An E.S.R. Study of the Photochemistry of Zirconocene(IV) Alkyls and Chlorides†

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Low temperature photolysis in PhMe or MeC_6H_{11} of various zirconocene(IV) alkyls, aryls, chlorides, cyclopentadienyls, or hydrides $[Zr(\eta\text{-}C_5H_5)_2(R)X]$ leads to the e.s.r. characterisation of a number of Zr^{III} complexes: $[Zr(\eta\text{-}C_5H_5)_2R]$ (**1**) and $[Zr(\eta\text{-}C_5H_5)R_2]$ as well as their phosphine adducts, $[Zr(\eta\text{-}C_5H_5)_2Cl]$, and a Zr^{III} hydride (**2**); the primary photo-products from $[Zr(\eta\text{-}C_5H_5)_2R_2]$ (*e.g.*, R = CH_2Ph) are (**1**) and R·, with (**2**) derived from (**1**) by a dark reaction.

Little is known about the photochemical behaviour of organozirconium(IV) compounds, especially with respect to their reduction to Zr^{III}.[1,2] We now report results on $[Zr(\eta\text{-}C_5H_5)_2R_2]$ (R = Ph, $C_6H_4Me\text{-}p$, CH_2Ph, or CH_2SiMe_3) (see Scheme 1) and $[Zr(\eta\text{-}C_5H_5)_2Cl(X)]$ (X = $\eta\text{-}C_5H_5$, Cl, H, or Me) (see Scheme 2). A feature of this work is the characterisation of a number of organozirconium(III) species (**1**)—(**4**), and phosphine adducts (**1a**) and (**3a**); such complexes are exceedingly rare.[2]

Photolysis (Pyrex-filtered light from a 1 kW high-pressure Hg-Xe lamp) of $[Zr(\eta\text{-}C_5H_5)_2Ph_2]$ in toluene, deoxygenated and sealed in a quartz tube under argon, at ambient temperature gave an e.s.r. spectrum consisting of a 6.6 G doublet centred at $g = 1.987$. On turning off the light, the doublet first increased slightly in intensity and then slowly decreased. Very similar results were obtained with $[Zr(\eta\text{-}C_5H_5)_2(C_6H_4Me\text{-}p)_2]$.

At room temperature photolysis of $[Zr(\eta\text{-}C_5H_5)_2(CH_2Ph)_2]$ yielded a broad signal which resolved into a doublet when the irradiation was stopped. The signal observed during photolysis at −50 °C could be analysed in terms of doublet (a = 6.6 G, $g_{av} = 1.987$) which overlapped a 1 : 2 : 1 triplet (a, *ca.* 3 G). The latter exhibited ^{91}Zr satellites with a separation of 23.5 G. When the experiment was repeated at −85 °C these signals became broad and poorly resolved but we were then able to characterise the spectrum of the benzyl radical.

A more complicated picture emerges from the photolysis of $[Zr(\eta\text{-}C_5H_5)_2(CH_2SiMe_3)_2]$ but at −90 °C we successfully detected the transient $\cdot CH_2SiMe_3$. At −48 °C, in addition to broad signals, we observed what is probably a quintet [$a(^1H)$ = 2.4 G], which we assign as (**3**) (R = CH_2SiMe_3). At higher temperatures it was possible to identify a doublet identical with that found in the other systems.

These results provide strong evidence that the principal primary photolytic process is metal–carbon bond homolysis in $[Zr(\eta\text{-}C_5H_5)_2R_2]$ to yield the Zr^{III} complex (**1**) and R· (Scheme

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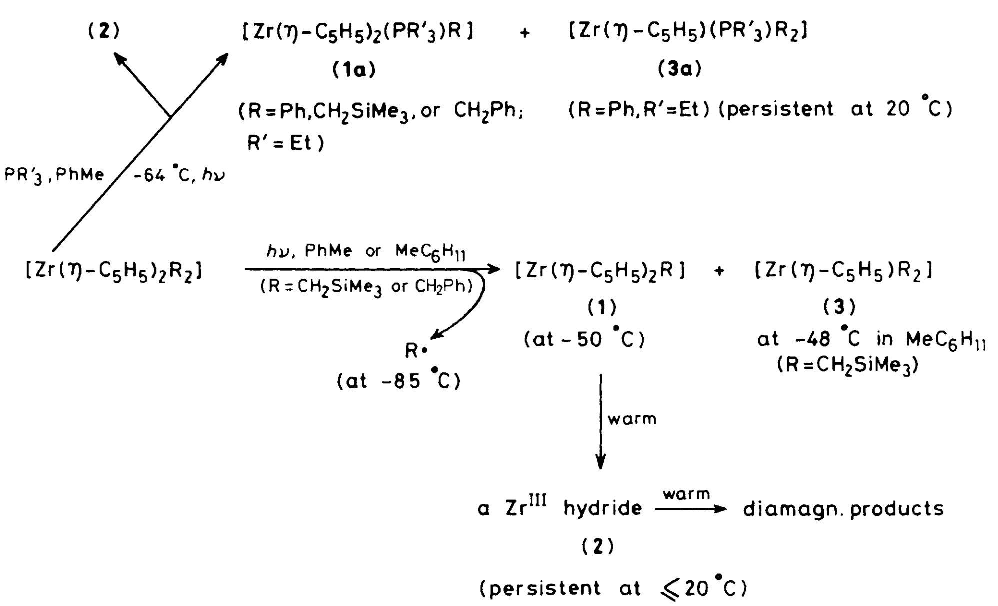
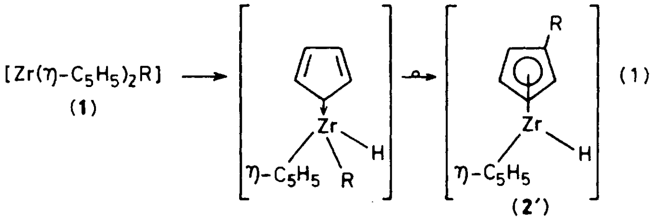
† No reprints available.

