

AN ESR STUDY OF THE PHOTOLYSIS OF DICYCLOPENTADIENYLTITANIUM DICHLORIDE

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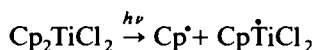
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Summary

ESR spectroscopy has been used to monitor the radicals which are formed when dicyclopentadienylyltitanium dichloride is photolysed in solution alone or in the presence of various reagents (oxygen, ethers, pyridine, phosphines, 2-methyl-2-nitropropane, nitrosodurene, biacetyl, and 3,6-di-*t*-butyl-1,2-benzoquinone). The direct observation of the spectrum of the cyclopentadienyl radical, and the unambiguous resolution of the hyperfine coupling by two chlorine atoms in the spin adduct which the titanium fragment forms with 2-methyl-2-nitropropane suggests that, at least in tetrahydrofuran, the principal reaction is, as commonly accepted:



However, under some conditions (e.g. in ether solvent, or in the presence of pyridine, particularly at low temperatures), the spectra of two different titanium(III) radicals, with resolvable hyperfine structure, can be observed, and this simple model needs to be extended.

Introduction

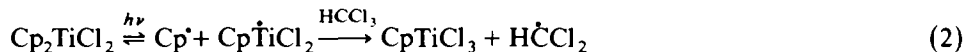
The cyclopentadienyl derivatives of a variety of Main Group metals have now been shown to undergo homolysis of the Cp–metal bond when they are irradiated with ultraviolet light (eq. 1), and reactions of this type have been exploited as a source of substituted cyclopentadienyl radicals, and of metal-centred radicals, for studies by ESR spectroscopy [1]. Cyclopentadienylytin(IV) compounds, which are σ -bonded, have been studied the most thoroughly, but the unimolecular homolysis of eq. 1 applies equally well to the π -bonded η^5 -cyclopentadienylytin(II) compounds. A

brief review of the field is given in ref. 2.



Relatively little is known about the photolysis of cyclopentadienyl derivatives of transition metals, though frequently the Cp-metal bond is now relatively strong (as it is, for example, in ferrocene) and photoreaction involves some other bond in the molecule [3].

Most work in this field has been carried out on titanocene dichloride, $\eta^5\text{-Cp}_2\text{TiCl}_2$. In 1974, Harrigan, Hammond, and Gray [4] showed that irradiation of Cp_2TiCl_2 in chloroform or carbon tetrachloride gave clean conversion to CpTiCl_3 ; in benzene, the reaction was relatively slow and there was convincing evidence for the formation of $\text{Cp}\dot{\text{T}}\text{iCl}_2$. It was concluded that excitation is followed by unimolecular homolysis of the Cp-Ti^{IV} bond to give a Ti^{III} species which can abstract halogen from the solvent. The low quantum yield (2×10^{-2}) was ascribed to the reversibility of the primary process (eq. 2).



Similar results were obtained by Brubaker [5], who also showed that irradiation of Cp_2TiCl_2 in benzene led to the exchange of Cp ligands between molecules, and, in benzene/methanol mixture, to methanolysis to give CpTi(OMe)Cl_2 [6,7].

Photolysis of Cp_2TiCl_2 in tetrahydrofuran in the cavity of an ESR spectrometer [8] was reported to show initially a singlet, g 1.976, showing satellites due to hyperfine interaction with Ti isotopes. On prolonged photolysis, a second singlet, g 1.953 developed, and both signals persisted for at least 18 h after the photolysis. This illustrates the most obvious difference between the behaviour of the metallic fragments from the titanium(IV) compounds and the corresponding derivatives of Main Group metals such as tin(IV) [1]. Whereas the radicals $\text{L}_3\text{Sn}^\bullet$ decay at a diffusion-controlled rate to give irreversibly the ditins L_3SnSnL_3 [9] (unless the ligands L are very bulky [10]), $\text{Cp}\dot{\text{T}}\text{iCl}_2$, which can be prepared by reduction of CpTiCl_3 [11], is in thermal equilibrium with the solvated monomer and the dimer (which is probably chlorine-bridged), and shows a persistent ESR spectrum under a variety of conditions.

Results and discussion

We describe here a study by ESR spectroscopy of the photolysis of dicyclopentadienyltitanium(IV) dichloride (titanocene dichloride) and of the properties and reactions of the resulting paramagnetic fragments. It should be born in mind that this technique would not detect directly any non-radical fragments, nor any radical which has a very short life-time (e.g. H^\bullet) or a very broad spectrum (e.g. Cl^\bullet). Our results confirm and extend those of previous workers in this field, particularly Tsai and Brubaker's [8], though we differ with them on one point of interpretation. We discuss first the cyclopentadienyl radical which is formed, and then the titanium(III) fragment.

