Tributyltin(IV) Penta(methoxycarbonyl)cyclopentadienides $[SnBu_3L_2]^+$-$[C_5(CO_2Me)_5]^-$. *X*-Ray Crystal Structure of the Diaquatributyltin(IV) Salt, $[SnBu_3(OH_2)_2][C_5(CO_2Me)_5]$,† and Electron Spin Resonance Spectrum of the Radical $C_5(CO_2Me)_5^{\bullet}$

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The ionic penta(methoxycarbonyl)cyclopentadienide salts of the diligated tributyltin(IV) cation, $[SnBu_3L_2][C_5(CO_2Me)_5]$ [L = H_2O, O=P$(NMe_2)_3$, or $HCONMe_2$], have been isolated, and the crystal structure of the diaqua compound has been determined. The cation and anion have approximate C_{3v} and D_{5h} symmetry respectively, and, in the anion, the methoxycarbonyl groups are twisted out of the plane of the ring by between 29.2 and 53.2°. If 1,2,3,4,5-penta(methoxycarbonyl)cyclopentadiene, or its dehydrodimer, $(MeO_2C)_5C_5C_5(CO_2Me)_5$, is photolysed, the e.s.r. spectrum of the persistent radical $C_5(CO_2Me)_5^{\bullet}$ is observed, a(H) = 0.61 G.

Since the discovery of ferrocene in 1951,[1] the cyclopentadienyl compounds have occupied a central place in organometallic chemistry. Derivatives of tin(IV) and tin(II) are well known, and early work on these compounds is reviewed in ref. 2. The tin(IV) compounds such as $SnBu_3(C_5H_5)$ and $Sn(C_5H_5)_4$[3] show monohapto fluxional bonding, but tin(II) compounds such as $Sn(C_5H_5)_2$,[4] $Sn(C_5H_5)Cl$,[5] and $Sn(C_5Ph_5)_2$[6] are pentahapto bonded.

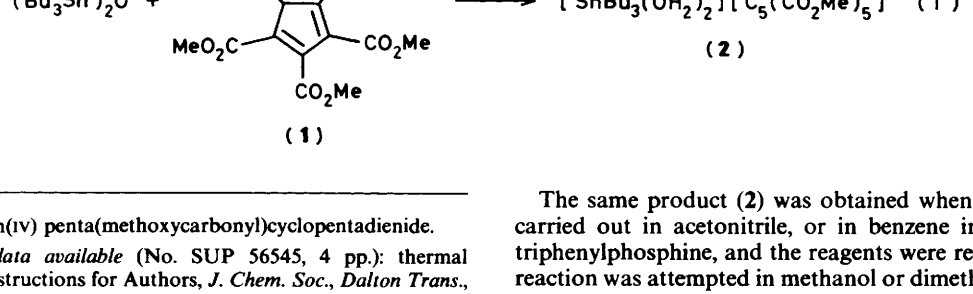
Surprisingly little attention has been paid until recently to the penta(methoxycarbonyl)cyclopentadienyl metallic compounds, although the precursor, 1,2,3,4,5-penta(methoxycarbonyl)cyclopentadiene, $C_5H(CO_2Me)_5$ (1), has been readily available since 1967.[7] Up to 1981, only the silver(I)[8] and the iron(II)[8] derivatives were known, but since then, Bruce *et al.* have reported the isolation of derivatives of lithium,[9,10] sodium, potassium, rubidium, caesium, thallium(I),[10] magnesium, calcium, strontium, barium, zinc, cadmium,[11] chromium,[12] manganese,[13,14] iron, cobalt, nickel, and copper,[14] and of the compounds $[Ru(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5(CO_2Me)_5\}]$, $[RuH_2(PPh_3)_2(\eta^5\text{-}C_5H_5)][C_5(CO_2Me)_5]$,[15] $[Os(NCMe)(PPh_3)_2(\eta^5\text{-}C_5H_5)][C_5(CO_2Me)_5]$,[16] $[Au\{C_5(CO_2Me)_5\}(PPh_3)]$, $[Au(PPh_3)][C_5(CO_2Me)_5]\cdot MeOH$,[17] $[\{Ag[C_5(CO_2Me)_5](OH_2)\}_n]\cdot 1.5nH_2O$, $[Ag\{C_5(CO_2Me)_5\}L_2]$, and $[Rh\{\eta^5\text{-}C_5H_2(CO_2Me)_3\}_2][C_5(CO_2Me)_5]$.[18]

The protic parent (1) was shown to have a fulvenoid structure in which the $C_5(CO_2Me)_5$ group acts as a bidentate ligand as shown previously.[9,10] The first group of metallic derivatives listed above similarly have at least one bidentate $C_5(CO_2Me)_5$ group, and sometimes one monodentate $C_5(CO_2Me)_5$ group. The remaining compounds show η^2, η^3, or η^5 bonding to the $C_5(CO_2Me)_5$ ring, but the ruthenium, osmium, rhodium, and gold derivatives contain the free $[C_5(CO_2Me)_5]^-$ anion as shown.

