Spin Trapping of Cyclopentadienyl Radicals using Nitroso Compounds and Nitrones

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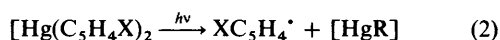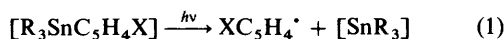*Department of Chemistry, University of Victoria, British Columbia, Canada V8W 2Y2*

Cyclopentadienyl radicals $C_5H_4X^{\cdot}$ (X = H or Me) generated in various solvents either chemically or photochemically from $Hg(C_5H_4X)_2$ have been trapped using nitrosodurene (ND), phenyl(t-butyl)nitrone (PBN), and 3,4-dihydro-2,2-dimethyl-2H-pyrrole N-oxide (DMPO) to afford radical adducts identifiable by e.s.r. spectroscopy. For X = H the ND adduct (1) gives rise to a six-line e.s.r. spectrum in toluene having $a(N)$ ca. 13.5 G and $a(H)$ ca. 6.5 G. In contrast, production of (1) by photolysis in $CHCl_3$ is accompanied by the appearance of a species (7) with a four-line e.s.r. spectrum, assigned to the $H^{\cdot}/ND$ (aminoxyl) adduct. For X = Me, with ND as spin trap, overlapping e.s.r. spectra which correspond to adduct formation at points of maximum spin-density [C(1) and C(3), C(4)] are resolved. Similar spin trapping of radicals derived photolytically from C_5Me_5H is also described.
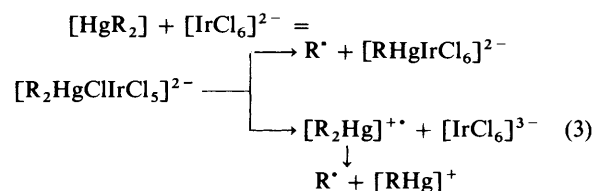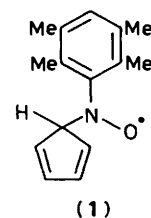
The photochemistry of cyclopentadienylmetal (cpM) compounds is receiving increasing attention. In particular Davies and his co-workers have found that photolysis of η^1-cyclopentadienyltin derivatives such as $[Bu_nSn(\eta^1\text{-}C_5H_5)_{4-n}]$ ($n = 0$, 2, or 3) results in a strong e.s.r. spectrum of the cyclopentadienyl radical with no evidence for formation of butyl radicals.[1] This behaviour has been developed as a general route to the hitherto poorly characterized family of annulene radicals $XC_5H_4^{\cdot}$, mainly by using appropriate tin[2,3] and mercury[3] species as precursors. It has thus been established that homolysis of the M–cp bond is a dominant process in the photofragmentation of η^1-cp compounds of the main-group elements. In contrast, it has proved difficult to gauge the importance of corresponding steps in the photodecomposition of η^5-cp transition-metal complexes[4–6] primarily because of difficulties associated with the detection of e.s.r. signals due to cyclopentadienyl radicals in the presence of a variety of other paramagnetic products. Since the familiar metallocenes including $[M(\eta^5\text{-}C_5H_5)_2]$ (M = Fe, Ru, or Co⁺) are photostable,[7] it is the equally accessible[8] and chemically topical[9] M^{IV} species formed by Ti, Zr, Hf, Th, and U that have been examined in this context, by Gianotti,[5] by Brubaker,[6] and most recently again by Davies,[10] who has reviewed possible pitfalls inherent in identification of cyclopentadienyl radicals by spin trapping rather than by direct observation. We discuss here how the spin-trapping technique may be successfully applied to this same group of radicals.

