Journal of Organometallic Chemistry, 264 (1984) 253–261
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

AN ESR STUDY OF THE PHOTOLYSIS OF CYCLOPENTADIENYLZIRCONIUM COMPOUNDS *

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(Received August 26th, 1983)

Summary

ESR spectroscopy has been used to study the photolysis of the compounds $(C_5H_5)_2ZrCl_2$, $(Me_5C_5)_2ZrCl_2$, $(C_5H_5)_2ZrMe_2$, $(C_5H_5)_2ZrMeCl$ and $(C_5Me_5)_2ZrMe_2$ in fluid solution.

With the first two compounds, the primary reaction is the loss of the cyclopentadienyl radical, and with the second two it is the loss of the methyl radical, but from $(C_5Me_5)_2ZrMe_2$, both the cyclopentadienyl and methyl radicals could be identified.

In every case, the spectrum of a zirconium(III) radical could be observed at high field, but frequently this could be resolved into a doublet, indicating the formation of an unidentified zirconium(III) hydride.

Various reagents were added to intercept the initially formed zirconium(III) species, and the following spin adducts have been identified with varying degrees of certainty: $C_5H_5Zr(Cl_2)OO^{\cdot}$, $Me_5C_5Zr(Cl_2)OO^{\cdot}$, $C_5H_5Zr(Cl_2)ON(Bu^t)O^{\cdot}$, $(C_5H_5)_2Zr(Cl)ON(Bu^t)O^{\cdot}$, $(C_5Me_5)_2Zr(Cl)ON(Bu^t)O^{\cdot}$, $(C_5H_5)_2\dot{Z}rMe(PPh_3)$, $(C_5H_5)_2Zr(Me)OCMeCMeO^{\cdot}$, $2,5\text{-}Bu^t_2\text{-}6[(C_6H_5)ZrCl_2O]C_6H_2O^{\cdot}$, $2,5\text{-}Bu^t_2\text{-}6[(C_5H_5)_2Zr(Me)O]C_6H_2O^{\cdot}$, and $2,5\text{-}Bu^t_2\text{-}6[(C_5H_5)Zr(Me_2)O]C_6H_2O^{\cdot}$.

Introduction

A substantial amount of work has now been carried out on the photolysis of cyclopentadienyl derivatives of Main Group metals [1]. Whatever other ligands may be present on the metal, and whether the cyclopentadienyl group be η^1 or η^5 bonded (e.g. $C_5H_5SnBu_3$ or $(C_5H_5)_2Sn$ respectively), in all the examples studied as yet the

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* Dedicated to Professor R. Calas on the occasion of his 70th birthday (April 8th, 1984) in recognition of his outstanding work in organometallic chemistry during more than 30 years.

0022-328X/84/$03.00

initial reaction involves homolysis of the cyclopentadienyl–metal bond to give a cyclopentadienyl radical and a metal radical [1–3]. The same pattern of behaviour applies to pentamethylcyclopentadienyl derivatives [4].

Within the series of transition metals, most work has been carried out on the cyclopentadienyl derivatives of titanium and zirconium, and we recently reported an ESR study of the photolysis of dicyclopentadienyltitanium dichloride [5]. We now describe a similar study of a series of zirconium derivatives, namely $(C_5H_5)_2ZrCl_2$, $(Me_5C_5)_2ZrCl_2$, $(C_5H_5)_2ZrMeCl$, $(C_5H_5)_2ZrMe_2$, and $(Me_5C_5)_2ZrMe_2$.

The state of published work in this field is as follows.

