

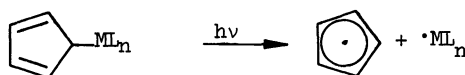
PHOTOLYTIC REACTIONS OF CYCLOPENTADIENYLMETALLIC COMPOUNDS

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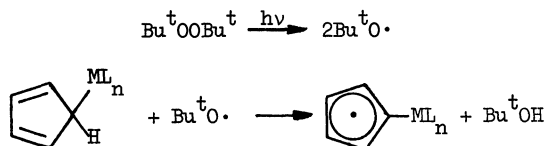
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Abstract - Bonds to the cyclopentadienyl ring readily undergo homolysis because the cyclopentadienyl radical is resonance stabilized. Two aspects of this reactivity are discussed.

First, a wide variety of cyclopentadienylmetallic compounds undergo photolysis with ultraviolet light, providing a route to metal-centred radicals. The properties of some of these radicals have been studied by e.s.r. spectroscopy.



Second, t-butoxyl radicals react with some other cyclopentadienylmetallic compounds by abstraction of hydrogen to give metal-substituted cyclopentadienyl radicals.



By this and other methods a series of these radicals have been prepared where M = C, Si, Ge, or Sn. Their e.s.r. spectra can be interpreted to show the mode of interaction of the ML_n substituents with the π-electron system.

INTRODUCTION

Since their foundations one hundred and fifty years ago, the fields of organometallic chemistry and of free radicals have developed in close association, and work by Bunsen, Frankland, Gomberg, and Paneth provided land-marks in both histories.

This interdependence has continued as the two fields have expanded rapidly in recent years. One topic which has attracted much attention is the process of bimolecular homolytic substitution (S_H2) which frequently occurs very rapidly at a metal centre (eqn. 1, M = Mg, Zn, B, Al, Sn, P, Sb etc.) [Ref. 1].



These reactions often occur very much more rapidly than the corresponding reactions at hydrogen (ML_n-R = H-R), presumably because the metal usually carries vacant p or d orbitals which can accommodate the attacking radical, the electropositive metal can readily release electrons to an electronegative radical to promote a charge-transfer mechanism, and many metal-carbon bonds are rather weak.

Attack at the atom proximate to the metal, (eqn. 2) is relatively rare, and only organosilicon radicals (L-MR_n = H-SiR₃) and organotin radicals (L-MR_n = H-SnR₃ or R₃Sn-SnR₃) are commonly prepared by this route.

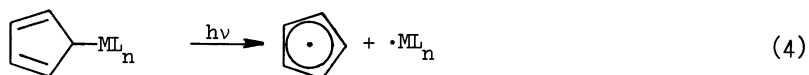


In this lecture we shall be concerned with the place of cyclopentadienylmetallic compounds in this scheme of things, and we shall see that they provide an important context

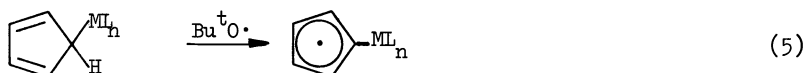
for the operation of a further mechanism (eqn. 3), namely that in which the R-M bond undergoes unimolecular homolysis.



Although many cyclopentadienylmetallic compounds (e.g. ferrocene) are characterised by their unreactivity, others are very reactive and the stability associated with the cyclopentadienyl (5-annulene) structure causes many of their reactions to be homolytic. This manifests itself in two main ways. First, the Cp-M bond is often uniquely photosensitive for a carbon-metal bond, providing a new source of metal centred radicals and of cyclopentadienyl radicals (eqn. 4).



Second, if bimolecular homolytic substitution does not readily occur at the metal centre, hydrogen may be abstracted from the ring to give a metal-substituted cyclopentadienyl radical (eqn. 5).



PHOTOLYSIS OF THE Cp-M BOND

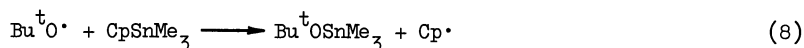
The photosensitivity of the cyclopentadienyl-metal bond was first observed with the tin(IV) derivatives. If simple alkyltin compounds are irradiated in solution with u.v. light in the cavity of an e.s.r. spectrometer, no significant e.s.r. signal can be detected. Under the same conditions, cyclopentadienyltin(IV) compounds, $\eta^5\text{-CpSnL}_3$ (L = Cp, alkyl, aryl, Cl, MeCO₂, etc.) show a strong sextet spectrum of the cyclopentadienyl radical (Ref. 2); this obscures the spectrum of the radical $\cdot\text{SnL}_3$, but this radical can be identified by virtue of its characteristic reactions with reagents such as alkenes, alkyl halides, and 1,2-diones. It seems therefore, that simple unimolecular homolysis is involved (eqn. 6).



