2 h. The initially clear solution became straw coloured after *ca.* 10 min, which deepened in colour when heated longer under reflux. Unchanged insoluble tin(II) dimethoxide was removed from the cool mixture by filtration under argon. Removal of the excess of acetylacetone *in vacuo* yielded a pale orange viscous oil which upon distillation afforded pure *bis(pentane*-2,4-*dionato)tin*(II) as a yellow oil.

(ii) *From bis(methylcyclopentadienyl)tin*(II). To bis(methylcyclopentadienyl)tin(II) (2·57 g, 9·3 mmol) dissolved in benzene (10 ml) was added hexafluoroacetylacetone (excess) also in benzene (10 ml). An immediate darkening of the solution from yellow to orange took place, and removal of the solvent *in vacuo*, followed by sublimation [50 °C (bath)/10^{-2} mmHg] of the resulting material yielded *bis*(1,1,1,5,5,5-*hexafluoropentane*-2,4-*dionate*)*tin*(II) as glistening white crystals.

(iii) *From tin*(II) *halides.* To hexafluoroacetylacetonatosodium (1·15 g, 5·0 mmol), dispersed as a suspension in benzene (25 ml), was added dropwise a solution of tin(II) chloride (0·47 g, 2·5 mmol) in THF (10 ml). The solid dissolved gradually during the addition, and a yellow colour became apparent. After the addition was complete, sodium chloride was slowly precipitated, which was filtered off; *bis*(1,1,1,5,5,5-*hexafluoropentane*-2,4-*dionato*)*tin*(II) was isolated as in (ii).

Formation of the 2,2′-*Bipyridyl and* 1,10-*Phenanthroline Complexes of* [Sn(tfac)$_2$] *and* [Sn(hfac)$_2$].—The *complexes* were immediately precipitated on the addition of ether solutions of 2,2′-bipyridyl or 1,10-phenanthroline to [Sn(tfac)$_2$] or [Sn(hfac)$_2$] also in ether.

Data are presented in Table 4.

Reaction of [Sn(hfac)$_2$] *and* SnCl$_2$.—Equimolecular quantities (5 mmol) of [Sn(hfac)$_2$] and SnCl$_2$ were dissolved in dry THF and refluxed for 1 h. The pale yellow solution of [Sn(hfac)$_2$] became paler, and after 1 h the solution was colourless. Concentration of this solution afforded a white *powder* (Found: C, 16·5; H, 0·30. Calc. for C, 16·6; H, 0·28%), which yielded [Sn(hfac)$_2$](sublimate) and SnCl$_2$ (residue) on attempted sublimation at 100 °C/0·1 mmHg.

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