We report here a study of the synthesis, structure, and properties of some penta(methoxycarbonyl)cyclopentadienyl derivatives of tributyltin(IV). A preliminary note on the structure of one of the derivatives has already been published.[19]

Discussion

Preparation of Tin(IV) *Salts*, $[SnBu_3L_2][C_5(CO_2Me)_5]$.—Penta(methoxycarbonyl)cyclopentadiene (1) has an acid strength similar to that of HCl.[7] It reacts with bis(tributyltin) oxide in benzene to give diaquatributyltin(IV) penta(methoxycarbonyl)cyclopentadienide (2) as a stable crystalline solid (m.p. 147 °C), equation (1)



$$(Bu_3Sn)_2O + (1) \longrightarrow [SnBu_3(OH_2)_2][C_5(CO_2Me)_5] \quad (1)$$

(2)

(1)

The same product (2) was obtained when the reaction was carried out in acetonitrile, or in benzene in the presence of triphenylphosphine, and the reagents were recovered when the reaction was attempted in methanol or dimethyl sulphoxide.

The existence of the dihydrated trialkyltin ion has been recognised in aqueous solution,[20] but the only previous report of the isolation of a crystalline salt appears to be the

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† Diaquatributyltin(IV) penta(methoxycarbonyl)cyclopentadienide.

* *Supplementary data available* (No. SUP 56545, 4 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. unit employed: G = 10^{-4} T.

preparation of the tetraphenylborate $[SnMe_3(OH_2)_2][BPh_4]$ by Wada and Okawara.[21]

When the reaction was attempted in pyridine as solvent, the pyridinium salt, $[C_5H_5NH][C_5(CO_2Me)_5]$, was isolated; Bruce *et al.*[22] have recently described a number of related quaternary ammonium salts, $[NR_4][C_5(CO_2Me)_5]$.

When the reaction was carried out in dimethylformamide (dmf), or when the diaqua complex **(2)** was treated with dmf, the dmf complex $[SnBu_3(OCHNMe_2)_2][C_5(CO_2Me)_5]$ **(3)** was formed, and similarly the hmpt complex $[SnBu_3\{OP(NMe_2)_3\}_2][C_5(CO_2Me)_5]$ **(4)** was isolated when **(2)** was treated with hexamethylphosphorotriamide (hmpt).

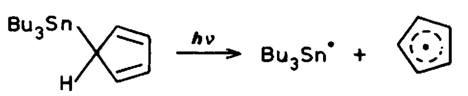
No stable acetone complex could be isolated. In acetone solution, the diaqua complex **(2)** (*ca.* 0.5 g in 2.5 cm^3) showed a ^{119}Sn chemical shift which was strongly temperature dependent, varying linearly from -6.8 at 185 K to $+48$ at 315 K, $d\delta/dT = 0.42$ K^{-1}: clearly the aqua complex is involved in a temperature-dependent, mobile equilibrium, in which at least one of the ligands at tin is probably acetone. Blunden and Hill[23] have shown that tributyltin methanesulphonate or ethanesulphonate in water both show $\delta(^{119}Sn)$ $+22$, and they ascribe this to the formation of the $[SnBu_3(OH_2)_2]^+$ cation in solution.

The ^{13}C n.m.r. spectra confirm that, in solution in deuterioacetone, the protic parent **(1)** has C_{2v} symmetry, and that its anion in the diaqua complex **(2)** has D_{5h} symmetry.

The ^{119}Sn Mössbauer spectra of the complexes **(2)**, **(3)**, and **(4)** show quadrupole coupling values of 4.20, 3.99, and 3.94 mm s^{-1} respectively, within the range which is normally observed for *trans*-trigonal bipyramidal complexes, SnR_3X_2.