The cyclopentadienyl radical. Photolysis in the ESR cavity of Cp_2TiCl_2 in toluene or tetrahydrofuran, alone or in the presence of other reagents such as oxygen, pyridine, triphenylamine, bipyridyl, biacetyl, or nitrosodurene, showed the character-

istic sextet spectrum of the cyclopentadienyl radical as illustrated in Fig. 1–5. This is the first direct evidence that the cyclopentadienyl radical is formed: previous evidence was indirect, depending on spin-trapping experiments with nitrosodurene, and, as we point out below, is not unambiguous.

The only reaction of cyclopentadienyl radicals that we have observed by the ESR technique is their bimolecular decay at a diffusion-controlled rate (to give presumably dihydrofulvalene) [12], and neither in the work described here, or previously, have we been able to intercept them with an added reagent. For example, the spectrum of the Cp• radical can still be observed when Cp₂TiCl₂ (or cyclopentadienyl derivatives of Sn^{II}, Sn^{IV}, Pb^{II}, Pb^{IV} or Hg) are photolysed in the presence of oxygen and no spectrum which might be ascribed to the CpOO• radical is observed*.

This does not of course preclude the possibility of building up an observable concentration of a longer-lived radical adduct by reaction of the cyclopentadienyl radical with a spin trap, and two reports of reactions involving nitrosodurene have appeared. Tsai and Brubaker [8] reported that when (C₅H₅)₂TiCl₂ or (C₅D₅)₂TiCl₂ was photolysed in the presence of nitrosodurene, the spectrum of the cyclopentadienyl(duryl)nitroxyl radical was observed, with *a*(N) 13.0, *a*(H) 13.0, or *a*(N) 13.0, *a*(D) 2.0 G, *g* 2.005, respectively; for convenience in discussion we will refer to these as spectra A and A'. With (MeC₅H₄)₂TiCl₂, spectra ascribed to two isomeric duryl(methylcyclopentadienyl)nitroxyl radicals were observed, the first with *a*(N) 13.0 G, *a*(H) 13.0 G, *g* 2.005, (spectrum B) and the second with *a*(N) 13.0 G, *g* 2.005 (spectrum C).

On the other hand, Gianotti and his coworkers [13] found that Cp₃UMe and Cp₃UBu reacted thermally with nitrosodurene to give a spectrum (D) which was tentatively ascribed to the cyclopentadienyl(duryl)nitroxyl radical, which showed different hyperfine coupling constants from those reported in ref. 8: *a*(N) 13.56, *a*(H) 6.22 G in tetrahydrofuran, or *a*(N) 15.5 *a*(H) 5.6 G in toluene.

Values of *a*(Hβ) in alkyl(duryl)nitroxyl radicals, R(Me₄C₆H)NO• are known to vary widely with the steric demands of the alkyl group R (e.g. R = Me, *a*(3Hβ) 12.17 G; R = Me₂CH, *a*(Hβ) 6.92 G; R = Ph₂CH, *a*(Hβ) 1.43 G) [14], and with the solvent and temperature. It is difficult therefore to predict with confidence the value of *a*(Hβ) when R = C₅H₅, but a reasonable model is probably the 4-arylcyclohexa-2,5-dienyl(duryl)nitroxyl radicals, which show *a*(Hβ) ca. 9 G [15].

We have been able to reproduce Brubaker's results [8]. Photolysis of Cp₂TiCl₂ in toluene containing nitrosodurene, at -56°C, gave initially a triplet, *a*(N) 27.2 G, *g* 2.0050 (Spectrum E). As the temperature was raised, this spectrum was rapidly replaced by a second spectrum showing hyperfine coupling to one nitrogen and one hydrogen atom; the coupling constants were similar, so that the spectrum approximates to a quartet, and they varied with temperature and with solvent, but at room temperature, in toluene, *a*(N) = 13.8, *a*(H) = 15.3 G. If tetrahydrofuran was added, the spectrum of the cyclopentadienyl radical, and of a strong singlet due to a titanium species, also became apparent. This is illustrated in Figure 1, where (at -47°C), the quartet shows *a*(N) 14.0, *a*(H) 15.0 G, *g* 2.0051 (Spectrum F).

However, if nitrosodurene was photolysed alone in toluene, it showed the

* Metal peroxy radicals (e.g. Bu₃SnOO• or Ph₃PbOO•), however, can often be observed [1d,12] (see below).

superimposed spectra of a triplet, $a(N)$ 13.5 G (Spectrum G), and of again a "quartet", $a(N)$ 14.0, $a(H)$ 15.0 G (at -60°C) (Spectrum H).