Photolysis of $(C_5H_5)_2ZrCl_2$ shows the ESR spectrum of the $C_5H_5^{\cdot}$ radical [1,6], and if the reaction is carried out in the presence of t-butyl chloride it can be used as a preparative route to $C_5H_5ZrCl_3$ [7]. The reaction is therefore thought to proceed as shown in eq. 1.

$$(C_5H_5)_2ZrCl_2 \rightarrow C_5H_5^{\cdot} + C_5H_5\dot{Zr}Cl_2 \xrightarrow{Bu^tCl} C_5H_5ZrCl_3 \qquad (1)$$

Photolysis of $(C_5H_5)_2ZrMeCl$ shows a singlet ESR spectrum, g 1.980, $a(^{91}Zr)$ 40.3 G, which was ascribed to the zirconium(III) species resulting from homolysis of the Zr–Me bond (eq. 2) [6].

$$(C_5H_5)_2ZrMeCl \xrightarrow{h\nu} (C_5H_5)_2\dot{Zr}Cl + Me^{\cdot} \qquad (2)$$

The behaviour of $(C_5H_5)_2ZrMe_2$ is more complicated. The ultimate products are $(C_5H_5)_2Zr$ and methane [8], and the precursor showed an eratic CIDNP effect [9]. The ESR spectrum of the zirconium species now appears as a doublet, a(1H) 7.00 G, g 2.000, suggesting a transfer of hydrogen from a ligand to the metal, and the spectrum of this zirconium(III) species increased in intensity when the light was shuttered, implying that it can be thermally regenerated, perhaps from $(C_5H_5)_2Zr$ [10]. Some of the reactions which might be involved are shown in eq. 3.

$$\begin{tikzcd} (C_5H_5)_2ZrMe_2 \arrow[r, rightleftharpoons, "h\nu"] & (C_5H_5)_2\dot{Zr}Me + Me^{\cdot} \arrow[r] \arrow[d, "h\nu"] & MeH \\ & Me^{\cdot} + (C_5H_5)_2Zr{:} \arrow[r] & \text{a zirconium(III) hydride} \end{tikzcd} \qquad (3)$$

No work appears to have been published on the photolysis of pentamethylcyclopentadienylzirconium compounds.

Results and discussion

$(C_5H_5)_2ZrCl_2$

Our conclusions regarding the photolysis of $(C_5H_5)_2ZrCl_2$ are illustrated in Scheme 1. Irradiation in toluene, xylene, or tetrahydrofuran, alone or in the presence of the various reagents discussed below, showed the ESR spectrum of the cyclopentadienyl radical; an example is shown in Fig. 1. Addition of di-t-butyl peroxide as a photolytic source of t-butoxyl radicals enhanced the intensity of the spectrum, suggesting that displacement of the $C_5H_5^{\cdot}$ radical by bimolecular (S_H2) attack of the t-butoxyl radical at zirconium may be superimposed on the unimolecular homolysis.

The effect of adding acetaldehyde was much more pronounced. We have no evidence for any thermal reaction between $(C_5H_5)_2ZrCl_2$ and acetaldehyde. An S_H2