The pentahapto cyclopentadienyltin(II) compounds similarly show the spectrum of the Cp⁵ radical, but an insoluble solid separates, and the fate of the tin moiety is unknown.



The intensity of the spectrum of the Cp⁵ radical from CpSnMe₃ [Ref. 3] (though not so obviously from CpSnBu₃) is enhanced if di-t-butyl peroxide or acetone is added to the solution. Presumably, under these conditions, an S_H2 reaction at the tin centre by t-butoxyl radicals (eqn. 8) or ketone triplets supplements the unimolecular process.



Variation of the metal

Similar studies have been carried out on the cyclopentadienyl derivatives of other metals, CpML_n. When the metal M is lithium, mercury, tin(IV), tin(II), lead(IV), lead(II), titanium(IV), or zirconium(IV), the spectrum of the cyclopentadienyl radical is observed according to equation (4). Cyclopentadienyl derivatives of beryllium, magnesium, boron, silicon, and germanium show at best only a very weak spectrum, but, in the presence of di-t-butyl peroxide, the compounds Cp₂Be, CpBeCl, Cp₂Mg, and CpGeCl₃ undergo an S_H2 reaction at the metal centre to give the cyclopentadienyl radical (cf. eqn. 8). Under the same conditions, t-butoxyl radicals abstract hydrogen from the cyclopentadienyl ring of the compounds CpSiR₃ and CpGeR₃ (R = alkyl) to give the corresponding metallocyclopentadienyl radicals by reaction (5) [Refs. 4 and 5].

Mixed alkylcyclopentadienylmetallic compounds

When the metal carries both cyclopentadienyl and alkyl (R) groups, cleavage of the Cp-M and R-M bonds may be in competition. Irradiation of alkylcyclopentadienyltin(IV) compounds

gives only the cyclopentadienyl radical but cyclopentadienyltriethyl-lead gives Cp· above -50 °C and Et· below -100 °C, and both in between [Refs. 2 and 6]. Bis(cyclopentadienyl) zirconium dichloride give a rather weak Cp· spectrum, but Cp₂ZrMe₂ gives only the methyl radical, and the intensity of the spectrum is increased when di-*t*-butyl peroxide is added [Ref. 7].

Cyclopentadienylmethylberyllium reacts with *t*-butoxyl radicals to show predominantly the spectrum of the cyclopentadienyl radical below -60 °C, but at -30 °C the concentrations of cyclopentadienyl and methyl radicals are approximately equal [Ref. 8].

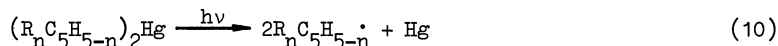
We hoped the alkylcyclopentadienylmercury compounds, CpHgR, might give the radicals Cp· and Me· in equal concentration, providing a useful new source of alkyl radicals and a method of following the kinetics of the reactions of the alkyl radicals (eqn. 9).



However, with cyclopentadienylmethyl mercury at the normal concentration, the principal species which are observed are Cp· at -75 °C, and Me· at -130 °C; only with a very low concentration of reagent, does the stoichiometry of the reaction appear to approach that of equation (9) [Ref. 9].

Ring-substituted cyclopentadienylmetallic compounds

If the cyclopentadienyl ring carries one alkyl substituent, the trialkyltin derivatives are much less photosensitive [Ref. 2], but the trimethyltin derivatives, RC₅H₄SnMe₃ still undergo an S_H2 reaction with *t*-butoxyl radicals (cf. eqn. 7) to provide a source of the radicals RC₅H₄· [Ref. 3]. The alkylated cyclopentadienylmercury compounds, however, retain their photosensitivity. All the isomers of the methylcyclopentadienyl radicals, Me_nC₅H_{5-n}·, n = 0 - 5, have been prepared by reaction (10) [Ref. 10], and a similar route has been used for preparing radicals such as EtC₅H₄·, PrⁱC₅H₄·, Bu^tC₅H₄·, and Me₃SiC₅H₄· [Ref. 2].