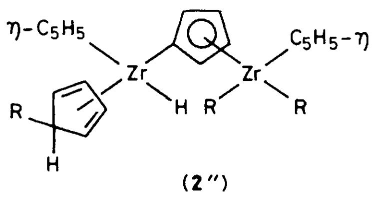


Scheme 1. Paramagnetic zirconium(III) complexes (**1**)—(**3**), and tertiary phosphine adducts (**1a**) and (**3a**), from photolysis of dialkyl- or diphenyl-zirconocene(IV), [Zr(η-C_5H_5)$_2$$R_2$]. The following e.s.r. parameters [g_{av}, $a(^{91}Zr)$, and $a(^1H)$ or $a(^{31}P)$ in G, respectively] were recorded: (**1**) (1.979, 23.5, *ca.* 3); (**2**) [1.987, $a(^{91}Zr)$ not observed, 6.6]; (**3**), [$a(^1H)$ = 2.4 G]; (**1a**) [1.988, 19—19.5, $a(^{31}P)$ 23.7—24.2]; and (**3a**) [1.996, 23.2, $a(^{31}P)$ 19.5].

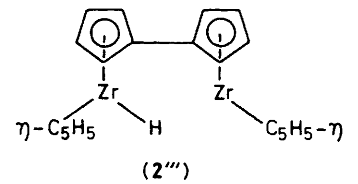


(2′)

(1)



(2″)



(2‴)

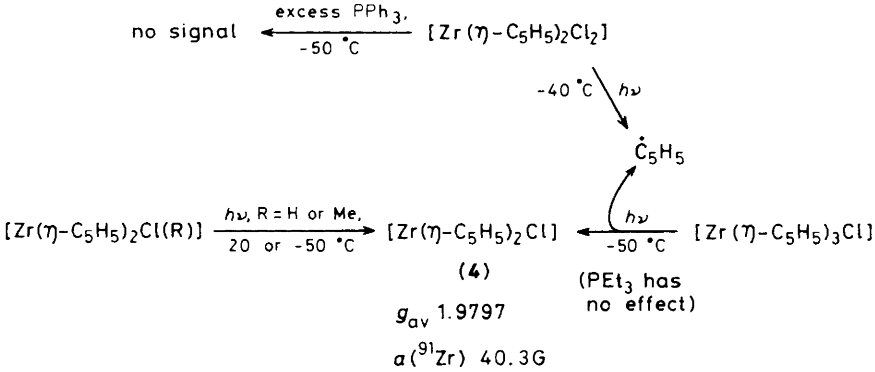
1). It is particularly significant that in two cases (R = CH_2SiMe_3 or CH_2Ph) we have been able directly to detect these transient species, since previous work has relied either on spin-trapping merely to establish the presence of $R^{\cdot}$[1] or CIDNP[3] (for R = Me). The spectra of complexes (**1**), exhibiting ^{91}Zr satellites, are typical of Zr^{III}.[2,4]

The structure of the species (**2**) giving rise to the 6.6 G doublet is more problematical. The same spectrum was observed in all four systems. A similar doublet (a = 7.0 G) has been detected in the photolysis of [Zr(η-C_5H_5)$_2$$Me_2$].[1] The doublet splitting in (**2**) must be due to a single proton and it seems likely that it originates from the $^-C_5H_5$ ligand. We have obtained the same spectrum from either [Zr(η-C_5H_5)$_2$(C_6D_5)$_2$] in toluene or [Zr(η-C_5H_5)$_2$$Ph_2$] in perdeuteriotoluene but have yet to perform an experiment with a $^-C_5D_5$ ligand. Complex (**2**) seems to be formed by a thermal reaction since the spectrum grows in intensity on ceasing irradiation and its precursor may be a transient [Zr(η-C_5H_5)$_2$].[1] (Evidence for such a transient molecule comes from trapping experiments, *e.g.*, with C_4H_6.[2])

Our failure to detect ^{91}Zr satellites for the hydride (**2**) is curious, because they are readily detectable for other Zr^{III} complexes. This may indicate the presence of a dimer or polymer, since these would be expected to tumble more slowly in solution than a monomer and hence have broader satellite lines.