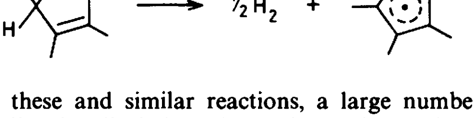
Nugent *et al.*[24] have recently described the preparation of solvated trialkyltin salts, $[SnR_3(NCMe)_n][X]$ ($X = SbX_6$, BF_4, or ClO_4), from the reaction between the trialkyltin bromide or hydride and AgX. When R = Me, Et, Pr, or Bu, non-integral values of *n* between 1 and 2 were observed, but, when R was a more bulky group such as t-butyl, neopentyl, or cyclohexyl, salts could be isolated with an integral value of $n = 2$. Their crystallographic studies[24] are compared below with ours.

The Penta(methoxycarbonyl)cyclopentadienyl Radical.—One of our interests in the cyclopentadienes is in their use as sources of cyclopentadienyl radicals. If tributyl(cyclopentadienyl)tin is irradiated with u.v. light in an e.s.r. cavity, the spectrum of the cyclopentadienyl radical is observed, equation (2).[25]



(2)

Cyclopentadiene itself does not show the formation of the $C_5H_5^{\bullet}$ radical under these conditions, but pentamethylcyclopentadiene and related polyalkylcyclopentadienes are unique among hydrocarbons in that, when they are irradiated with u.v. light, hydrogen is evolved, and a strong spectrum of the polyalkylcyclopentadienyl radical is apparent, equation (3).[26,27,28]



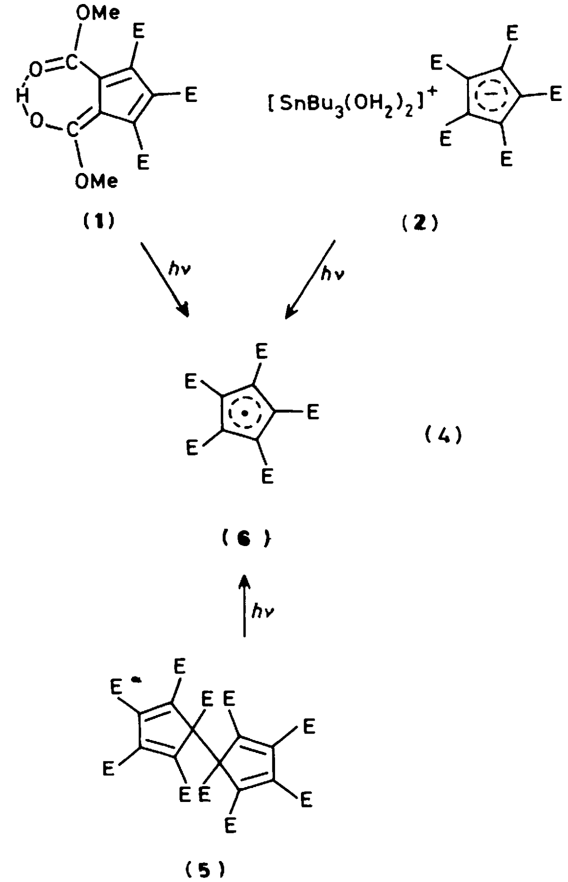
(3)

By these and similar reactions, a large number of cyclopentadienyl radicals have been observed, carrying alkyl, silyl, germyl, or stannyl groups.[25–32]

Relatively few cyclopentadienyl radicals carrying electronegative substituents have been studied. The $C_5F_5^{\bullet}$ radical has been generated,[33] and like the $C_5H_5^{\bullet}$[34] and $C_5Me_5^{\bullet}$[26] radicals, it has been shown to decay at a diffusion-controlled rate.[35] A persistent radical is generated when hexachlorocyclopentadiene is photolysed in solution,[36] but we have not been able to simulate the spectrum on the basis of five equivalent chlorine atoms,[37] and a different spectrum is observed when $HgPh(C_5Cl_5)$,[38] C_5Cl_5H, or $(C_5Cl_5)_2$[39] is photolysed.[37] The identification of the $C_5Cl_5^{\bullet}$ radical, and also, by implication, of the $C_5Br_5^{\bullet}$ radical from C_5Br_6,[40] hence is questionable.

We were therefore interested in observing the penta(methoxycarbonyl)cyclopentadienyl radical by e.s.r. spectroscopy.

Photolysis of penta(methoxycarbonyl)cyclopentadiene **(1)** or of its dehydrodimer **(5)** in dichloromethane solution gave rise to a persistent e.s.r. spectrum consisting of an even multiplet of ten or more lines, $a(nH) = 0.61$ G, $\Delta H_{pp} = 0.3$ G, $g = 2.0034$, independent of temperature from 173 to 273 K. Under the same conditions, the cyclopentadienide **(2)** gave an unresolved spectrum with the same *g* value. We ascribe these spectra to the penta(methoxycarbonyl)cyclopentadienyl radical **(6)**; when the radical is derived from the anion, the lines in the spectrum may be broadened by rapid electron exchange between the product and its precursor, equation (4) ($E = CO_2Me$).



