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AN ELECTRON SPIN RESONANCE STUDY OF THE EFFECT OF THE CYCLOPENTADIENYL LIGAND ON THE PROPERTIES OF TIN(III) RADICALS AND THEIR ADDITION PRODUCTS *

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Summary

A series of cyclopentadienyltin(III) radicals have been prepared by the reaction:

$$Bu_{4-n}Cp_nSn \xrightarrow{h\nu} Bu_{3-n}Cp_nSn^{\cdot} + Cp^{\cdot}$$

The substitution reactions of these radicals with alkyl bromides, and their addition reactions with ethylene, biacetyl, 3,6-di-t-butyl-1,2-benzoquinone, and nitrocompounds, have been studied by ESR spectroscopy. The apparent reactivity decreases as the number of Cp ligands increases, and in this, and in the ESR parameters of the $Sn^{(IV)}$ adducts which are formed, the Cp ligands resemble chloro groups rather than alkyl groups. This is supported by the quadrupole splitting which is observed in the Mössbauer spectra of alkylcyclopentadienyl tin compounds.

In η^1-$Sn^{(IV)}$ compounds this effect may be ascribed to carbon—metal hyperconjugation (σ—π-interaction), but as yet there is no evidence whether $CpSn^{(III)}$ radicals are $\sigma(\eta^1)$ or $\pi(\eta^{2-5})$ bonded.

Introduction

Trialkyltin radicals, $R_3Sn^{\cdot}$, can readily be derived from the corresponding hexalkylditins, R_3SnSnR_3, or trialkyltin hydrides, R_3SnH, and the properties of these radicals have been extensively investigated [1]. In contrast, very little is known about the properties of tin-centred radicals carrying ligands other than simple saturated alkyl groups, because suitable routes to these radicals have not previously been available.

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* Dedicated to Professor G.A. Razuvaev on the occasion of his 85th birthday.

We have recently shown that a variety of such novel radicals, $R_{3-n}X_nSn^{\cdot}$, can be prepared by the photolysis of the corresponding cyclopentadienyltin(IV) compounds (eq. 1) [2], and the properties of the radicals $Bu_{3-n}Cl_nSn^{\cdot}$ (n = 0—3) derived from this route, were studied by ESR spectroscopy [3] *.

$$R_{3-n}X_nSnCp \xrightarrow{h\nu} R_{3-n}X_nSn^{\cdot} + Cp^{\cdot} \quad (1)$$

It became apparent in this work that alkyl and cyclopentadienyl groups were not equivalent as ligands on a tin(III) radical, and that the reactivity of a radical was significantly altered when an alkyl ligand was replaced by cyclopentadienyl. We report here a comparative study by ESR spectroscopy of the properties of the various tin-centred radicals $R_{3-n}X_nSn^{\cdot}$, where R = alkyl and X = Cl or Cp, as reagents for alkyl bromides, alkenes, biacetyl, 3,6-di-t-butyl-1,2-benzoquinone, and nitro compounds.

Experimental

Preparation of reagents

The preparation of the compounds Bu_3SnCp, Bu_2SnCp_2, $BuSnCp_3$, Cp_4Sn, $BuCpSnCl_2$, and $Bu_2CpSnCl$, from cyclopentadienylsodium and the appropriate tin halides, has already been described [4,5].

3,6-Di-t-butyl-1,2-benzoquinone was prepared by the di-t-butylation of catechol with isobutylene in the presence of titanium catecholate [6], followed by oxidation of the product with silver oxide [7]. The quinone was obtained from hexane as dark green crystals, m.p. 199—201°C (lit. [7] 199—201°C). ^1H NMR (CCl_4) τ8.75 (s, 18H, t-Bu), 3.12 (s, 2H, C_6H_2). Found: C, 75.8; H, 9.12. Calcd. for $C_{14}H_{20}O_2$: C, 76.4; H, 9.09%.

ESR experiments

The cyclopentadienyltin compounds and the co-reagents were mixed in roughly equimolar amounts in sodium-dried toluene in Suprasil silica tubes. The solutions were degassed and sealed under nitrogen, and photolysed in the cavity of a Varian E4 ESR spectrometer with light from a 500 W high pressure mercury arc focussed through quartz lenses. Overlapping signals were resolved with a Telmore subharmonic generator. g-Values were determined by direct measurement of magnetic field and frequency, or by comparison with that of the cyclopentadienyl radical (2.0025).