Hydrogen as a metalloid

In both homolytic and heterolytic reactions, hydrogen often behaves like a main-group metal, and it is interesting to compare the properties of the cyclopentadienes themselves with those of their metallic derivatives. Cyclopentadiene, C₅H₅-H is much less photosensitive than the derivatives C₅H₅-ML_n (ML_n = SnBu₃, PbMe₃, 1/2 Hg etc.), but under carefully controlled conditions, it shows a good e.s.r. spectrum of the C₅H₅· radical when it is irradiated with u.v. light (cf. eqn. 4) [Refs. 9 and 11]. The intensity of the spectrum is enhanced when di-*t*-butyl peroxide is added (cf. eqn. 7), but some addition of *t*-butoxyl radicals to the diene system also occurs. Progressive introduction of alkyl groups increases the photosensitivity, and the 1,2,3,4,5-pentaalkylcyclopentadienes under u.v. irradiation give very strong spectra of the pentaalkylcyclopentadienyl radicals [e.g. eqn. 11, Ref 10 and 12]



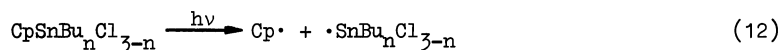
The enhanced stability of the pentamethylcyclopentadienyl radical which this implies, suggests that the use of the compounds Me₅C₅ML_n might provide an extension of reaction (4) by which a wider range of metal-centred radicals could be prepared.

PROPERTIES OF THE ·ML_n RADICALS

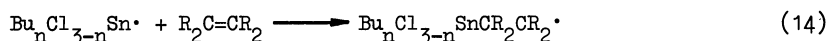
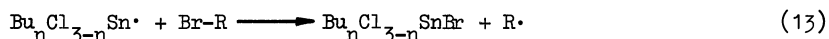
The versatility of reaction (4) makes it possible to prepare a wide variety of radicals ·ML_n, and to study the dependence of the properties of those radicals on the nature of the ligands L.

Tin-centred radicals

The radicals Bu_nCl_{3-n}Sn·, n = 0 - 3, were prepared by reaction (12), and their reactions were monitored by e.s.r. spectroscopy [Ref. 13].



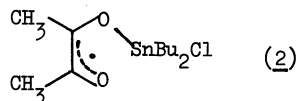
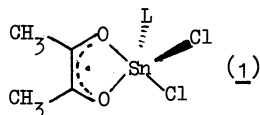
The two most characteristic reactions of trialkyltin radicals are their abstraction of halogen from alkyl halides, and their addition to alkenes (eqns. 13 and 14, n = 3).



In both these reactions, the reactivity of the tin radicals is reduced by chloro ligands. This is reasonable if it is accepted that the SOMO of the radical interacts with the LUMO of higher energy of the alkyl bromide or alkene, and that the SOMO energy is lowered by electron attracting chloro ligands.

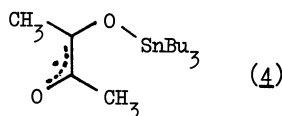
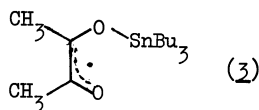
Most metal-centred radicals form persistent semidione adducts with 1,2-diones: these adducts may have a variety of structures, and a comparison of the e.s.r. spectra of the products formed from biacetyl and the butylchlorotin radicals has made it possible to identify these structures [Ref. 13].

First, the radicals $\text{Cl}_3\text{Sn}\cdot$ and $\text{BuCl}_2\text{Sn}\cdot$, formed by reaction (10), react with biacetyl to give adducts with e.s.r. spectra which show two slightly non-equivalent methyl groups, and, at low temperature, hyperfine coupling to one unique chlorine atom. Above 10°C the two methyl groups become equivalent, and hyperfine coupling occurs to more than one chlorine atom. We take this to imply that the biacetyl acts as a bidentate ligand bridging apical and equatorial positions at trigonal bipyramidal tin, so that the methyl groups are pseudo-apical, and there is a unique chlorine atom in the apical position, as shown in (1, L = Cl or Bu). At higher temperatures, positional exchange of the ligands about the tin occurs, and renders equivalent the two methyl groups, and the two or three chlorine atoms.