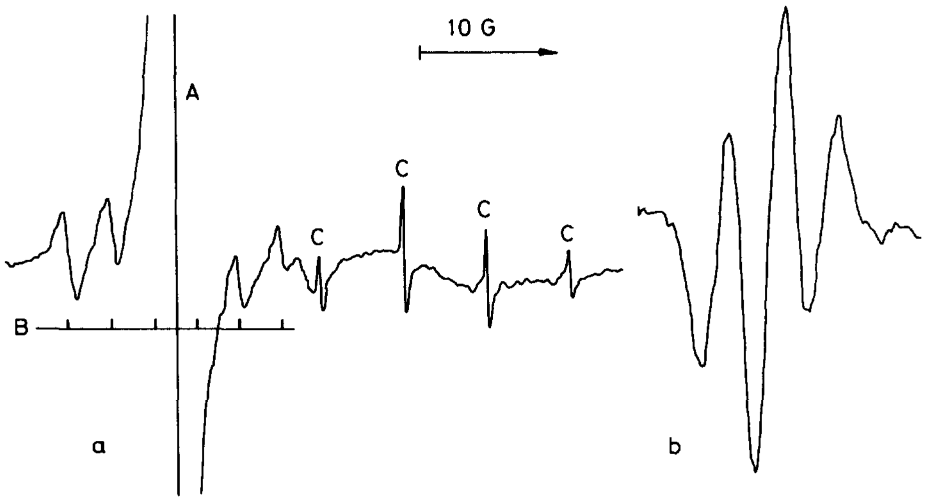

Fig. 1. (a) ESR spectrum obtained from the photolysis of $(C_5H_5)_2ZrCl_2$ in benzene at −20°C in the presence of oxygen, showing the $C_5H_5ZrCl_2OO^{\cdot}$ radical (A) with the ^{91}Zr satellites (B), and the central lines of the $C_5H_5^{\cdot}$ radical (C). (b) Spectrum obtained from the photolysis of $(C_5H_5)_2ZrCl_2$ in toluene in the absence of oxygen at +25°C, showing signals due to zirconium(III) radicals, *g* 1.9906 G.

reaction by the carbonyl triplet at zirconium, similar to that which we have established at boron [11], and at tin [12] appears unlikely because no spectrum of the radical $CH_3\dot{C}HOZr(C_5H_5)Cl_2$ could be detected, and the enhancing effect is probably due to photosensitization by the aldehyde.

Unless the sample tubes were rigorously outgassed, the photolysis was accompanied by the appearance of a strong, persistent, broad singlet at low field, *g* 2.0145, ΔH_{pp} 1.3 G, showing satellites due to ^{91}Zr coupling *, $a(^{91}Zr)$ 3.35 G (see Fig. 1). We have shown that the cyclopentadienyl radical does not show the spectrum of a peroxyl radical under these conditions [4], and the provenance, persistance, *g*-value, line shape, and hyperfine coupling characterise this signal as being due to a zirconium peroxyl radical, $(C_5H_5)Zr(Cl_2)OO^{\cdot}$. No example of a zirconium peroxyl radical has been reported previously, but the titanium analogue, $(C_5H_5)Ti(Cl_2)OO^{\cdot}$, obtained by a similar method, showed *g* 2.0129, ΔH_{pp} 0.8 G [5].

If air was carefully excluded, this low-field peroxyl singlet was replaced by a group of three lines at high field (see Fig. 1) which could be interpreted as either a triplet, a(2H) 3.8 G, *g* 1.9906, or, more probably, as an overlapping singlet and a doublet with a(1H) 7.6 G, with the same *g*-values. This signal or signals can be ascribed to zirconium(III) species, the multiplet coupling resulting from an unidentified zirconium hydride. Similar formation of a hydride species was observed with $(C_5H_5)_2TiCl_2$ [5].

Some metal-centred radicals such as $R_3Sn^{\cdot}$ or $R_3Si^{\cdot}$ will abstract bromine from an alkyl bromide so that the ESR spectrum of the alkyl radical can be observed, and a reaction of this type is assumed to be involved in the preparation of $(C_5H_5)ZrCl_3$ by

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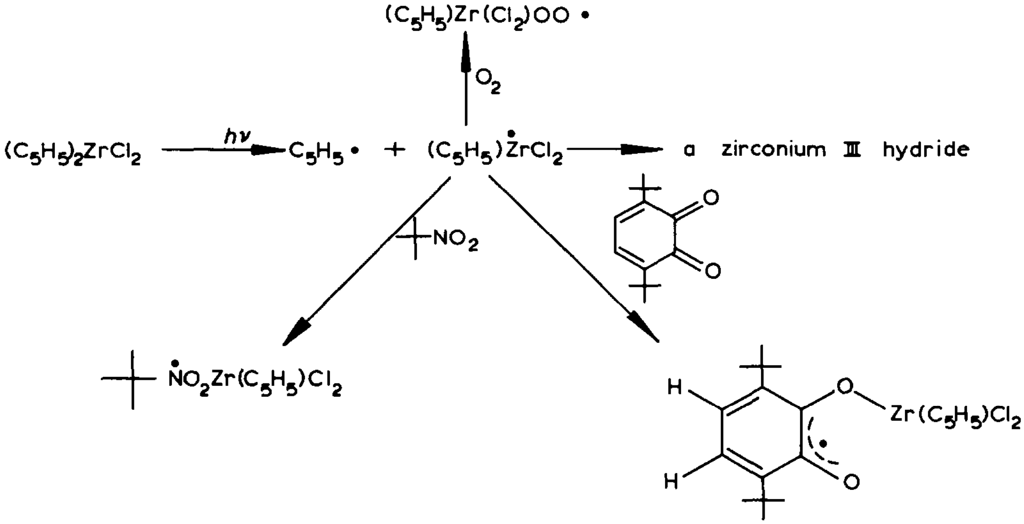
* ^{91}Zr, *I* 5/2; natural abundance 11.23%.