Kinetic measurements on the fluxional tin derivatives of 3,6-di-t-butyl-1,2-benzoquinone were carried out by computer simulation of the spectra using the program ESREXN written by Dr. J. Heinzer, and obtained from the QCPE at the University of Indiana.

Results

The ESR spectra of the radicals which were formed when the cyclopentadienyl compounds were photolysed in the presence of the co-reagents were monitored over a range of temperature. Details of the spectra of the adducts which

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* Throughout this paper, Cp = cyclopentadienyl.

TABLE 1

COMPARATIVE ESR PARAMETERS FOR THE ADDUCTS OF BUTYLCYCLOPENTADIENYLTIN AND BUTYLCHLOROTIN RADICALS WITH BIACETYL, $Bu_{3-n}X_nSnOCMeCMeO^{\cdot}$ (X = Cp or Cl)

n	T (°C)		a(xH)(G)		$a(^{117/119}Sn)$(G)		g	
	Cp	Cl	Cp	Cl	Cp	Cl	Cp	Cl [a]
0		+19	8.6(6 H)		8.5		2.0040 [b]	
		−20	7.2(6 H)		—		2.0045 [c]	
1	−65	−65	11.2 (3 H) 7.0(3 H)	10.6(3 H) 7.5(3 H)	—	—	2.0042	2.0039
2	−10	+10	8.5(6 H) [d]	9.5 (6 H) [e]	65.3/68.4	—	2.0026	2.0028
3	−10	+10	8.7(6 H)	9.5(6 H) [e]	65.8/69.0	—	2.0026	2.0030

[a] Values for the chloro compounds are taken from ref. 4. [b] Assigned to the *cis*-isomer [4]. [c] Assigned to the *trans*-isomer [5]; a strong alternating line-width effect is apparent. [d] The spectrum also shows the presence of a broad singlet, g 2.0090, ΔH_{pp} 1.0 G. [e] Hyperfine coupling by >1Cl is also apparent. At −20°C, a(3 H) 9.98 G, a(3 H) 9.10 G, a(1 Cl) 0.88 G.

were formed with biacetyl, 3,6-di-t-butyl-1,2-benzoquinone, and nitro compounds are given in Tables 1, 2, and 3 respectively, and the ^{119m}Sn Mössbauer parameters are listed in Table 4.

Discussion

Reactions involving ethyl bromide or ethylene

The two most characteristic reactions of trialkyltin radicals are the abstraction of bromine from alkyl bromides, and the addition to alkenes [reviewed in refs. 1 and 8]. Both reactions can readily by observed by ESR spectroscopy, and the former reaction provides the most convenient general route to alkyl radicals for ESR studies [9]. When the $R_3Sn^{\cdot}$ radical is derived from a trialkyltin hydride, a chain reaction is set up, and both reactions then find application in organic synthesis.

$$R_3Sn^{\cdot} + Br{-}R' \rightarrow R_3SnBr + R'^{\cdot}\ (\xrightarrow{R_3SnH} R'H + R_3Sn^{\cdot}) \tag{2}$$

$$R_3Sn^{\cdot} + C{=}C \rightarrow R_3SnCC^{\cdot}\ (\xrightarrow{R_3SnH} R_3SnCCH + R_3Sn^{\cdot}) \tag{3}$$

TABLE 2

ESR PARAMETERS FOR THE ADDUCTS OF STANNYL RADICALS $R_{3-n}X_nSn^{\cdot}$ WITH 3,6-DI-T-BUTYL-1,2-BENZOQUINONE

$R_{3-n}X_nSn^{\cdot}$	T (°C)	a(xH) (G)	$a(^{117/119}Sn)$ (G)	g
Bu_3Sn [a]	−40	3.6(2 H)	12.8/13.6	2.0036
Bu_2ClSn [b]	−14 +104	2.6(1 H) 4.9(1 H) 3.6(2 H) [e]	23.6/25.0	2.0037
Cl_3Sn [c]	−31	3.9(2 H) [f]		2.0033
Cp_3Sn [d]	−50	3.8(2 H)	7.4	2.0033

[a] From VI + Bu_4Sn, Bu_3SnCp, or Bu_6Sn_2, or from the reaction of 1,2,3,6-(HO)(Bu_3SnO)(t-Bu)$_2C_6H_2$ with t-butoxyl radicals. [b] From VI + Bu_3SnCl or $Bu_2CpSnCl$. [c] From VI + $BuSnCl_3$. [d] From VI + Cp_4Sn. [e] For the degenerate rearrangement, E = 44.4 kJ mol^{-1}, log A = 13.6, whence k(333 K) = 2.8×10^6 s^{-1}. [f] a(1 Cl) 0.6 G.