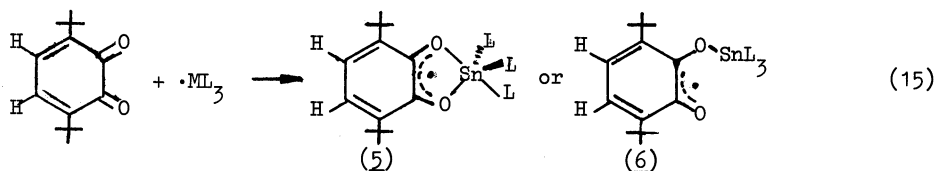


The radical $\text{Bu}_2\text{ClSn}\cdot$ on the other hand gives an adduct which shows severely non-equivalent methyl groups and no hyperfine coupling to chlorine. This would be compatible with biacetyl acting as a (probably cis) monodentate ligand to give the structure (2) which is non-fluxional.

Finally, the Bu_3Sn radical reacts to give two radicals. One, with a spectrum consisting of a regular binomial sextet, appears to be the rapidly fluxional monodentate cis-derivative (3). The other, which shows a strong alternating line width effect, is assigned the more slowly fluxional trans-structure (4).



Within this family of radicals, we conclude then that the introduction of chloro instead of alkyl ligands at the metal first reduces the mobility of the metal and then anchors it with an increased coordination number. A similar picture emerges from a study of the adducts which the radicals form with 1,4-di-*t*-butyl-2,3-benzoquinone (eqn. 15) [Ref. 14].



When $\text{ML}_3 = \text{SnBu}_3$, the spectrum of the adduct consists of a triplet which shows an alternating line width effect at low temperature. When $\text{ML}_3 = \text{SnBu}_2\text{Cl}$, the spectrum consists of a doublet of doublets at low temperature, and a triplet at higher temperatures. Both these adducts therefore appear to have the monodentate structure (6), and the fluxional mobility is in the sequence $\text{Bu}_3\text{Sn} > \text{Bu}_2\text{ClSn}$. When $\text{ML}_3 = \text{BuCl}_2\text{Sn}$ or Cl_3Sn , the two hydrogen atoms in the ring are equivalent, and hyperfine coupling occurs to one unique chlorine atom: these derivatives, like the corresponding derivatives from biacetyl, therefore appear to have the chelated structure (5).

Similar studies have been carried out on cyclopentadienyltin radicals, where the interesting question (as yet unanswered) arises as to whether the cyclopentadienyl ligand is monohapto, as it is in tin(IV) compounds, or pentahapto, as it is in tin(II) compounds. In its effect on the properties of the radicals, and on the structures of the radical adducts, the cyclopentadienyl ligand behaves as though it has an electronegativity closer to Cl than to alkyl [Ref. 15].

PROPERTIES OF THE ML_n GROUPS AS SUBSTITUENTS

By reactions (5) and (10), cyclopentadienyl radicals can be generated containing a variety of substituents, and the e.s.r. spectra of these radicals can then be interpreted in terms of the electronic interaction between the substituents and the π -electron system. This approach is based on that which is well-established for the substituted benzene radical anions, but the cyclopentadienyl system has a number of advantages. The routes (eqns. 5 and 10) to the neutral radicals are tolerant towards a wider variety of substituents, and the reactions can be carried out in non-polar solvents, and there is no counterion to complicate the interpretation. Further, the substituent interacts with a low-energy bonding M.O. rather than a higher energy antibonding M.O. as it does in the radical anions, so that the information gained will be more relevant in other chemical situations. As the [3]-annulenes (cyclopropenyls) are σ -radicals, these [5]-annulenes (cyclopentadienyls) are the simplest π -delocalised annulenes that can be studied.

The interpretation of the spectra has been described elsewhere [Refs. 2, 3, and 4]. In the cyclopentadienyl radical, the unpaired electron is shared equally between two degenerate orbitals, ψ_A and ψ_S . Of these, ψ_A has zero coefficient at C(1), and only ψ_S will interact with a substituent, being destabilized by electron release and stabilized by electron attraction. The unpaired electron will occupy, wholly or principally, the upper of these two orbitals, and the e.s.r. spectrum will be characteristic of the spin density distribution in this occupied orbital. If the perturbation induced by the substituent is smaller than kT , the unpaired electron will populate both orbitals according to the Boltzmann equation, and a population-weighted average of the spectra characteristic of the ψ_A and ψ_S electron distributions will be observed.