(1) (2) (6) (5) (4)

A typical example of the spectrum is shown in Figure 1. The relative intensities of the lines varied somewhat with the conditions under which the spectra were recorded, but were consistent with the central lines of a multiplet, $a(15H) = 0.61$ G. This hyperfine coupling constant is surprisingly large for a methoxycarbonylalkyl radical where the spin density (ρ) on the α-carbon atom is 0.2; for comparison, the methoxycarbonylmethyl radical $MeOCOCH_2^{\bullet}$ ($\rho = 1$) shows $a(3H) = 1.55$ G, $g = 2.0032$ (in water).[41] In the radical $MeOCOCH_2^{\bullet}$, the methoxyl group can be regarded as being attached at the nodal centre of a heteroallylic system; perhaps in the cyclopentadienyl radical the planarity of the allylic system is interrupted by the twisting of the methoxycarbonyl groups out of the plane of the ring, as it is in the cyclopentadienyl anion (see below), permitting the methyl group to spend more time nearer the W conformation with respect to the singly occupied p orbital, in which hyperfine coupling may be larger.

The generation of the radical (**6**) from the protic precursor (**1**) and its dehydrodimer (**5**) bears a formal similarity to the formation of the radical $C_5Me_5^{\bullet}$ by photolysis of C_5Me_5H or of $(C_5Me_5)_2$, though in (**1**) the hydrogen atom is lost from an enolic OH group, whereas in C_5Me_5H it is lost from sp^3 carbon in the ring. In the photolysis of C_5Me_5H, this hydrogen atom combines with a hydrogen atom from a methyl group, equation (3); in the case of the photolysis of (**1**), the evolution of a gas is not apparent, and we do not know the fate of the hydrogen atom which is lost.

If the radical (**6**) is indeed formed from the tin salt (**2**), the reaction can be regarded as photo-assisted electron transfer, leading to the equivalent products of the carbon–metal bond homolysis of reaction (2).

With the exception of the $C_5Cl_5^{\bullet}$ and $C_5Br_5^{\bullet}$ radicals, the identification of which we question, the penta(methoxycarbonyl)cyclopentadienyl radicals (**6**) are unique among the cyclopentadienyl radicals in that they are persistent; once the radicals (**6**) have been generated from either compound (**1**) or (**5**) as shown in equation (4), the intensity of the e.s.r. spectra showed no diminution in intensity during one hour after the light had been shuttered. Such persistence is more typical of a radical ion than a neutral radical, but it seems most unlikely that a radical anion could be long-lived in the presence of the strong acid (**1**).

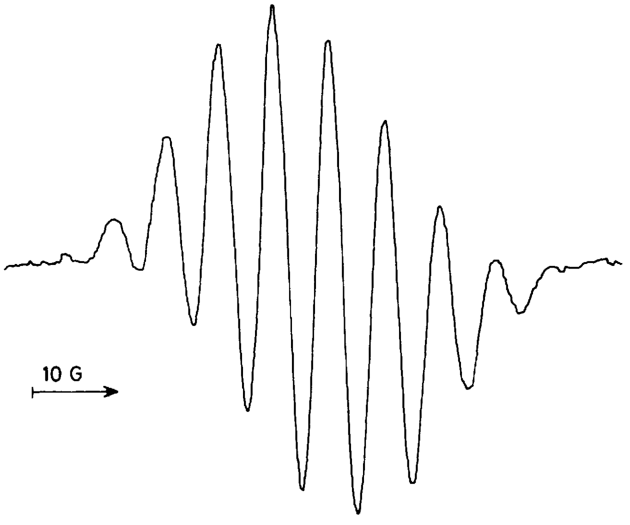


Figure 1. The e.s.r. spectrum of the radical $C_5(CO_2Me)_5^{\bullet}$

Crystal Structure of $[SnBu_3(OH_2)_2][C_5(CO_2Me)_5]$.—The structure of the crystalline diaqua salt (Figure 2) was determined by single-crystal X-ray diffraction. Bond lengths and angles are given in Table 1, and fractional atomic co-ordinates in Table 2.