SCHEME 1



photolysis of $(C_5H_5)_2ZrCl_2$ in the presence of t-butyl chloride. However, photolysis of $(C_5H_5)_2ZrCl_2$ in the presence of ethyl bromide did not show the ESR spectrum of the ethyl radical, and abstraction of bromine by the zirconium radical cannot be fast enough to establish a detectable concentration of ethyl radicals under our conditions; similar negative results were reported previously for the $(C_5H_5)\dot{T}iCl_2$ radical obtained by photolysis of $(C_5H_5)_2TiCl_2$ [5].

Metal-centred radicals are characterised also by adding to 1,2-dicarbonyl compounds. However, photolysis of $(C_5H_5)_2ZrCl_2$ in the presence of biacetyl at −30°C in tetrahydrofuran showed the spectrum of the $C_5H_5^{\bullet}$ radical, and a spectrum with *a*(3H) 14.2, *a*(3H) 1.75, *a*(1H) 2.0 G, *g* 2.0052. The doublet coupling indicates that this is the protic rather than the metallic derivative of the semidione; for *trans*-HOCMeCMeȮ in toluene, we have previously reported *a*(3H) 13.4, *a*(3H) 2.6, *a*(1H) 2.1 G [3].

In a similar experiment, 3,6-di-t-butyl-1,2-benzoquinone showed a spectrum with *a*(1H) 3.8, *a*(1H) 3.4, $a(^{91}Zr)$ 1.2 G, *g* 2.0044 at −20°C in toluene; under these conditions, the dione acts as a monodentate group, and the zirconium moiety, presumably, $(C_5H_5)\dot{Z}rCl_2$ is not migrating rapidly between the two oxygen atoms (see Scheme 1). At +32°C, the central pair of lines could not be resolved at first or third derivative, but the spectrum was weaker, and it is not clear whether rapid migration was occurring. In the spectrum of the titanium analogue, the ring protons of the quinone moiety remain magnetically non-equivalent up to +80°C [5].

Metallic radicals are also reactive towards nitro compounds, and again various modes of bonding are possible [13]. Photolysis of $(C_5H_5)_2ZrCl_2$ in the presence of nitromethane, nitroethane, or 2-nitropropane gave only weak spectra, but with 2-methyl-2-nitropropane in toluene the spectrum shown in Fig. 2 was obtained, showing *a*(N) 27.0, *a*(1Cl) 1.5 G, *g* 2.0040 from −40 to −4°C, but *a*(2Cl) 1.6 G above −4°C. In tetrahydrofuran, the former spectrum predominated to a higher temperature (see Fig. 2) but above +33°C, both spectra could be observed.