TABLE 3

ESR PARAMETERS OF THE ADDUCTS OF ORGANOTIN RADICALS WITH NITROCOMPOUNDS, $RN(O^{\cdot})OSnBu_{3-n}X_n$ ($X = Cp$ or Cl), IN TOLUENE

R	SnX_3	T (°C)	a(G)			g
			N	(x)H	Sn	
CH_3	$SnBu_3$	–26	28.5	10.2(3)	3.6	2.0051
	$SnBu_2Cp$	–26	28.5	10.8(3)	7.2	2.0048
	$SnBu_2Cl$	–23	28.5	11.8(3)	14.4	2.0044
	$SnCp_3$			[a]		
CH_3CH_2	$SnBu_3$	+3	28.5	9.1(2)		2.0060
	$SnBu_2Cp$	–10	28.5	9.1(2)		2.0047
	$SnBuCl_2$			[b]		
$(CH_3)_3C$	$SnBu_3$	+27	28.9		4.5	2.0052
		–64	28.9		6.5	
	$SnBu_2Cp$	+27	29.0		7.9	2.0049
		–61	29.0		10.5	
	$SnBuCp_2$	+27	28.5		10.3	2.0034
		–37	28.5		12.3	
	$SnCp_3$			[c]		
	$SnBu_2Cl$	+27	29.0		15.6	2.0047
		–42	29.0		17.7	
	$SnBuCl_2$	+45	30.0	[d]		
4-ClC_6H_4	$SnBu_3$	+50	14.0	3.4(2) [e] 1.25(2)		2.0048
	$SnBu_2Cp$	+51	14.2	3.5(2) [f] 1.25(2)		2.0047
	$SnBu_2Cl$			[g]		
	$SnBuCl_2$			[g]		

[a] Only the spectrum of the $Cp^{\cdot}$ radical was observed. [b] The principal spectrum which was observed was that of the $Cp^{\cdot}$ radical, and the spectrum of the adduct was very weak. [c] Initially, only the spectrum of the $Cp^{\cdot}$ radical was observed; after 20—30 minutes photolysis, the spectrum of the radical t-$Bu_2NO^{\cdot}$ was apparent. [d] a(2 Cl) 0.62 G. [e] a(Cl) 0.28 G. [f] a(Cl) 0.31 G. [g] Very weak unresolved spectrum.

TABLE 4

MÖSSBAUER SPECTRA OF BUTYLCYCLOPENTADIENYLTIN COMPOUNDS, $Bu_{4-n}SnCp_n$

n	δ (mm s^{-1}) [a]	ΔEq (mm s^{-1})
0	1.35	0.00
1	1.36	1.39
2	1.46	1.47
4	1.52	0.00

[a] At 80 K, with respect to SnO_2 at room temperature.

The successive replacement of butyl ligands by cyclopentadienyl ligands in the radicals $Bu_{3-n}Sn^{\cdot}Cp_n$ progressively reduces their reactivity towards both reagents *. Thus the photolysis of dibutylbiscyclopentadienyltin in the presence of ethyl bromide showed a spectrum of the ethyl radical (eqs. 4 and 5) rather weaker than that observed from tributylcyclopentadienyltin under

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* The reaction $CpR_2\dot{S}n^{(III)} \rightarrow Cp^{\cdot} + R_2\ddot{S}n^{(II)}$ might in principle contribute to this apparent unreactivity, but we do not believe it is a major factor because photolysis of $Cp(MeC_5H_4)SnBu_2$ gives mainly $Cp^{\cdot}$ and relatively little $MeC_5H_4^{\cdot}$.

the same conditions, and butyltriscyclopentadienyltin and tetrakiscyclopentadienyltin showed only a strong spectrum of the cyclopentadienyl radical.

$$\mathrm{Bu_2SnCp_2} \xrightarrow{h\nu} \mathrm{Bu_2\dot{S}nCp + Cp^{\bullet}} \tag{4}$$

$$\mathrm{Bu_2\dot{S}nCp + BrC_2H_5 \rightarrow Bu_2SnCpBr + C_2H_5^{\bullet}} \tag{5}$$