The diaquatrialkyltin cation has a symmetry close to D_{3h}, with the O–Sn–O angle 178.4(2)°, and the Sn–O bond lengths 2.295(4) and 2.326(5) Å. It is interesting that in the cation $[Sn(cyclo\text{-}C_6H_{11})_3(NCMe)_2]^+$, the two axial Sn–N bond lengths are long and unequal at 2.374(3) and 2.472(3) Å [N–Sn–N 177.2(1)°], and it was suggested that this resulted from the different conformations of the cyclohexyl groups.[24]

In the cyclopentadiene anion, the ring atoms occupy, within experimental error, a regular pentagon with the C–C bond lengths 1.402(9)—1.420(8) Å; the methoxycarbonyl groups are twisted out of the plane of the ring by between 29.2 and 53.2°. Similar structures for the anion have been identified in the salts $[NMe_4][C_5(CO_2Me)_5]$,[22] $[Rh\{\eta^5\text{-}C_5H_2(CO_2Me)_3\}][C_5(CO_2Me)_5]$,[18] $[RuH_2(PPh_3)_2(\eta^5\text{-}C_5H_5)][C_5(CO_2Me)_5]$,[15] and $[Au(PPh_3)][C_5(CO_2Me)_5]\cdot MeOH$.[17]

Experimental

1,2,3,4,5-*Penta(methoxycarbonyl)cyclopentadiene*.—The reaction between dimethyl acetylenedicarboxylate and dimethyl malonate in the presence of pyridine and glacial acetic acid gave 1,1,2,3,4,5,6,7-octa(methoxycarbonyl)cyclohepta-3,5-diene in 91% yield. This was refluxed with aqueous potassium acetate to yield 1,2,3,4,5-penta(methoxycarbonyl)cyclopentadiene (54%) as off-white crystals, m.p. 147 °C[7,42] (Found: C, 50.4; H, 4.45. Calc. for $C_{15}H_{16}O_{10}$: C, 50.6; H, 4.55%); $\delta(^1H)$ ($CDCl_3$) 3.92 (9 H, br s, OMe), 4.05 (6 H, br s, OMe), 20 (1 H, br s, OH); $\delta(^1H)$ (D_2O) 3.75 (15 H, s, OMe), 4.60 (s, DOH); $\delta(^{13}C)$ 53.4 (3 C, OMe), 56.0 (2 C, OMe), 107.0 (2 C, ring), 118.2 (1 C, ring), 134.4 (2 C, ring), 164 (1 C, CO), 168.2 (2 C, CO), 172.8 (2 C, CO); i.r., 1 600 (H-bonded C=O), 1 730 cm^{-1} (C=O).

Bi[1,2,3,4,5-*penta(methoxycarbonyl)cyclopenta*-2,4-*dienyl*].—Oxidative coupling of the cyclopentadiene to the bi(cyclopentadienyl) was carried out with $(NH_4)_2Ce(NO_3)_6$ in aqueous methanol in 48% yield.[43] $\delta(^1H)$ ($CDCl_3$) 3.68 (6 H, s, OMe), 3.80 (12 H, s, OMe), and 3.82 (12 H, s, OMe).

$[SnBu_3(OH_2)_2][C_5(CO_2Me)_5]$.—Bis(tributyltin) oxide (2.09 g, 3.51 mmol) was added to a saturated solution of penta(methoxycarbonyl)cyclopentadiene (2.5 g, 7.02 mmol) in benzene. The salt immediately began to separate as white needles. After 3 d these were collected, washed with diethyl ether, and dried (3.37 g, 74%); decomposition (white→green) at 92 °C (Found: C, 47.5; H, 6.65. $C_{27}H_{46}O_{12}Sn$ requires C, 47.6; H, 6.80%); $\delta(^1H)$ ($CDCl_3$) 0.88 (9 H, t, CH_2CH_3), 1.15 (6 H, m,