As spectra F and H appear to be indistinguishable, it is questionable whether either represents the cyclopentadienyl(duryl)nitroxyl radical*. An interpretation equally consistent with the evidence would be that spectra A, B, F, and H represent instead the radical $(\text{Me}_4\text{C}_6\text{H})(\text{H})\text{NO}\cdot$, and A' represents the radical $(\text{Me}_4\text{C}_6\text{H})(\text{D})\text{NO}\cdot$; a hyperfine coupling $a(H)$ ca. 15 G would not be unreasonable in such a radical (e.g. $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{N}(\text{H})\text{O}\cdot$, $a(H) = 12.6$ G) [16]. Allowing for the normal dependence of nitroxyl hyperfine couplings on temperature and solvent, spectra C and G could relate to the same radical, perhaps $(\text{Me}_4\text{C}_6\text{H})_2\text{NO}\cdot$, and spectrum E may refer to a spin-trapped oxygen radical, perhaps a peroxytitanium species $(\text{Me}_4\text{C}_6\text{H})(\text{CpCl}_2\text{TiOO})\text{NO}\cdot$; for comparison the radical $(\text{Me}_4\text{C}_6\text{H})(\text{Bu}'\text{O})\text{NO}\cdot$ shows $a(N)$ 25.2 G, g 2.0054 [14].

Nitrosodurene was therefore added to a solution of cyclopentadienylpotassium in tetrahydrofuran in order to generate the potassium salt of *N*-cyclopentadienyl-*N*-durylhydroxylamine. The product showed a strong ESR spectrum $a(N)$ 13.25, $a(H)$ 5.5 G, g 2.0063 at 288 K. These values are close to those reported by Gianotti [13] (spectrum D), and we take them to relate to the authentic cyclopentadienyl(duryl)-nitroxyl radical.

It is not necessary that Gianotti's radical (D), or the assumed cyclopentadienyl-hydridonitroxyl radical (A, B, F, and H) should be formed by simple addition of the appropriate free radical to nitrosodurene, and indeed we note that Maillard and Gianotti [17] were unable to observe the formation of the radical $(\text{Me}_4\text{C}_6\text{H})(\text{H})\text{NO}\cdot$ from the photolysis of alkylcobaloximes or of tributyltin hydride in the presence of nitrosodurene. They suggested that the radical was rapidly reduced further to the diamagnetic hydroxylamine $(\text{Me}_4\text{C}_6\text{H})(\text{H})\text{NOH}$, and it is possible that the Cp_2TiCl_2 is less reactive in donating this second hydrogen atom.

This emphasises once again that the spin trapping technique is a poor alternative to the direct observation of a radical, and that results obtained using spin-traps should be interpreted with a great deal of caution.

The titanium(III) radical. The low solubility of Cp_2TiCl_2 in non-coordinating solvents limits the useful results which can be obtained under these conditions. Photolysis of Cp_2TiCl_2 in degassed toluene showed only a weak spectrum of the $\text{Cp}\cdot$ radical, and no clear signal which could be ascribed to a Ti^{III} species, but in toluene saturated with air, the $\text{Cp}\cdot$ radical could be observed from -80°C up to -10°C , together with a strong persistent singlet, g 2.0129, ΔH_{pp} 0.8 G, with no detectable satellites due to titanium coupling. The conditions of formation, persistence, high g factor, and absence of hyperfine structure, characterise this as a titaniumperoxyl radical, probably $\text{CpCl}_2\text{TiOO}\cdot$. For comparison, the g factors of Group IVB peroxy radicals which can be prepared in the same way are $\text{Bu}_3\text{SnOO}\cdot$ 2.0260 [12] and $\text{Ph}_3\text{PbOO}\cdot$ 2.0280 [1d].

We have mentioned above that we have never observed cyclopentadienyl radicals to react with oxygen under these conditions. If the cyclopentadienylperoxyl radical were to be formed, it would be expected to show a lower g -factor and the presence of

* The intensity of the spectrum of the cyclopentadienyl radical was unchanged when nitrosodurene was added to a solution of BuCpSnCl_2 or of CpSnPh_3 , irradiated with UV light, and no spectrum A was observed, but when CpPbPh_3 was treated similarly, the spectrum A did develop.