A dinuclear hydride might arise through either (σ,π)-$C_5H_4^{2-}$ or (π,π)-$\bar{C}_5H_4$-$C_5H_4^-$ bridging [transformations $2M(\eta^5\text{-}C_5H_5) \rightarrow M(\eta^5,\eta^1\text{-}C_5H_4)_2M$ or $M(\eta^5:\eta^5\text{-}C_{10}H_8)M$ are recognised as an important facet of low oxidation state organotransition metal chemistry[5]]. Such a ligand might in turn derive from an initial α-elimination as shown in equation (1) (which has a precedent in titanocene chemistry[6]). Alternative formulations of the hydride (**2**) are then (**2′**), (**2″**), or (**2‴**); the latter two being formed from (**1**) and either [Zr(η-C_5H_5)$_2$$R_2$] or (with loss of RH) Zr(η-C_5H_5)$_2$, respectively. [We thank a referee for suggesting structures (**2″**) and (**2‴**).]

In order to stabilise the Zr^{III} intermediates formed during photolysis of [Zr(η-C_5H_5)$_2$$R_2$] we have performed a number of experiments in the presence of an added tertiary phosphine. Thus when [Zr(η-C_5H_5)$_2$$Ph_2$] is irradiated at −64 °C with PPh_3 present, we see, in addition to the 'hydride' doublet, a second larger doublet with ^{91}Zr satellites which we assign to [Zr(η-C_5H_5)$_2$(Ph)(PPh_3)], (**1a**), (R = Ph = R′ in Scheme 1). When the PPh_3 is replaced by PEt_3, two doublets are observed. One is assigned to [Zr(η-C_5H_5)$_2$(Ph)(PEt_3)], (**1a**, R = Ph, R′ = Et). The second, which is the more stable at higher temperatures, is also formed by leaving the solution at room temperature and is probably (**3a**, R = Ph, R′ = Et). Species related to (**1a**) have been detected from the other compounds when it is also possible to resolve hyperfine structure for the



Scheme 2. A paramagnetic zirconium(III) complex (**4**) from photolysis in PhMe of zirconocene(IV) chlorides.

methylene protons of the ligands $^-CH_2Ph$ or $^-CH_2SiMe_3$. Thus for $[Zr(\eta\text{-}C_5H_5)_2(CH_2Ph)(PPh_3)]$ we find $a(^{31}P) = 20.7$ G, $a(^1H) = 4$ G, $a(^{91}Zr) = 16.5$ G, $g_{av} = 1.984$ and for $[Zr(\eta\text{-}C_5H_5)_2(CH_2SiMe_3)(PEt_3)]$: $a(^{31}P) = 19.2$ G, $a(^1H) = 4.6$ G, $a(^{91}Zr) = 19.9$ G, $g_{av} = 1.988$. These coupling constants are similar to those recently reported for other Zr^{III} phosphine complexes.[7]

The above results are summarised in Scheme 1.

We have also investigated the photolysis of the compounds $[Zr(\eta\text{-}C_5H_5)_2Cl(R)]$, Scheme 2. When R = H or Me, the e.s.r. signals consist of a singlet ($g_{av} = 1.980$) with satellites, $a(^{91}Zr) = 40.3$ G. This species has a half-life of about 1 min at room temperature and is unaffected by the presence of added tertiary phosphine. The same spectrum, which we assign to $[Zr(\eta\text{-}C_5H_5)_2Cl]$, (**4**), has been obtained during the photolysis of $[Zr(\eta\text{-}C_5H_5)_3Cl]$. A similar singlet was also observed from $[Zr(Ar)(\eta\text{-}C_5H_5)_2Cl]$ (Ar = $C_6H_2Bu^t_3$-2,4,6) along with the characteristic sextet of $\cdot C_5H_5$. The cyclopentadienyl radical was also detectable on photolysis of $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ in toluene; this result may have a bearing on reports of photolysis of the dichloride in presence of (a) Bu^tCl {to give $[Zr(\eta\text{-}C_5H_5)Cl_3]$}[8] and (b) $[Zr(\eta\text{-}C_5D_5)_2Cl_2]$ {to give an equilibrium mixture containing $[Zr(\eta\text{-}C_5H_5)(\eta\text{-}C_5D_5)Cl_2]$}.[9]

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