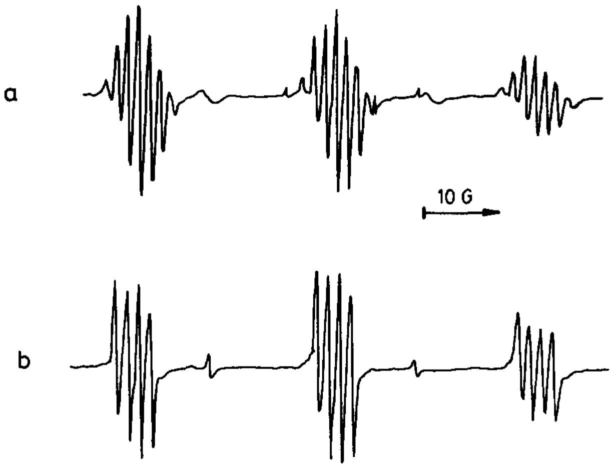


Fig. 2. ESR spectra obtained from the photolysis of $(\mathrm{C_5H_5})_2\mathrm{ZrCl_2}$ in the presence of $\mathrm{Bu^tNO_2}$. (a) In toluene at −4°C; a(N) 27.0, a(2Cl) 1.5 G. (b) In tetrahydrofuran at −3°C; a(N) 27.5, a(1Cl) 1.6 G.

The species showing hyperfine coupling to two chlorine atoms is presumably the radical $\mathrm{Bu^tN(\dot{O})OZrCpCl_2}$ resulting from spin-trapping of $\mathrm{Cp\dot{Z}rCl_2}$. The second species is apparently a monochloro derivative, which might perhaps be formed by an electron-transfer process followed by nucleophilic displacement of chloride ion by the nitroalkane radical anion (eq. 4 and 5).

$$\mathrm{Cp_2ZrCl_2 + Bu^tNO_2 \rightarrow Cp_2\overset{+}{\dot{Z}}rCl_2 + Bu^tNO_2^{\cdot-}} \qquad (4)$$

$$\mathrm{Bu^tNO_2^{\cdot-} + Cp_2ZrCl_2 \rightarrow Bu^tN(\dot{O})OZrCp_2Cl + Cl^-} \qquad (5)$$

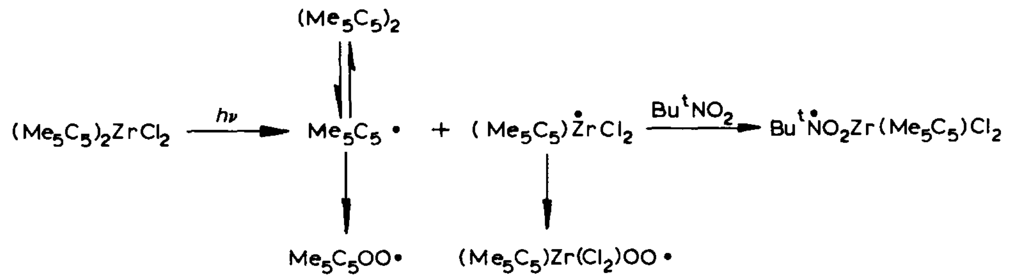
In comparison, $(\mathrm{C_5H_5})_2\mathrm{TiCl_2}$ under the same conditions, gave a spectrum showing hyperfine coupling to two equivalent chlorine atoms from −76 to +12°C (a(N) 17.6, a(2Cl) 0.83 G, g 2.0053; see Fig. 2 of ref. 5) and addition of the $\mathrm{Bu\dot{S}nCl_2}$ radical gave a spectrum with a(N) 30.0, a(2Cl) 0.31 G [14].

$(\mathrm{Me_5C_5})_2\mathrm{ZrCl_2}$

The behaviour of $(\mathrm{Me_5C_5})_2\mathrm{ZrCl_2}$ was similar to that of $(\mathrm{C_5H_5})_2\mathrm{ZrCl_2}$. Photolysis in degassed tetrahydrofuran gave only the spectrum of the $\mathrm{Me_5C_5^{\cdot}}$ radical, the intensity of which increased with time presumably because its decay to give the dehydro dimer is reversible (see Scheme 2) [4].