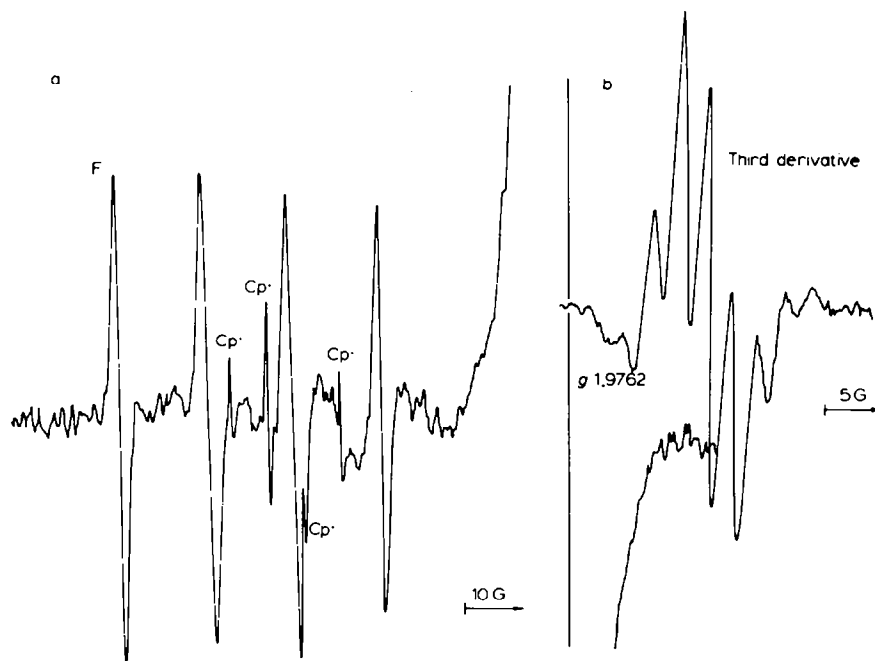


Fig. 1. (a) ESR spectrum from the photolysis of a mixture of Cp_2TiCl_2 and nitrosodurene in toluene/THF at -47°C ; (b) the third derivative of the principal signal, at -30°C .

doublet hyperfine structure, like that which is seen in the cyclopentylperoxyl radical (g 2.0154, $a(\text{H}\gamma)$ 7.4 G) [18] or the cyclopent-3-enylperoxyl radical (g 2.0152, $a(\text{H}\gamma)$ 7.7 G) [19].

In ethereal solvents, or in the presence of coordinating solutes (including nitrosodurene), Cp_2TiCl_2 is much more soluble, and strong, persistent, spectra of Ti^{III} species can then be observed directly. Figure 2 shows the ESR spectrum which is obtained from the photolysis of Cp_2TiCl_2 in toluene/tetrahydrofuran; the first derivative signal is a singlet, ΔH_{pp} 4 G at -14°C , g 1.9768, showing satellites due to coupling to titanium, $a(^{47/49}\text{Ti})$ 13 G*. Essentially the same singlet is seen when nitrosodurene is present (g 1.9762, ΔH_{pp} 6 G, at -1°C , $a(\text{Ti})$ 13 G), (Fig. 1) and, as Brubaker reported [8] there was no evidence for spin-trapping of the Ti^{III} species by the nitrosodurene.

This Ti^{III} radical is similar to that obtained by Brubaker (g 1.976, $a(\text{Ti})$ ca. 13 G) from the photolysis of Cp_2TiCl_2 in tetrahydrofuran [8], and by Symons (g 1.977, $a(\text{Ti})$ 13 G) from the γ -radiolysis of CpTiCl_3 in a methyltetrahydrofuran glass at 77 K, followed by annealing at higher temperatures [20]. Both authors ascribed this spectrum to the radical CpTiCl_2 (presumably solvated by the tetrahydrofuran or methyltetrahydrofuran), which, together with our observation of the spectrum of the cyclopentadienyl radical, would be in accord with the reaction involving simple

* ^{47}Ti , 7.75% abundance, I 5/2, γ -0.3148; ^{49}Ti , 5.51% abundance, I 7/2, γ -0.3149.