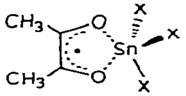
Similarly, whereas photolysis of $\mathrm{Bu_3CpSn}$ in ethylene as solvent showed the spectrum of the cyclopentadienyl radical and of the radical $\mathrm{Bu_3SnCH_2CH_2^{\bullet}}$ (reproduced in ref. 4), photolysis of $\mathrm{Bu_2Cp_2Sn}$, $\mathrm{BuCp_3Sn}$, or $\mathrm{Cp_4Sn}$ under the same conditions showed only a strong spectrum of the cyclopentadienyl radical.

In these two reactions, the effect of the cyclopentadienyl ligand is parallel to that of the chloro ligand in attenuating the reactivity of the tin-centred radicals. In the chlorotin radicals, this effect was tentatively ascribed to the electronegativity of the chlorine in lowering the energy of the SOMO of the radical, and reducing the interaction between the SOMO and the LUMO of the alkyl halide or alkene.

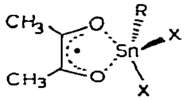
This analogy between the ligand effect of the Cp and Cl groups, and its possible interpretation in terms of electronegativity is developed in the subsequent discussion.

Reactions involving biacetyl

Butylchlorotin radicals, $\mathrm{Bu_{3-n}X_nSn^{\bullet}}$, react with biacetyl to show the ESR spectra of the corresponding tin semidiones, $\mathrm{Bu_nCl_{3-n}SnOCMeCMeO^{\bullet}}$. At low temperatures, the trichloro and dichloro derivatives show hyperfine coupling by one unique chloro ligand, and the two methyl groups of the semidione are slightly non-equivalent. This was interpreted as implying that the biacetyl moiety acted as a bidentate ligand at trigonal bipyramidal tin, rendering non-equivalent the apical and equatorial chloro ligands about the tin, and the two methyl groups (Formulae I and II; X = Cl); at higher temperatures (>10° C), rapid positional exchange rendered the different sites indistinguishable.



(I)



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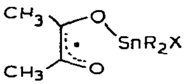
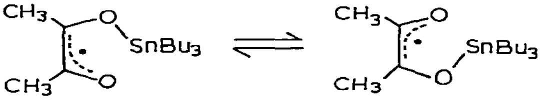


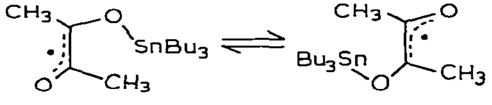
(III)

The monochloro derivative, on the other hand, showed no hyperfine coupling to chlorine, and the two methyl groups were more severely non-equivalent over the whole range of temperature which could be studied. This was interpreted as implying a non-fluxional monodentate structure (III).

Finally, the reaction of the $\mathrm{Bu_3Sn^{\bullet}}$ radical with biacetyl showed the ESR spectra of two radicals, one of which was a regular binomial septet, and the other of which showed a severe alternating line-width effect. These two spectra were assigned to the rapidly fluxional *cis*-monodentate structure (IV) and the more slowly fluxional *trans*-monodentate structure (V) respectively.



(IV)



(V)

Fig. 1. ESR spectrum obtained from the photolysis of $BuSnCp_3$ and biacetyl in the presence of ethyl bromide, in toluene at −10°C.

Photolysis of butylcyclopentadienyltin compounds in the presence of biacetyl shows the spectra of the cyclopentadienyl radical and of the adduct of the tin radical with the dione (e.g. eqns. 6 and 7).

$$BuSnCp_3 \xrightarrow{h\nu} Cp^{\bullet} + BuCp_2Sn^{\bullet} \quad (6)$$

$$BuCp_2Sn^{\bullet} + OCMeCMeO \rightarrow BuCp_2SnOCMeCMeO^{\bullet} \quad (7)$$

As ethyl bromide does not react with the di- or tri-cyclopentadienyltin radicals, but it broadens the spectrum of the cyclopentadienyl radical beyond detection, only the spectrum of the adduct radical is observed when the reaction is carried out in the presence of an excess of ethyl bromide. An example of such a spectrum, showing a binomial septet for the tin derivative of the semidione together with the satellites due to $^{117/119}Sn$ coupling (and in this particular case an extra singlet which is labelled with an asterisk) is shown in Fig. 1.