In tetrahydrofuran, no signal that might be ascribed to a zirconium(III) species could be detected, but in toluene a persistent broad signal developed, g ca. 1.9580, ΔH_{pp} 18.5 G. If air was present this signal was replaced by a strong broad singlet at g ca. 2.0148, and the spectrum of the pentamethylcyclopentadienyl radical was very weak. In toluene, the line at low field could be resolved into two lines with g 2.0170 and 2.0153 (and no pentamethylcyclopentadienyl radical could be detected). We have shown previously that the $\mathrm{Me_5C_5^{\cdot}}$ radical, unlike cyclopentadienyl itself, does react with oxygen to give the radical $\mathrm{Me_5C_5OO^{\cdot}}$, g 2.0151 [4] and therefore we ascribe the other signal with g 2.0170 to the radical $\mathrm{(Me_5C_5)Zr(Cl_2)OO^{\cdot}}$.

SCHEME 2



Again, 2-methyl-2-nitropropane proved to be a good trap for the zirconium radical, and between −10 and −20°C it gave a spectrum consisting of a triplet of quartets, a(N) 27.5, a(1Cl) 1.73 G, g 2.0041.

$(C_5H_5)_2ZrMe_2$

Experiments with alkylzirconocenes are complicated by the fact that the alkylzirconium group shows a reactivity towards oxygen [15], protic reagents, and polar double bonds [16] similar to that of a Grignard reagent. This limits the coreagents which can be added to probe the properties of the zirconium radicals.

Photolysis of $(C_5H_5)_2ZrMe_2$ in toluene shows the ESR spectrum of the methyl radical as the only organic fragment; a doublet ascribed to a zirconium(III) hydride developed at high field (a(H) 6.5, ΔH_{pp} 3.5 G, g 1.9842) and increased in intensity when the light was shuttered. Samuel, Maillard, and Gianotti [10] report a(1H) 7.00 G, g 2.0000.

If air was admitted to the sample, or even if air was passed through the solution during photolysis, no spectrum of the $(C_5H_5)_2Zr(Me)OO^{\cdot}$ radical could be observed. Brindley and Scotton [15] have shown that $(C_5H_5)_2ZrMe_2$ reacts with oxygen by a homolytic chain reaction involving the propagation steps 6 and 7.

$$Me^{\cdot} + O_2 \rightarrow MeOO^{\cdot} \tag{6}$$

$$MeOO^{\cdot} + (C_5H_5)_2ZrMe_2 \xrightarrow{k_p} (C_5H_5)_2Zr(Me)OOMe + Me^{\cdot} \tag{7}$$

The rate of self initiation, R_i was found to be 1.2×10^{-7} mol $l^{-1}s^{-1}$, and the propagation rate constant, k_p, was ca. 9.2×10^3 l $mol^{-1}s^{-1}$ at 40°C; under the experimental conditions, consumption of the reactant was complete in about 10 min.

In our ESR experiments, our inability to detect the radical $(C_5H_5)_2Zr(Me)OO^{\cdot}$ is probably due to the fact that it is rapidly removed by a peroxydemethylation reaction at zirconium, analogous to that of reaction 7; further, the rate of production of radicals by photolysis would give a rate of initiation of about 10^{-3} mol $l^{-1}s^{-1}$, and under these conditions, the reactant would rapidly be consumed.

Photolysis of $(C_5H_5)_2ZrMe_2$ in the presence of triphenylphosphine in toluene at −44°C gave a strong spectrum consisting of a doublet of quartets, which we ascribe to the radical $(C_5H_5)_2\dot{Z}rMe(PPh_3)$, a(P) 21.0, a(3H) 7.0 G, g 1.9876. This supports the picture of homolysis of one of the Zr–Me bonds, followed by trapping of the zirconium(III) fragment before a zirconium(III) hydride is formed. Similar complexes have been reported from the photolysis of $(C_5H_5)_2ZrR_2$ (R = CH_2SiMe_3 or CH_2Ph) in the presence of tertiary phosphines [6].

If $(C_5H_5)_2ZrMe_2$ was photolysed in the presence of ethyl bromide between −50 and −70°C, the spectrum of the ethyl radical was superimposed on that of the methyl radical. Any thermal reaction between ethyl bromide and the zirconocene would be expected to follow the same course as the known reaction with alkyltitanium(IV) compounds [17], and give propane and $(C_5H_5)_2ZrMeBr$ and $(C_5H_5)_2ZrBr_2$. The appearance of the ethyl radical thus probably indicates that the radical $(C_5H_5)_2\dot{Z}rMe$ is more reactive than $(C_5H_5)\dot{Z}rCl_2$ in abstracting bromine. This would be parallel to the ligand effect on the reactivity of tin(III) radicals, which drops as the number of chloro ligands increases [3].