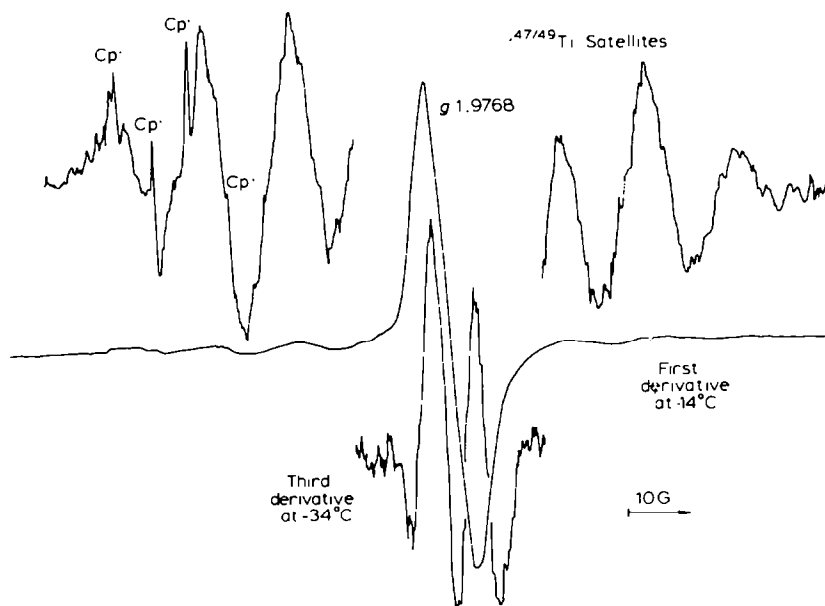


Fig. 2. ESR spectrum from the photolysis of Cp₂TiCl₂ in tetrahydrofuran at -14°C (first derivative) and at -34°C (third derivative). The upper insets show at higher gain, the ^{47/49}Ti satellites in the former spectrum, and the central lines of the spectrum of the cyclopentadienyl (Cp•) radical.

cleavage of the cyclopentadienyltitanium bond (eq. 3).



This interpretation is supported by experiments in which 2-methyl-2-nitropropane was used as a spin trap. Neumann has shown that nitro compounds, RNO₂ can serve as useful traps for metal-centred radicals, [•]ML_n, by giving the persistent nitroxyl radicals RN(O•)OML_n or aminyl radicals, RNOML_n [21], and we have used Me₃CNO₂ for trapping the metal radicals derived from cyclopentadienyltin [1c] and cyclopentadienyllead compounds [1d].

No reaction is apparent when Cp₂TiCl₂ and Me₃CNO₂ are mixed in toluene, but when the mixture is photolysed, the spectrum shown in Fig. 3 is generated. The minor component is the binomial sextet of the cyclopentadienyl radical, and the major component is a radical, *g* 2.0054, showing the triplet splitting characteristic of a large spin density on nitrogen, *a*(N) 17.62 G, and further septet splitting from two equivalent chlorine atoms, *a*(Cl) 0.83 G. A computer simulation of the septet at lowest field, which is not distorted by lines from the cyclopentadienyl radical, is shown in the inset to Fig. 3. The high *g* factor suggests that this is a nitroxyl rather than an aminyl radical [1c,d,21] the Ti^{III} radical from reaction 3 being trapped by reaction 4.



Thus far, the results appear to be straightforward. The first complication arises when the signals ascribed to Cp•TiCl₂ are examined under higher resolution. The contours of the apparent singlets show clearly that they are in fact unresolved

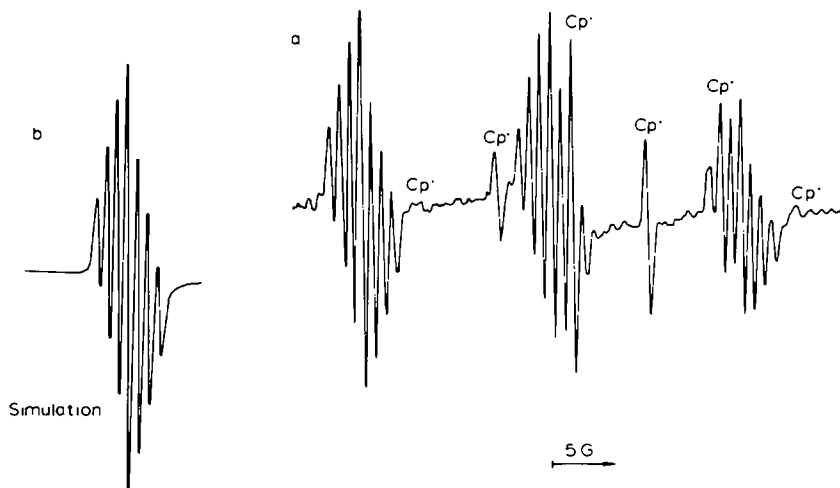


Fig. 3. (a) ESR spectrum from the photolysis of Cp_2TiCl_2 in the presence of 2-methyl-2-nitropropane in toluene at -33°C ; (b) computer simulation of the septet at lowest field, $a(2\text{Cl})$ 0.83 G, ΔH_{pp} 0.375 G.

multiplets, and these can be resolved when the spectra are recorded as the third rather than the first derivatives. The observed spectra are shown as insets to Fig. 1 and 2, and it will be seen that they now appear as, apparently, a quintet or a doublet, respectively.