Results and Discussion

Convenient access to cyclopentadienyl radicals is provided[1–3] by the unimolecular photolytic reactions (1) and (2), starting

$$[R_3SnC_5H_4X] \xrightarrow{h\nu} XC_5H_4^{\cdot} + [SnR_3] \qquad (1)$$

$$[Hg(C_5H_4X)_2] \xrightarrow{h\nu} XC_5H_4^{\cdot} + [HgR] \qquad (2)$$

from organotin or organomercury derivatives, respectively. The chemical generation of alkyl radicals from alkylmercurials has also been explored, initially by Kochi et al.[11] With $[IrCl_6]^{2-}$, an inner-sphere electron transfer is believed to take place via a bimetallic intermediate which subsequently fragments to alkyl radicals and metallic products [equation (3)]. Availability of

(1)

$$[HgR_2] + [IrCl_6]^{2-} =$$

$$[R_2HgClIrCl_5]^{2-} \longrightarrow \begin{cases} \longrightarrow R^{\cdot} + [RHgIrCl_6]^{2-} \\ \\ \longrightarrow [R_2Hg]^{+\cdot} + [IrCl_6]^{3-} \quad (3) \\ \qquad\qquad \downarrow \\ \qquad R^{\cdot} + [RHg]^{+} \end{cases}$$

both photochemical and reductive pathways to cyclopentadienyl radicals from the mercury compounds led us to adopt these derivatives as precursors in the study reported here. We have found that either approach conducted in the presence of a spin trap such as nitrosodurene (ND), nitrosobenzene (NB), or phenyl(t-butyl)nitrone† (PBN) allows the appropriate radical adduct to be observed by e.s.r. spectroscopy. We have also examined trapping of the $C_5Me_5^{\cdot}$ radical, which was generated photolytically directly from pentamethylcyclopentadiene.[12]

The adduct (1) of $C_5H_5^{\cdot}$ with ND obtained via reaction between $[Hg(C_5H_5)_2]$ and $K_2[IrCl_6]$ in acetic acid solution gave rise to the six-line e.s.r. spectrum illustrated in Figure 1. The same spectrum was observed when $[Hg(C_5H_5)_2]$ was photolysed with ND in a variety of solvents, with g values in the range 2.006—2.007 and a minor variation in the hyperfine coupling constants $a(N)$ and $a(H)$: respectively 13.5 and 6.5 G (toluene); 13.2 and 5.3 G (benzene); 13.2 and 5.6 G (tetrahydrofuran); 13.6 and 7.3 G ($CHCl_3$); and 13.8 and 5.7 G (HOAc). The values in tetrahydrofuran solution (± 0.15 G) are essentially identical with those reported by Davies;[10] indeed the coupling constants (Table) for (1) closely resemble those reported[13,14] for other radical adducts with ND possessing only one β-hydrogen atom, for example isopropyl and

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† N-(t-Butyl)benzylideneamine N-oxide.

Table. Spin adducts of cyclopentadienyl radicals

| Radical	Source	Spin trap	Solvent	$a(N)/G$	$a(H_\beta)/G$
C_5H_5	$[Hg(C_5H_5)_2]$; $h\nu$	ND	Toluene	13.5	6.5
C_5H_5	$[Hg(C_5H_5)_2]$; $h\nu$	ND	Benzene	13.2	5.3
C_5H_5	$[Hg(C_5H_5)_2]$; $h\nu$	ND	Tetrahydrofuran	13.2	5.6
C_5H_5	$[Hg(C_5H_5)_2]$; $K_2[IrCl_6]$	ND	HOAc	13.8	5.7
C_5H_5	$[Hg(C_5H_5)_2]$; $h\nu$	PBN	Toluene	14.5	2.9
C_5H_5	$[Hg(C_5H_5)_2]$; $K_2[IrCl_6]$	PBN	HOAc	14.3	2.7
C_5H_5	$[Hg(C_5H_5)_2]$; $h\nu$	DMPO	Toluene	13.8	20.4
C_5D_5	$[Hg(C_5D_5)_2]$; $h\nu$	ND	Benzene	13.4	a
C_5D_5	$[Hg(C_5D_5)_2]$; $K_2[IrCl_6]$	ND	HOAc	13.7	a
C_5D_5	$[Hg(C_5D_5)_2]$; $h\nu$	DMPO	Toluene	13.8	20.7
C_5H_4Me	$[Hg(C_5H_4Me)_2]$; $h\nu$	ND	Toluene	13.5	b
				13.4	6.3
C_5H_4Me	$[Hg(C_5H_4Me)_2]$; $h\nu$	ND	HOAc	14.5	b
				14.2	6.2
C_5H_4Me	$[Hg(C_5H_4Me)_2]$; $K_2[IrCl_6]$	DMPO	Toluene	14.0	20.4
C_5Me_5	C_5Me_5H; $h\nu$	ND	Toluene	13.4	b
C_5Me_5	C_5Me_5H; $h\nu$	DMPO	Toluene	14.2	20.8
				14.4	19.2 (2H)
				c	c
C_5Me_5	C_5Me_5H; $h\nu$	PBN	Toluene	14.1	2.8