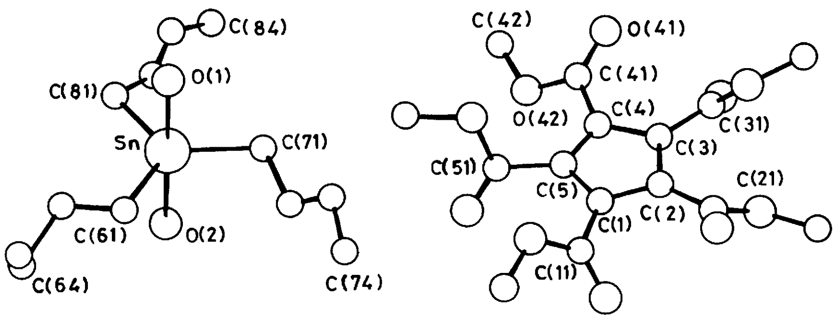


Figure 2. The structure of $[SnBu_3(OH_2)_2][C_5(CO_2Me)_5]$

Table 1. Bond lengths (Å) and angles (°) for $[SnBu_3(OH_2)_2][C_5(CO_2Me)_5]$

Sn–O(1)	2.295(4)	C(2)–C(21)	1.473(10)	C(21)–O(22)	1.331(9)	C(52)–O(52)	1.489(9)
Sn–O(2)	2.326(5)	C(3)–C(4)	1.409(9)	C(22)–O(22)	1.470(9)	C(61)–C(62)	1.444(18)
Sn–C(61)	2.190(14)	C(3)–C(31)	1.457(10)	C(31)–O(31)	1.217(8)	C(62)–C(63)	1.771(27)
Sn–C(71)	2.155(12)	C(4)–C(5)	1.402(9)	C(31)–O(32)	1.325(8)	C(63)–C(64)	1.199(29)
Sn–C(81)	2.189(11)	C(4)–C(41)	1.457(9)	C(32)–O(32)	1.464(9)	C(71)–C(72)	1.731(28)
		C(5)–C(51)	1.497(9)	C(41)–O(41)	1.222(8)	C(72)–C(73)	1.031(50)
C(1)–C(2)	1.419(10)	C(11)–O(11)	1.218(8)	C(41)–O(42)	1.330(8)	C(73)–C(74)	1.544(43)
C(1)–C(5)	1.406(10)	C(11)–O(12)	1.337(8)	C(42)–O(42)	1.450(8)	C(81)–C(82)	1.673(30)
C(1)–C(11)	1.458(10)	C(12)–O(12)	1.440(9)	C(51)–O(51)	1.184(9)	C(82)–C(83)	1.117(53)
C(2)–C(3)	1.420(8)	C(21)–O(21)	1.206(9)	C(51)–O(52)	1.340(10)	C(83)–C(84)	1.399(51)

O(1)–Sn–O(2)	178.4(2)	C(4)–C(3)–C(31)	125.9(6)	C(4)–C(41)–O(41)	124.2(7)
O(1)–Sn–C(61)	88.4(4)	C(3)–C(4)–C(5)	108.1(5)	C(4)–C(41)–O(42)	113.0(7)
O(1)–Sn–C(71)	90.5(4)	C(3)–C(4)–C(41)	127.5(6)	O(41)–C(41)–O(42)	122.8(7)
O(1)–Sn–C(81)	92.0(3)	C(5)–C(4)–C(41)	124.2(7)	C(41)–O(42)–C(42)	116.8(6)
O(2)–Sn–C(61)	90.0(4)	C(1)–C(5)–C(4)	108.6(5)	C(5)–C(51)–O(51)	125.6(9)
O(2)–Sn–C(71)	90.5(4)	C(1)–C(5)–C(51)	125.5(8)	C(5)–C(51)–O(52)	111.3(8)
O(2)–Sn–C(81)	88.6(3)	C(4)–C(5)–C(51)	125.9(8)	O(51)–C(51)–O(52)	122.9(7)
C(61)–Sn–C(71)	119.2(6)	C(1)–C(11)–O(11)	124.5(7)	C(51)–O(52)–C(52)	115.5(6)
C(61)–Sn–C(81)	120.8(4)	C(1)–C(11)–O(12)	112.5(7)		
C(71)–Sn–C(81)	120.0(5)	O(11)–C(11)–O(12)	122.9(7)	Sn–C(61)–C(62)	105.0(10)
		C(11)–O(12)–C(12)	116.8(6)	Sn–C(71)–C(72)	107.4(12)
C(2)–C(1)–C(5)	107.8(6)	C(2)–C(21)–O(21)	124.8(8)	Sn–C(81)–C(82)	111.9(12)
C(2)–C(1)–C(11)	124.4(7)	C(2)–C(21)–O(22)	112.1(7)		
C(5)–C(1)–C(11)	127.7(8)	O(21)–C(21)–O(22)	123.1(7)	C(61)–C(62)–C(63)	109.9(15)
C(1)–C(2)–C(3)	107.5(7)	C(21)–O(22)–C(22)	115.8(7)	C(71)–C(72)–C(73)	115.1(42)
C(1)–C(2)–C(21)	126.5(7)	C(3)–C(31)–O(31)	124.9(7)	C(81)–C(82)–C(83)	100.2(39)
C(3)–C(2)–C(21)	126.1(8)	C(3)–C(31)–O(32)	113.3(6)	C(62)–C(63)–C(64)	105.2(25)
C(2)–C(3)–C(4)	108.0(7)	O(31)–C(31)–O(32)	121.8(7)	C(72)–C(73)–C(74)	105.6(46)
C(2)–C(3)–C(31)	126.1(7)	C(31)–O(32)–C(32)	115.7(6)	C(82)–C(83)–C(84)	96.5(44)