A further complication appears when the Ti^{III} radical is generated in toluene containing ether. Above about -10°C , the principal spectrum observed, apart from that of the cyclopentadienyl radical, was a broad (ΔH_{pp} 5.5 G) unresolved multiplet, g 1.9752, but at lower temperatures (down to -63°C) a clear multiplet could be observed at lower field, with g ca. 1.9831. Both signals could be resolved as their third derivatives as shown in Fig. 4. The group at high field now presented the same appearance as the multiplet illustrated in Fig. 1; the group at lower field appeared to contain 14 or 15 lines, which might arise from a doublet coupling superimposed on that derived from two chlorine atoms.

Similarly, with pyridine in toluene, two signals were observed. At room temperature, the only signal (apart from that of the cyclopentadienyl radical), was a line at g 1.9810, ΔH_{pp} 6.5 G (Fig. 5), which could be resolved as the third derivative, into a doublet (insert to Fig. 5). As the temperature was reduced, a second line, ΔH_{pp} 7 G, developed, now at higher field, g 1.9732 (see Fig. 5), which could not be resolved further as a higher derivative; below about -50°C , this line became dominant.

Complications of this nature were not observed when a phosphine rather than an amine was present. Photolysis of Cp_2TiCl_2 in toluene containing triphenylphosphine gave, from -80°C to -6°C , the cyclopentadienyl radical and a doublet, g 1.9769, which can reasonably be ascribed to the radical $\text{CpCl}_2\dot{\text{T}}\text{iPPh}_3$, $a(\text{P})$ 8.2 G, $a(\text{Ti})$ 13 G. Similarly, when triisopropylphosphine was present, the dominant spectrum was that of a doublet, presumably due to the radical $\text{CpCl}_2\dot{\text{T}}\text{iPPr}^i_3$, $a(\text{P})$ 7.5 G, g 1.9768. Tiroflet [22] has described the formation of a radical, perhaps $\text{Cp}_2\text{TiCl}_2\text{PMe}_2\text{Ph}^\cdot$, $a(\text{P})$ 22 G, g 1.9865, from the electrolytic reduction of Cp_2TiCl_2 in the presence of Me_2PhP .

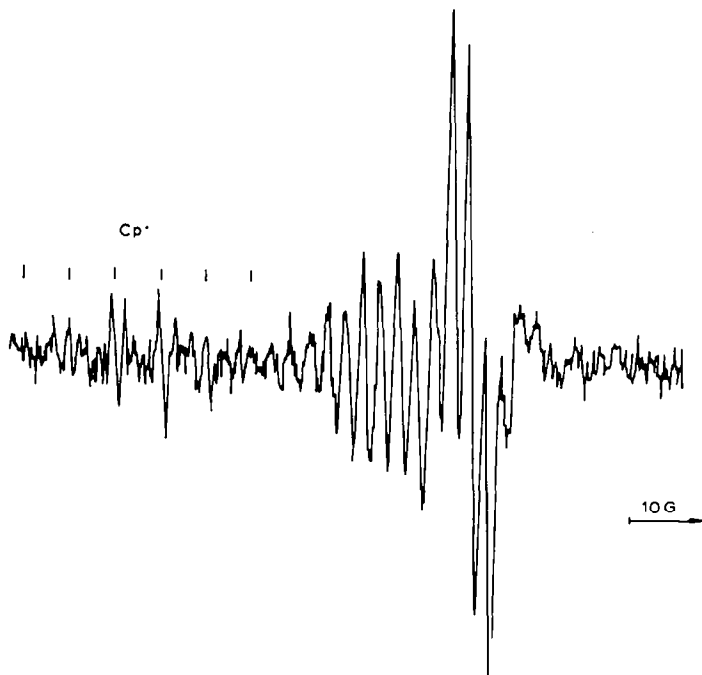


Fig. 4. Third derivative display of the ESR spectrum observed on photolysis of Cp_2TiCl_2 in diethyl ether at -52°C .