Acetaldehyde reacted exothermically with $(C_5H_5)_2ZrMe_2$, and photolysis of the product showed the spectrum of the methyl radical with a greatly increased intensity, and the spectrum of the cyclopentadienyl radical was also apparent. These radicals probably arise from photolysis of $(C_5H_5)_2Zr(Me)OCHMe_2$, and possibly also of $(C_5H_5)_2Zr(OCHMe_2)_2$, which are the expected products of the reaction.

Under the same conditions, biacetyl showed a spectrum consisting of a quartet of quartets, a(3H) 9.0, a(3H) 7.9 G, g 2.0038, but above 32°C, an alternating line-width effect caused some of the lines to broaden until, at 70°C, the spectrum approximated to a septet. Hyperfine coupling to zirconium at about 2.1 G, was apparent. The magnitude of the hydrogen hyperfine coupling constants characterises this as a *cis*-complex (eq. 8) which at low temperature is slowly fluxional on the ESR time scale; the groups R_3 are probably $(C_5H_5)_2Me$. For comparison, the adduct formed between the radical $(C_5H_5)_2BuSn^{\cdot}$ and biacetyl shows a(6H) 8.5, g 2.0025 in toluene at −10°C [14].

(8)

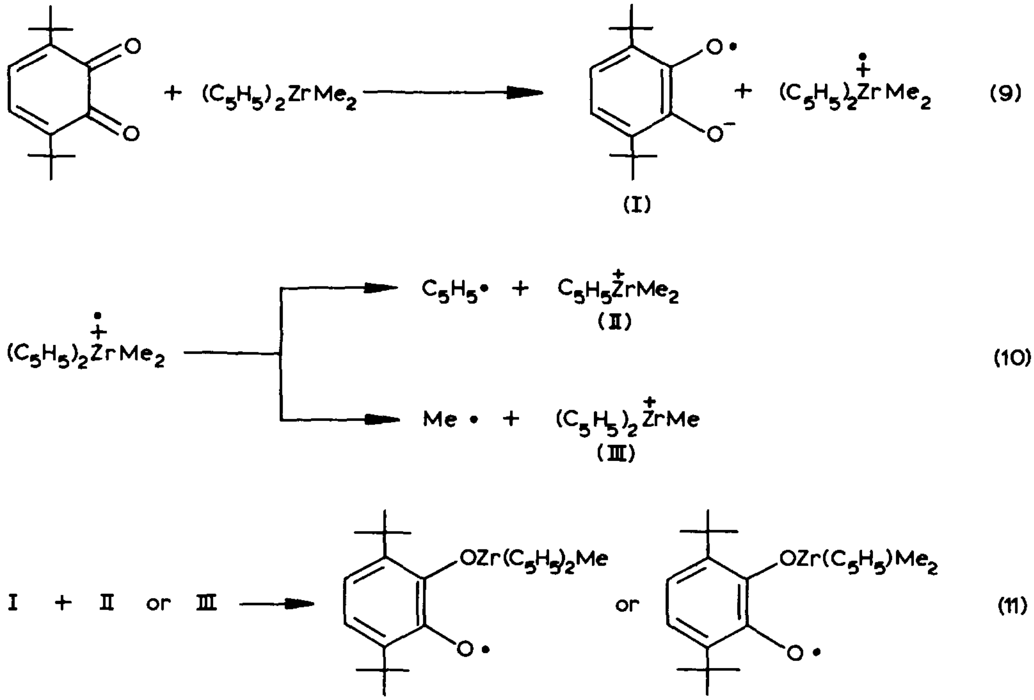
3,6-Di-t-butyl-1,2-benzoquinone reacted with $(C_5H_5)_2ZrMe_2$ at −40 to −70°C without photolysis, to show the spectra of two radicals a(1H) 3.3 and 3.9 G, g 2.0042, and a(1H) 3.2 and 3.8 G, g 2.0038, with relative intensities 5/2; neither showed evidence of fluxionality up to 70°C, when the spectra were lost. The radicals now results from an electron transfer process involving presumably the loss of a methyl radical or a cyclopentadienyl radical as shown in Scheme 3.