a Deuterium hyperfine coupling not resolved. b β-CH_3 proton hyperfine coupling not resolved. c Third spectrum superimposed: $a(15H) = 6.4$ G, i.e. C_5Me_5 (see ref. 12).
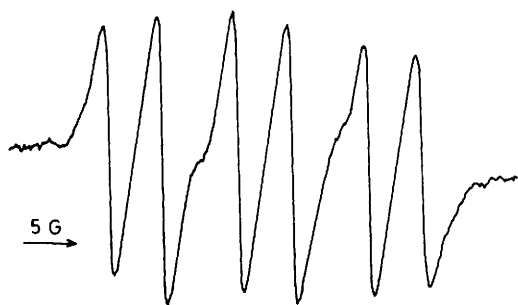

Figure 1. E.s.r. spectrum of adduct (1) formed by reaction of $[Hg(C_5H_5)_2]$ with $K_2[IrCl_6]$–HOAc in the presence of ND

cyclohexyl which will have steric characteristics similar to (1). An unexpectedly large difference in $a(H)$ exists between benzene and toluene as solvents although, more normally for such similar hydrocarbons, the $a(N)$ values are almost identical. We have also independently [5,10] observed the spectrum of (1) in toluene during photolysis of $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ and found the six-line spectrum to be essentially the same as that reported in the Table, i.e. $a(N)$ 13.4 G, $a(H)$ 6.2 G. Trapping of the isotopomeric radical C_5D_5· with ND gave rise to broadened triplets, $a(N)$ near 13.4 G, $\Delta_{pp} = 3$ G, in which deuterium coupling could not be resolved, whereas the adduct of C_5H_5· with NB showed $a(H)$ 3.2 G, again comparable directly with data available in the literature.[15]