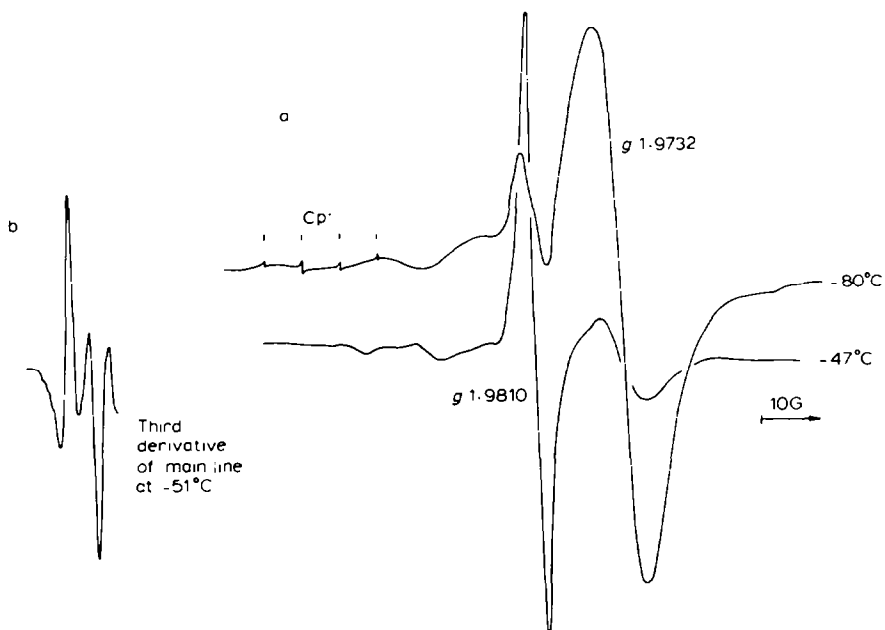


Fig. 5. (a) ESR spectrum from the photolysis of Cp_2TiCl_2 in toluene/pyridine mixture at -47°C and -80°C ; (b) the third derivative of the principal signal in the former spectrum.

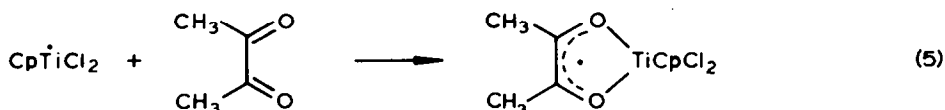
Not enough is known about the behaviour of titanium(III) compounds in solution to enable the two titanium radicals which we observe to be identified with any confidence, and attempts to assign the hyperfine coupling to particular protons or chlorine atoms* in the various possible mononuclear or binuclear solvated or unsolvated species would be largely speculative.

The commonly accepted model of the simple homolysis of the cyclopentadienyl-titanium bond (eq. 3) remains the best for the photolysis of Cp_2TiCl_2 in tetrahydrofuran at or near room temperature, but it provides an incomplete picture, particularly when other solvents or co-solvents are involved, and loss of hydrogen from a cyclopentadienyl ligand to give Ti-H species is a distinct possibility.

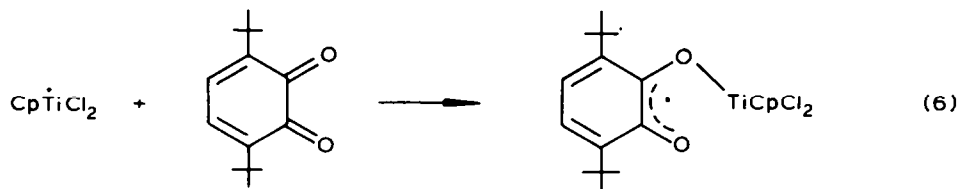
The behaviour of the Ti^{III} fragment towards some other co-reagents was examined briefly.

Photolysis of Cp_2TiCl_2 in toluene containing ethyl bromide or t-butyl bromide showed no spectrum of the corresponding alkyl radical. Any halogen-abstraction reaction by a Ti^{III} radical is apparently slower than it is by a silicon or tin radical, although this does not exclude the abstraction of chlorine from chloroform as shown in eq. 2.

Biacetyl is a very effective trap for metal-centred radicals, and the ESR spectra show a variety of types of bonding in the adducts. Photolysis of a solution of Cp_2TiCl_2 and biacetyl in toluene from -70°C to -14°C showed a strong spectrum of the cyclopentadienyl radical together with a septet, $a(6\text{H})$ 9.25 G, ΔH_{pp} 1.5 G, g 2.0034. Comparison with the adducts formed by organotin radicals [1b] suggests that this is a *cis*-complex, probably 5-coordinate rather than fast-fluxional (eq. 5), any hyperfine coupling to chlorine, or non-equivalence between the methyl groups being lost in the line width.



3,6-Di-t-butyl-1,2-benzoquinone similarly is a useful trap for metal-centred radicals and the structural possibilities for the adduct are relatively limited. Photolysis with Cp_2TiCl_2 in toluene gave a strong spectrum consisting of a doublet of doublets, $a(\text{H})$ 3.4 and 4.1 G at $+81^\circ\text{C}$, and 3.3 and 4.1 G at 34°C , g 2.0036, ΔH_{pp} 0.7 G, suggesting that a monodentate adduct is formed which is not rapidly fluxional on the ESR time scale.