The data in Table 1 show that the hyperfine coupling constants and *g*-values for the radicals $Bu_{3-n}X_nSnOCMeCMeO^{\bullet}$ where X = Cp run parallel with those where X = Cl. This might be taken to imply that these two ligands favour similar structures in the radicals, and within those structures, have similar effects on the ESR parameters.

Thus the low *g*-values (for semidione radicals) for $Cp_3SnOCMeCMeO^{\bullet}$ and $BuCp_2SnOCMeCMeO^{\bullet}$ are parallel to the values for the chloro analogues, $Cl_3SnOCMeCMeO^{\bullet}$ and $BuCl_2SnOCMeCMeO^{\bullet}$ respectively. The value of $a(^{117/119}Sn)$ for $Cp_2SnOCMeCMeO^{\bullet}$ (65.8/69.0 G, and temperature-independent over the range −40°C to 0°C) is much higher than that for the isomer of $Bu_3SnOCMeCMeO^{\bullet}$ for which a(Sn) could be measured (ca. 10 G, and strongly temperature-dependent) *, and emphasises the difference between butyl and

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* The value of a(Sn) for the radicals $Cl_3SnOCMeCMeO^{\bullet}$ and $BuCl_2SnOCMeCMeO^{\bullet}$ could not be measured because of the presence of hyperfine coupling by chlorine.

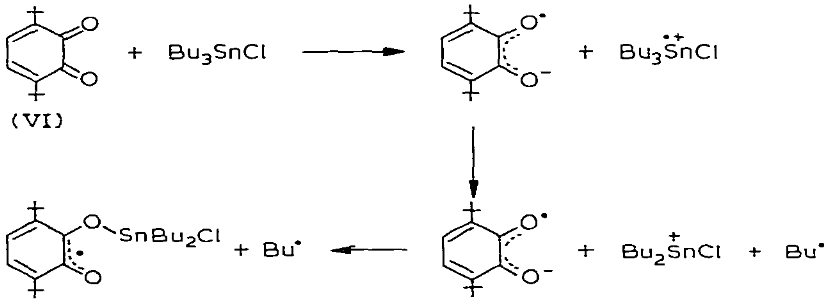
cyclopentadienyl groups as ligands for tin.

The low g-values and large hyperfine couplings to tin would be compatible with bidentate chelate structures (I and II) similar to those which we proposed for the chloro analogues, which involve increased occupancy of the d-orbitals of the tin by the unpaired electron [10]. If this is correct, it appears that the difference between the electronegativities of the butyl and cyclopentadienyl groups is not large enough to render the two methyl groups magnetically non-equivalent, as does occur with the chloro analogues at low temperature.

The monocyclopentadienyl and monochloro compounds $Bu_2XSnOCMeO^\bullet$ both have larger g-values and show similar hyperfine couplings to non-equivalent methyl groups. Apparently they have different structure from those of the compounds $Bu_{3-n}X_nSnOCMeCMeO^\bullet$ ($n = 3$ or 2), and its seems likely that they have similar structures to each other, namely the monodentate structure (III), non-fluxional on the ESR time-scale.

Reactions with 3,6-di-t-butyl-1,2-benzoquinone

3,6-Di-t-butyl-1,2-benzoquinone (VI) has been shown to be a very useful reagent for trapping organotin free radicals. The radicals (e.g. VII) are frequently formed by the electron transfer process shown in equation 8, without irradiation, when the quinone and organotin compound are mixed [11].



(VI)

(VII)

(8)

The radicals VII are persistent, have very simple ESR spectra (coupling to only two hydrogen atoms), and there is no possible ambiguity between *cis* and *trans* structures.

Table 2 lists the ESR parameters of some tin derivatives of 3,6-di-t-butylsemiquinone, prepared by the above type of reaction. As would be expected, a cyclopentadienyl radical is lost more readily than a butyl radical during the cleavage of the organotin radical cation. The presence of resolvable coupling by apparently one chlorine atom in the Cl_3Sn derivative suggests that it has a cyclic bidentate structure with trigonal bipyramidal tin, similar to the structure which was proposed for the analogous biacetyl derivative (I), but there is no direct evidence that the Cp_3Sn derivative adopts a similar structure.