Trapping of the radical derived from $[Hg(C_5H_4Me)_2]$ with ND to give the adduct (2) led to observation of the e.s.r. spectrum reproduced as Figure 2. This consists of two distinguishable patterns which we ascribe to bond formation at each of two different cp ring-carbon atoms, a triplet $[a(N)$ 14.5 G] due to the C(1) addition product (2A), together with a sextet $[a(N)$ 14.2 G, $a(H)$ 6.2 G] arising from addition at C(3), C(4), (2B). This interpretation is in agreement with recent calculations on substituted cp radicals which predict[2] that the spin density at either C(1) or C(3), C(4) will greatly exceed the corresponding term at C(2) or C(5), i.e. it is evident from the
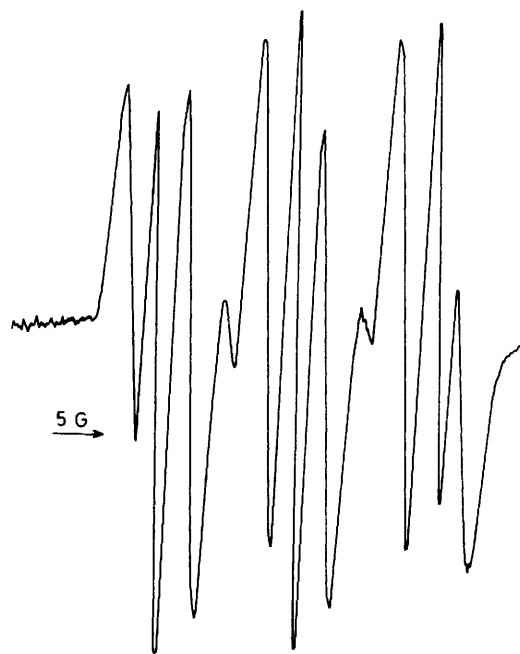
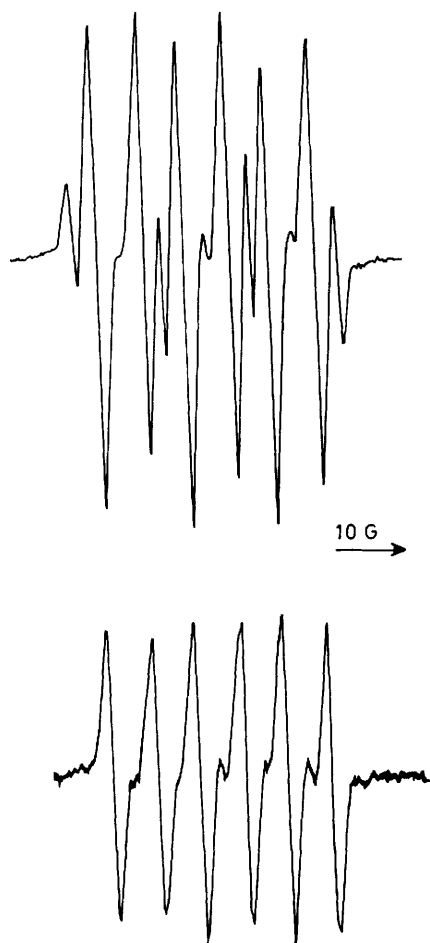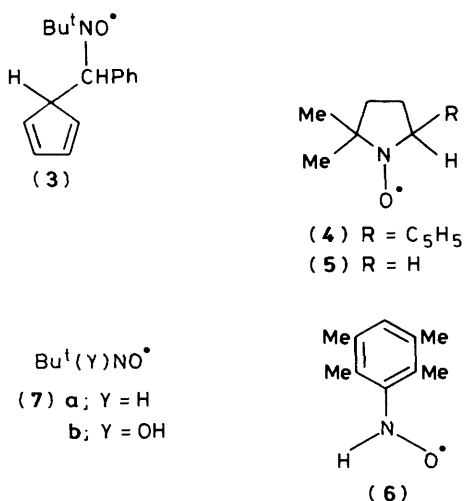**Figure 2.** E.s.r. spectrum of ND radical adducts (2A) and (2B)

(2A)

(2B)

(3)

(4) R = C$_5$H$_5$
(5) R = H

Bu^t(Y)NO$^•$

(7) a; Y = H
    b; Y = OH

(6)
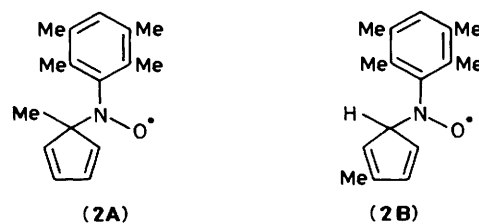
Figure 3. E.s.r. spectra observed on photolysis of [Hg(C$_5$H$_5$)$_2$] in CHCl$_3$ solution in the presence of ND: upper, during sample illumination; lower, after shuttering light source

spectra that addition is preferred[2] at points of maximum spin density.