* We note that Krusic and Tebbe [23] have recently reported hyperfine coupling by bridging hydrogen in the complex $\text{Cp}_2\text{Ti}(\mu\text{H})(\mu\text{Cl})\text{AlEt}_2$, $a(\text{H})$ 5.6 G, $a(\text{Ti})$ 10.0 G, g 1.9857.

Experimental

Samples were sealed under vacuum in Suprasil silica tubes, and photolysed in the cavity of a Varian E4 spectrometer, with light from a 500 W high pressure mercury arc, by the technique described previously [1]. Higher derivative signals were obtained using a Telmore subharmonic generator.

Two different specimens of nitrosodurene were used, and were authenticated by preparing the adducts with ethyl radicals, generated by photolysing a mixture of hexabutylditin and ethyl bromide.

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References

- 1 (a) P.J. Barker, A.G. Davies, and M.-W. Tse, *J. Chem. Soc., Perkin Trans. II* (1980) 941; (b) P.J. Barker, A.G. Davies, J.A.-A. Hawari, and M.-W. Tse, *ibid.*, (1980) 1488; (c) A.G. Davies and J.A.-A. Hawari, *J. Organometal. Chem.*, 201 (1980) 221; (d) A.G. Davies, C. Gaffney, P.G. Harrison, and J.A.-A. Hawari, *J. Chem. Soc., Perkin Trans. II*, (1982) 631.
- 2 A.G. Davies, *Pure Applied Chem.*, 54 (1982) 23.
- 3 Reviewed by (a) C.R. Bock and E.A. Koerner von Gustorf, *Adv. Photochem.*, 10 (1977) 221; (b) G.L. Geoffroy and M.W. Wrighton, *Organometallic Photochemistry*, Academic Press, New York, 1979, Chap. 5.
- 4 R.W. Harrigan, G.S. Hammond, and H.B. Gray, *J. Organometal. Chem.*, 81 (1974) 79.
- 5 E. Vitz and C.H. Brubaker, *J. Organometal. Chem.*, 82 (1974) C16.
- 6 E. Vitz, P.J. Wagner, and C.H. Brubaker, *J. Organometal. Chem.*, 104 (1976) C33.
- 7 E. Vitz and C.H. Brubaker, *J. Organometal. Chem.*, 107 (1976) 301.
- 8 Z.-T. Tsai and C.H. Brubaker, *J. Organometal. Chem.*, 166 (1979) 199.
- 9 G.B. Watts and K.U. Ingold, *J. Am. Chem. Soc.*, 94 (1972) 491; P.M. Blum, A.G. Davies and W.P. Neumann, unpublished work.
- 10 H.U. Buschhaus and W.P. Neumann, *Angew. Chem. Int. Ed. Engl.*, 17 (1978) 59; H.U. Buschhaus, W.P. Neumann, and Th. Apoussidis, *Liebigs Ann. Chem.*, (1981) 1190.
- 11 R.S.P. Coutts, R.L. Martin, and P.C. Wailes, *Austral. J. Chem.*, 24 (1971) 2533.
- 12 A.G. Davies and J. Luszyk, *J. Chem. Soc., Perkin Trans II*, (1981) 692, and unpublished work.
- 13 E. Klähne, C. Gianotti, H. Marquet-Ellis, G. Folcher, and R.D. Fischer, *J. Organometal. Chem.*, 201 (1980) 399.
- 14 S. Terabe, K. Kurama, and R. Konaka, *J. Chem. Soc. Perkin Trans. II* (1973) 1252.
- 15 T. Suehiro, M. Kamimori, K. Tokumaru, and M. Yoshida, *Chem. Letters*, (1976) 531.
- 16 P.B. Ayscough, F.P. Sargent, and R. Willson, *J. Chem. Soc. B*, (1966) 903.
- 17 P. Maillard and C. Gianotti, *Canad. J. Chem.*, 60 (1982) 1402.
- 18 J.E. Bennett and R. Summers, *J. Chem. Soc., Faraday Trans. II*, (1973) 1043.
- 19 A.J. Bloodworth and H.J. Eggelte, *Tetrahedron Lett.*, (1980) 2001.
- 20 M.C.R. Symons and S.P. Mishra, *J. Chem. Soc., Dalton Trans.*, (1982) 2258.
- 21 K. Reuter and W.P. Neumann, *Tetrahedron Lett.*, (1978) 5235.
- 22 N. El-Murr, A. Chaloyard, and J. Tiroflet, *J. Chem. Soc., Chem. Commun.*, (1980) 446.
- 23 P.J. Krusic and F.N. Tebbe, *Inorg. Chem.*, 21 (1982) 2900.