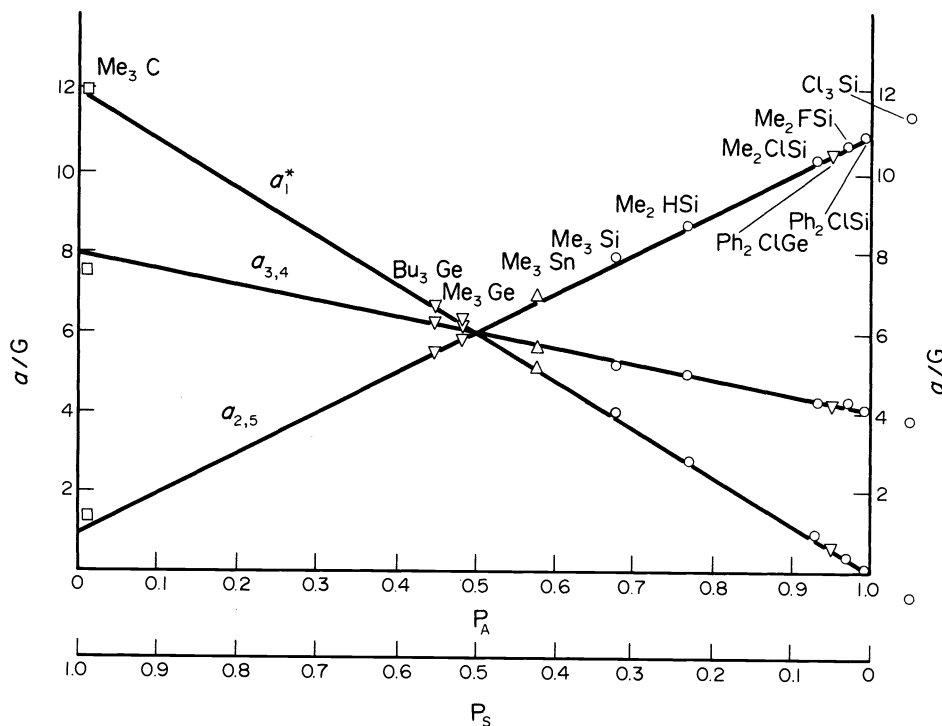


Figure. Plot of proton hyperfine coupling constants of the radicals $C_5H_4ML_3$ at $-100^\circ C$ against calculated populations of the ψ_A and ψ_S molecular orbitals.

Hückel coefficients are usually sufficient to predict the hyperfine couplings to be assigned to the pure ψ_A and ψ_S molecular orbitals, and in the Figure the predicted values of the hyperfine coupling constants for the radicals $C_5H_4ML_n$ are plotted against the orbital population. At the central point of intersection, the populations of ψ_A and ψ_S are equal, and the hyperfine coupling constants are equal to those in C_5H_5 . The divergence of the lines to the right of the centre indicates an increasing population of the ψ_A M.O. by the unpaired electron, and, to the left of the centre, ψ_S is increasingly populated. The observed values of the hyperfine coupling constants for the derivatives $C_5H_4ML_n$ have been added to this graph to give the best fit with the calculated lines [Ref. 5].

The substituent Me_3C , and other alkyl substituents, place the unpaired electron wholly in the ψ_{S} orbital. This is consonant with the generally accepted electron-releasing effect of alkyl groups. The Me_3Si group, on the other hand, acts as an electron attracting substituent [Refs. 4 and 5], because of π -d conjugation and π - σ^* hyperconjugation. The Me_3Ge substituent is almost electronically neutral in this situation, exerting a negligible electron repelling effect; presumably the inductive effect in the $\text{sp}^2\text{C}-\text{sp}^3\text{Ge}$ bond is almost cancelled by the two electron attracting mechanisms. With the Me_3Sn substituent, electron attraction again dominates, though the net effect is less than that of the Me_3Si group. We have not yet been able to observe the spectrum of the radical $\text{C}_5\text{H}_4\text{PbMe}_3\cdot$.

Further points on the graph illustrate the effect of changing the ligands at the metal centre. In particular the electron attracting power of the silyl substituent is progressively increased if the methyl ligands are replaced by hydrogen and then by chlorine.

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