Generation (either chemically or by photolysis) of C$_5$H$_5^•$ in solutions containing PBN as spin trap yielded products for which e.s.r. spectra were consistent with radical–nitrone adduct-

formation to give (3): with a(N) $ca.$ 14.2 G, a(H$_\beta$) 2.4—3.0 G (depending on experimental conditions). The six-line multiplets resembled those characteristic of known hindered secondary alkyl adducts.[13] Likewise, with the nitrone trap DMPO (3,4-dihydro-2,2-dimethyl-2H-pyrrole N-oxide), spectra typical[13] of a secondary alkyl radical adduct of DMPO were observed with a(N) 13.8—14.4 G and a(H$_\beta$) 20.4—20.8 G. The e.s.r. spectrum which resulted from photolysis of C$_5$Me$_5$H in the presence of DMPO is instructive: it consists of three superimposed patterns, that of the C$_5$Me$_5^•$ spin-trap adduct (4) (see Table); a second species (5) attributable to H-atom addition; and weak features attributable to[12] the C$_5$Me$_5^•$ radical itself.

Photolysis of [Hg(C$_5$H$_5$)$_2$] in CHCl$_3$ solution with ND as spin trap resulted in appearance of a more complex e.s.r. spectrum than that observed in other solvents. In addition to the sextet pattern for which spectral parameters have already been quoted, a further species (6) showing an apparent quartet (1:2:2:1) with line separation 13.5 G was evident. On shuttering the light source, the sextet persisted, while the quartet rapidly lost intensity (Figure 3). The four-line feature corresponds exactly to the multiplet ascribed elsewhere[6] to the cp radical adduct arising from photolysis of [Ti(η^5-C$_5$H$_5$)$_2$Cl$_2$], an assignment disputed by Davies,[10] who has suggested that the origin of this spectrum lies in formation of the H$^•$/ND (aminoxyl) radical adduct (6). Kalyanaraman et al.[16] have attributed a very similar four-line e.s.r. spectrum (spacing 14.2 G) which is observed after reduction of 2-methyl-2-nitroso-propane with aqueous NaBH$_4$ to the aminoxyl (7a) rather than to the hydroxyaminoxyl (7b) proposed previously.

Conclusions

It is clear that under appropriate conditions cyclopentadienyl radicals C$_5$H$_4$X$^•$ generated from photolysis or chemical reaction of [Hg(C$_5$H$_4$X)$_2$] may be trapped, giving rise to well resolved and intense e.s.r. spectra, typified by that observed for the ND adduct with X = H shown in Figure 1. The data reported here strongly support arguments advanced recently by Davies et al.,[10] i.e. that whereas Gianotti and his co-workers[5] have indeed identified formation of the adduct (1) in thermal reactions of ND with Ucp$_3$R (R = Me or Bu), the e.s.r. spectra observed by Tsai and Brubaker[6] on photolysis of [Ti(η^5-C$_5$H$_4$X)$_2$Cl$_2$] (X = H or Me) with ND are not a result of M–cp homolysis but rather arise from reduction of the spin trap.

Experimental

Cyclopentadiene and methylcyclopentadiene were obtained by thermal 'cracking' of the commercially available (Aldrich) dimers and were used to synthesize the diorganomercurials [Hg(C$_5$H$_4$X)$_2$] (X = H or Me) by published methods.[17] Perdeuteriocyclopentadiene (C$_5$D$_6$) was prepared in $ca.$ 95 atom % purity by base-catalysed exchange;[18] the spin traps nitrosodurene (ND), pentamethylnitrosobenzene, and nitroso-benzene (NB) were synthesized by literature methods.[14,19] Commercial 3,4-dihydro-2,2-dimethyl-2H-pyrrole N-oxide (DMPO) was resublimed prior to use.

E.s.r. spectra were recorded with a Bruker ER200tt spectrometer. Photolysis experiments were conducted in situ using a 2 kW high-pressure mercury arc focused through quartz optics (Oriel Corp.). Samples were prepared in quartz tubes and were outgassed with dry dinitrogen gas and sealed with rubber septa, or were degassed and sealed on a conventional high-vacuum system. The g values were measured by n.m.r. gaussmeter and external standard [diphenylpicrylhydrazyl (DPPH) or Mn^{2+}, $ca.$ 1% in MgO solution].

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