The most interesting entry in Table 2 is that for the adduct of the Bu_2ClSn radical which has a spectrum consisting of a doublet of doublets at low temperature and a triplet at high temperature, due to the degenerate exchange shown in equation 9.


(9)

Computer simulation of the spectra in the intermediate rates of exchange gave the activation parameters log $A = 13.6$, $E = 44.4$ kJ mol^{-1}, whence k(333 K) = 2.8×10^6 s^{-1}. The rate constant for the corresponding Me_2SnCl adduct has been reported to be k(333 K) = 2.5×10^6 s^{-1} [12].

The corresponding Bu_3Sn derivative showed a spectrum consisting of a sharp triplet down to —40° C. It is hardly conceivable that the Bu_3Sn derivative should have a higher coordination number than the Bu_2ClSn derivative. We therefore conclude that the Bu_3Sn group, like the Bu_2ClSn group, is 4-coordinate, but that the Bu_3Sn group is more rapidly fluxional so that the temperature cannot be reached at which its exchange process is slow. This lower mobility of the Bu_2ClSn group supports our assignment of the structures III, IV, and V to the biacetyl derivatives $Bu_2ClSnOCMeCMeO^{\cdot}$ and $Bu_3SnOCMeCMeO^{\cdot}$, on which, by analogy, our proposals for the structures of the corresponding cyclopentadienyl compounds are based.

Reactions involving nitro compounds

Reuter and Neumann [13] have recently shown that the photolysis of hexamethylditin in the presence of nitroalkanes or nitroarenes gave rise to persistent nitroxyl radicals (VIII) which showed high hyperfine couplings to nitrogen, e.g. R = t-Bu, a(N) = 30.1 G; R = Ph, a(N) = 14.1 G. We have therefore investigated the possibility of detecting the tin-centred radicals which are formed from the photolysis of cyclopentadienyltin compounds by the adducts which they might form with nitromethane, nitroethane, 2-methyl-2-nitropropane, and 1-chloro-4-nitrobenzene.

No radicals were observed when cyclopentadienyltin compounds and the nitro compounds were mixed without photolysis. An electron-transfer process similar to that which occurs with 3,6-di-t-butyl-1,2-benzoquinone is therefore

$$Me_3Sn^{\cdot} + RNO_2 \rightarrow \underset{\text{(VIII)}}{RN(O^{\cdot})OSnMe_3} \qquad (10)$$

not important. When the samples were irradiated, the spectrum of the cyclopentadienyl radical was observed, together usually with a spectrum resulting from the appropriate alkyl- or aryl-stannyloxynitroxyl radical (IX). The ESR parameters of these radicals are listed in Table 3.

$$Bu_{3-n}X_nSnCp \xrightarrow{h\nu} Bu_{3-n}X_nSn^{\cdot} + Cp^{\cdot} \qquad (11)$$

$$Bu_{3-n}X_nSn^{\cdot} + RNO_2 \rightarrow \underset{\text{(IX)}}{RN(O^{\cdot})OSnBu_{3-n}X_n} \qquad (12)$$

When the light was shuttered, the spectrum of the $Cp^{\cdot}$ radical decayed immediately, but the spectrum of the nitroxyl radicals (IX) persisted, the persistence increasing in the sequence R = Me (a few minutes) < Et < t-Bu (several hours). The relatively high values of a(N) when R = alkyl probably indicates that these are pyramidal σ-radicals; when R = aryl, delocalisation of the unpaired electron into the aromatic ring renders the radicals nearer planar at nitrogen, and a(N) decreases [13]. Changes in a(H) and a(Sn) may derive in part from the fact that the radicals may be monodentate static, monodentate fluxional, or bidentate, but it would be too speculative at this stage to attempt to analyse the results further in these terms.

The presence of either chloro or cyclopentadienyl ligands on the tin decreased the reactivity of the tin radicals towards the nitrocompounds, detracting from the intensity of the spectra of the radicals IX. For example, photolysis of Cp_4Sn in the presence of $MeNO_2$ or t-$BuNO_2$ showed initially the spectrum of only the $Cp^{\cdot}$ radical, but after 20—30 minutes, the sample containing t-$BuNO_2$ showed a strong persistent spectrum, a(N) 15.6 G, g 2.0061, with no hyperfine coupling to tin, which may be the di-t-butylnitroxyl radical formed by the reaction shown in equation (13).

$$Cp_3Sn^{\cdot} + \text{t-}BuNO_2 \rightarrow \text{t-}BuN(O^{\cdot})OSnCp_3 \xrightarrow{-Cp_3SnO^{\cdot}} \text{t-}BuN{=}O \overset{h\nu}{\rightarrow} \text{t-}Bu_2NO^{\cdot} \qquad (13)$$

The character of the cyclopentadienyl ligand in tin(IV) compounds

Structural and spectroscopic data on cyclopentadienyltin(IV) compounds might help to elucidate the character of the cyclopentadienyl ligand in tin(III) radicals.