$(Me_5C_5)_2ZrMe_2$

Whereas photolysis of $(C_5H_5)_2ZrMe_2$ showed the spectrum of only the methyl radical as described above, photolysis of $(Me_5C_5)_2ZrMe_2$ showed principally the spectrum of the $Me_5C_5^{\cdot}$ radical, although the methyl radical could also be detected at low temperature (−63°C) during the initial stage of the photolysis. The signal of a zirconium(III) species, g 1.9652, built up at high field as a broad singlet, ΔH_{pp} 10 G, which could not be resolved even as the third derivative.

This emphasises again that bonds to the Me_5C_5 ring are more readily cleaved than the corresponding bonds to the cyclopentadienyl ring itself, suggesting that the pentamethylation may confer thermodynamic stability on the radical. A previous notable example of this is the photosensitivity of pentamethylcyclopentadiene itself,

SCHEME 3



to give the pentamethylcyclopentadienyl radical and apparently a hydrogen atom, whereas, under the same conditions, cyclopentadiene itself does not react [4].

$(C_5H_5)_2ZrMeCl$

As would be expected from the behaviour of $(C_5H_5)_2ZrMe_2$, photolysis of $(C_5H_5)_2ZrMeCl$ showed the spectrum of the methyl radical, and the cyclopentadienyl radical was not detected. The signals for two zirconium(III) derivatives meanwhile developed at high field as broad singlets, one with *g* 1.9915, and a much weaker one with *g* 1.9783.

When the photolysis was carried out in the presence of ethyl bromide, the spectrum of the ethyl radical was also observed. The radicals $(C_5H_5)_2\dot{Z}rCl$ (eq. 13) and $(C_5H_5)_2\dot{Z}rMe$ are thus apparently more reactive towards ethyl bromide than is $(C_5H_5)\dot{Z}rCl_2$. This would be compatible with the reactivity of the corresponding tin(III) radicals which appears to follow the ligand sequence alkyl > C_5H_5 > Cl [14].

$$(C_5H_5)_2ZrMeCl \rightarrow (C_5H_5)_2\dot{Z}rCl + Me^{\cdot} \tag{12}$$

$$(C_5H_5)_2\dot{Z}rCl + C_2H_5Br \rightarrow (C_5H_5)ZrClBr + C_2H_5^{\cdot} \tag{13}$$

Conclusion

The contrasting relative ease of cleavage of bonds to zirconium (η^5-C_5H_5–Zr < Me–Zr) and to tin (η^1-C_5H_5–Sn > Me–Sn) reflects the relative strengths of the *pentahapto* and *monohapto* bonding. The cyclopentadienylzirconium bonding however can be weakened by pentamethylation of the ring, which apparently stabilises the cyclopentadienyl radical.

Caution must be exercised in discussing the behaviour of the initial zirconium(III) fragment because of the ESR evidence for the formation of unidentified zirconium(III) hydride species. Nevertheless, the absence of any hyperfine coupling to such hydride protons in the spectra of the spin adducts of the zirconium radicals suggests that the hydrogen transfer is subsequent to the initial homolysis, and that it is the initial zirconium(III) radicals which are trapped.

Experimental

The preparation of the cyclopentadienylzirconium compounds is described in ref. 15. Bis(pentamethylcyclopentadienyl)zirconium dichloride was prepared by Bercaw's method [18], then methylated with methyllithium [19].

The ESR experiments were carried out using a Varian E4 spectrometer, as described previously [5].

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