CH_2), 1.30 (6 H, m, CH_2), 1.55 (6 H, m, CH_2), 1.80 (4 H, br s, H_2O), 3.85 (15 H, s, OMe); $\delta(^{13}C)$ ($CDCl_3$) 12.52 (δ-CH_3), 17.96 (α-CH_2), 27.17 (γ-CH_2), 27.82 (β-CH_2), 51.78 (OMe), 111.5 (ring atoms), 168.55 (C=O); $\delta(^{119}Sn)$ ($CDCl_3$) 57.5; $\delta(^{119}Sn)$ $[(CD_3)_2CO]$ −6.8 at 185 K, −4.7 at 195 K, +11.5 at 235 K, +21.5 at 255 K, +38.2 at 295 K, +48.0 at 315 K; i.r., 1 660 cm^{-1} (CO); Mössbauer (at 77 K, *versus* SnO_2), δ +1.53 ± 0.02, ΔE_q 4.20 ± 0.02 mm s^{-1}.

The dihydrate was also obtained when the same reagents were mixed in acetonitrile or in benzene containing triphenylphosphine, and was recovered from solution in tetrahydrofuran or dimethyl sulphoxide.

$[SnBu_3(hmpt)_2][C_5(CO_2Me)_5]$.—The hydrate, $[SnBu_3(OH_2)_2][C_5(CO_2Me)_5]$ (0.2 g), was dissolved in the minimum volume of hexamethylphosphorotriamide. Half of the solvent was removed under reduced pressure, and the solution was allowed to stand. After 3 d colourless crystals had separated, and these were collected and washed with ether giving the hmpt complex, m.p. 67 °C (Found: C, 46.7; H, 7.85; N, 8.35. $C_{39}H_{78}N_6O_{12}P_2Sn$ requires C, 46.6; H, 7.85; N, 8.45%); $\delta(^1H)$ ($CDCl_3$) 0.90 (9 H, t, CH_3), 1.15 (6 H, m, CH_2), 1.35 (6 H, m, CH_2), 1.55 (6 H, m, CH_2), 2.60 [36 H, d, *J*(P–H) 12 Hz, NCH_3], 3.75 (15 H, s, OMe); i.r., 1 660 cm^{-1} (br, C=O); Mössbauer (at 77 K, *versus* SnO_2), δ +1.409 ± 0.013, ΔE_q 3.936 ± 0.013 mm s^{-1}.

$[SnBu_3(dmf)_2][C_5(CO_2Me)_5]$.—This compound, m.p. 85 °C (decomp.), was prepared in the same way from the hydrate in dimethylformamide, and also from bis(tributyltin) oxide, penta(methoxycarbonyl)cyclopentadiene, and dimethylformamide in dry toluene (Found: C, 49.5; H, 6.85; N, 3.20. $C_{33}H_{56}N_2O_{12}Sn$ requires C, 50.1; H, 7.15; N, 3.50%); $\delta(^1H)$ ($CDCl_3$) 0.90 (9 H, t, CH_3), 1.15 (6 H, m, CH_2), 1.35 (6 H, m, CH_2), 1.55 (6 H, m, CH_2), 2.80 (6 H, s, NMe), 2.97 (6 H, s, NMe), 3.75 (15 H, s, OMe), 7.80 (2 H, br s, CHO); i.r., 1 680 cm^{-1} (br, C=O); Mössbauer (at 77 K, *versus* SnO_2), δ +1.45 ± 0.02, ΔE_q 3.99 ± 0.02 mm s^{-1}.

Pyridinium Penta(methoxycarbonyl)cyclopentadienide.—A solution of the hydrate in pyridine was concentrated under reduced pressure to incipient crystallisation, then left to stand. The white crystals which separated were filtered off and washed with dry toluene yielding the pyridinium salt, m.p. 128 °C (Found: C, 55.1; H, 4.90; N, 3.10. $C_{20}H_{21}NO_{10}$ requires C, 55.2; H, 4.85; N, 3.20%).