At —60° C, crystalline Cp_4Sn has a distorted tetrahedral structure at tin with $<$C—Sn—C = 103—114°. The average C—Sn bond length is 2.27 Å, rather larger than the sum of the covalent radii. The planar cyclopentadienyl rings are η^1-bonded (though fluxional in fluid solution), but are bent towards the tin atom by an average of 5.1° [14].

The ^{119}Sn NMR chemical shifts of the compounds Me_nSnCp_{4-n} have been determined by Torocheshnikov, Tupciauskas, and Ustynyuk [15] to be as follows: Me_4Sn 0, Me_3SnCp +26, Me_2SnCp_2 +23.2, $MeSnCp_3$ —7.0, $SnCp_4$ —24.4 ppm. This variation emphasises again the difference between alkyl and cyclopentadienyl ligands, and was attributed to two competing electronic effects, namely deshielding of tin by carbon—metal hyperconjugation (σ—π interaction), and shielding by $p\pi$—$d\pi$ interaction.

Mössbauer spectroscopy can similarly give evidence of intramolecular electronic effects in organotin compounds, and Harrison and Zuckerman showed [16] that trimethylcyclopentadienyltin, like the alkylethynyltin compounds (and alkyltin chlorides) showed the presence of quadrupole splitting. Our own measurements on butylcyclopentadienyltin compounds are shown in Table 4.

These results again show that butyl and cyclopentadienyl groups when bonded to tin(IV) have significantly different electronic effects: in the mixed butylcyclopentadienyl compounds, an electric field gradient is set up at the nucleus which interacts with the nuclear quadrupole moment, and gives rise to the observed quadrupole splitting *.

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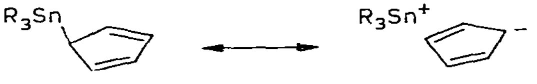
* A further apparent analogy between the Cp and Cl groups as ligands at tin(IV) is that whereas t-butoxyl radicals react with acyclic tetralkyltins by abstraction of hydrogen, Me_3SnCp, like the alkyltin halides, undergoes attack at tin [17]. The analogy may be misleading however as a cyclopentadienyl radical is replaced in one reaction and an alkyl radical in the other, and the ease of the cleavage of the Sn—Cp bond may be the controlling factor.

Conclusion

The work reported and reviewed in this paper has emphasized the difference in properties between the butyl and cyclopentadienyl groups as ligands for tin(III) and tin(IV), and suggests that the cyclopentadienyl groups may show in these compounds properties approaching those of a chloro ligand.

In the tin(IV) derivatives, this effect might be ascribed to carbon—metal hyperconjugation, which in valence bond terms represents the contribution that the polar canonical form X makes to the structure of the resonance hybrid.



(X)

Such an explanation might be carried over to the cyclopentadientyltin(III) radical. However, the $CpSn^{(IV)}$ compounds have fluxional *monohapto* structures, whereas $Cp_2Sn^{(II)}$ has an angular *bispentahapto* structure: in $Sn^{(III)}$ compounds, the cyclopentadienyl ligand might be bonded in *monohapto*, *polyhapto*, or *pentahapto* fashion, and there appears to be no reason for preferring one picture over the other on the present evidence.

We tried to answer this intriguing question by examining more closely the broad singlet marked with an asterisk (Fig. 1), which was obtained during the photolysis of $BuSnCp_3$, in the hope that it might be due to the presence of the radical $Bu\dot{S}nCp_2$ (although the *g*-value of 2.009 would be low for a trialkyltin radical, e.g. for $Me_3Sn^\cdot$, $g = 2.016$). Unfortunately, we were unable to resolve the signal and determine the pattern of proton hyperfine coupling. We hope that by the design of more persistent cyclopentadienyltin radicals we will be able to resolve the hyperfine structure in their ESR spectra, and determine their mode of bonding.

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