X-Ray Crystallography.—The crystal used for the *X*-ray work was sealed under nitrogen in a glass capillary. Unit-cell parameters and intensity data were obtained using a CAD4 diffractometer, with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) in a manner previously described in detail.[44]

Crystal data. $C_{12}H_{31}O_2Sn \cdot C_{15}H_{15}O_{10}$, *M* = 681, monoclinic, space group $P2_1/n$, a = 12.118(5), b = 19.203(3), c = 14.526(6) Å, β = 96.73(3)°, Z = 4, U = 3 357.2 Å^3, D_c = 1.348 g cm^{-3}, μ(Mo-K_α) = 8.1 cm^{-1}, *F*(000) = 1 416.

Intensity data were recorded using an $\omega/2\theta$ scan mode with $1.5 \leqslant \theta \leqslant 220°$. Of the 4 454 reflections measured, 2 259 satisfied the condition $I > 1.5\sigma(I)$ and were used for the analysis. The structure was solved *via* the heavy-atom method and refined *via* least squares. All Sn, O, and C atoms were refined anisotropically, except the C atoms of the butyl groups, which were refined isotropically. Hydrogen atoms were not included; unit weights were used. The final cycle of least-squares refinement gave R = 0.059 and R' = 0.067. An absorption correction was applied by the DIFABS method.[45]

All computations were made using programs in the Enraf-Nonius SDP11/34 system.

Mössbauer Spectroscopy.—Mössbauer spectra were measured by Mr. I. Sayer of the University of London Intercollegiate Research Service at Birkbeck College and by Dr.

Table 2. Fractional atomic co-ordinates, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Sn	0.366 25(8)	0.218 54(5)	0.013 42(7)
C(1)	0.417(1)	0.221 6(7)	0.447 7(8)
C(2)	0.396 1(9)	0.292 5(6)	0.467 1(8)
C(3)	0.330 6(8)	0.293 9(6)	0.541 9(7)
C(4)	0.312 0(8)	0.224 6(6)	0.568 1(7)
C(5)	0.365(1)	0.180 5(6)	0.510 3(9)
C(11)	0.479(1)	0.197 9(7)	0.373 6(8)
C(12)	0.588(1)	0.106 9(8)	0.322(1)
O(11)	0.487 7(7)	0.230 4(5)	0.302 8(5)
O(12)	0.532 2(7)	0.137 8(5)	0.393 9(6)
C(21)	0.434(1)	0.353 5(7)	0.418 2(9)
C(22)	0.383(2)	0.461 2(9)	0.345(1)
O(21)	0.529 5(7)	0.364 6(5)	0.406 2(6)
O(22)	0.350 8(8)	0.395 8(5)	0.387 7(8)
C(31)	0.287(1)	0.356 0(7)	0.582 7(9)
C(32)	0.310(1)	0.476 5(7)	0.612(1)
O(31)	0.196 8(7)	0.359 9(5)	0.611 4(6)
O(32)	0.355 7(7)	0.409 9(5)	0.585 7(7)
C(41)	0.256 3(9)	0.200 8(6)	0.645 9(9)
C(42)	0.147(1)	0.112 4(8)	0.703(1)
O(41)	0.260 4(7)	0.231 1(5)	0.720 2(5)
O(42)	0.198 0(8)	0.142 8(5)	0.627 5(6)
C(51)	0.368(1)	0.102 6(6)	0.515(1)
C(52)	0.328(2)	−0.003 6(8)	0.432(1)
O(51)	0.398(1)	0.069 3(5)	0.582 1(7)
O(52)	0.326 3(8)	0.074 0(5)	0.434 6(7)
O(1)	0.517 3(7)	0.219 2(6)	0.124 6(6)
O(2)	0.215 8(7)	0.216 0(6)	−0.101.8(6)
C(61)*	0.470(2)	0.168(2)	−0.081(2)
C(71)*	0.359(2)	0.331(1)	0.017(2)
C(81)*	0.268(2)	0.157(1)	0.101(2)
C(62)*	0.447(3)	0.095(2)	−0.074(2)
C(73)*	0.463(8)	0.410(5)	−0.061(6)
C(83)*	0.199(6)	0.222(4)	0.202(5)
C(63)*	0.491(4)	0.050(3)	−0.169(3)
C(64)*	0.583(3)	0.045(2)	−0.153(3)
C(72)*	0.428(4)	0.362(2)	−0.072(3)
C(74)*	0.524(4)	0.425(2)	−0.146(3)
C(82)*	0.161(4)	0.202(2)	0.133(3)
C(84)*	0.115(4)	0.269(3)	0.215(4)

* Atom refined isotropically.

P. J. Smith of International Tin Research Institute, and are quoted at 85 K with respect to SnO_2.

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