Inorganica Chimica Acta, 176 (1990) 107–112

Spin trapping of radicals formed during the photolysis of the dimeric iron carbonyl complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$

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(Received February 12, 1990; revised May 14, 1990)

Abstract

The generation of free radicals by photolysis of dimeric iron complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ has been studied by EPR and spin trapping. Unlike $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, no evidence for homolytic C_5Me_5–Fe cleavage was found for $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$. Photolytic scission of the Fe–Fe bond appears to be the dominating free radical process in both complexes. The resulting iron-centered free radicals react readily with dioxygen to form iron peroxyl radicals which may abstract hydrogen from C–H bonds. In addition, electron transfer has been observed between photoexcited $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ and the spin trap 2-methyl-2-nitrosopropane, which leads to a variety of secondary radicals. Unlike the situation with monohalocarbons, no carbon-centered radicals were detected when the photolysis was carried out in CCl_4 and $CFCl_3$, respectively.

Introduction

Photolysis of dimeric organometallic complexes provides a convenient method of generating catalytically-active metallo-radicals [1–5]. Several papers have dealt with the photochemistry of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ [6–11]. It has been shown by Giannotti and Merle [7] that the complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ undergoes a net Fe–Fe bond cleavage forming $[(\eta^5\text{-}C_5H_5)Fe(CO)_2X]$ (X = Cl, Br) when photolyzed with polychromatic light (350 nm < λ < 600 nm) in halocarbons such as CCl_4, $CHCl_3$, $CHBr_3$ and CH_2Cl_2. The complex $](\eta^5\text{-}C_5H_5)Fe(CO)_2X]$ undergoes secondary photolysis leading to ferrocene and iron(II) halides, FeX_2.

The behaviour of the $^{\bullet}Fe(CO)_2(C_5H_5)$ radical towards halocarbons has also been studied by other authors [8–11]. Wrighton *et al.* [8] have measured the quantum yields for the photoreaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in both CCl_4 and benzene/0.1 M PPh_3, while flash photolysis studies [9–12] and low-temperature experiments [13] led to the conclusion that an isomerization of the ground state structure rather than Fe–Fe bond cleavage is the primary step in the photoreaction of the dimeric $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ complex. Although isomerization may be the major pathway in the photolysis for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, there is also clear evidence for the formation of $^{\bullet}Fe(CO)_2(C_5H_5)$ radicals; photolysis of a mixture of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ leads to the cross-coupling product $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Mo(CO)_3\eta^5\text{-}C_5H_5)$ [6]. In addition, EPR spin-trapping studies [14–18] using nitroso spin traps as well as time-resolved IR measurements [12, 13, 19] have revealed the formation of $^{\bullet}Fe(CO)_2(C_5H_5)$ radicals.

On photolyzing $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in the presence of aromatic nitroso compounds, spin adducts of the $^{\bullet}Fe(CO)_2(C_5H_5)$ radical were observed. Two additional spin adducts tentatively assigned to differently bound $^{\bullet}C_5H_5$ radicals were observed by Carlton *et al.* [18]. However, at least the assignment for the spin adduct with $a_N = a_H = 1.41$ mT is probably incorrect and it should rather be assigned to the

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0020-1693/90/$3.50

hydronitroxide Ar–N($^{\bullet}$O)–H (Ar = duryl) [20]. This nitroxide may be formed by reduction of the nitroso compound and subsequent protonation.

In the presence of dioxygen the radical $^{\bullet}Fe(CO)_2(C_5H_5)$ forms the adduct $^{\bullet}OOFe(CO)_2(C_5H_5)$ which gives rise to an ESR signal at $g = 2.025$ detected at a lower temperature [18, 21].

To date far spin-trapping experiments have been restricted to the unsubstituted $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and little is known about the photochemical behaviour of iron complexes with substituted cyclopentadienyl ligands [22]. It was the aim of this work to study the formation of radicals during the photolysis of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$. For comparison, spin-trapping experiments using a variety of spin traps have also been carried out for unsubstituted $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.

Experiments

The photolysis was carried out directly in the EPR cavity. The light beam of a 100 W high-pressure mercury lamp (HANOVIA) was focused onto the window of the cavity after passage through an appropriate filter (350–600 nm band-pass filter and 401 nm BALZER interference filter, respectively).

All experiments were performed at room temperature (295 K). Unless otherwise stated, all samples were purged with purified argon for at least 30 min prior to photolysis. An H-shaped mixing chamber attached to a fused quartz flat cell was used. An ER 200 tt (Bruker) spectrometer operating at X-band was used for the EPR experiments with DPPH serving as the standard for the determination of g values. The field calibration was carried out by measuring the hyperfine splitting of di-tert-butyl nitroxide in benzene ($a_N = 1.536$ mT). All coupling constants were determined by at least three independent measurements. The experimental error was ±0.008 mT for the coupling constants and ±0.005 for the g values.

The complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ were synthesized according to literature procedures [22, 23].

The following nitroso compounds, which were prepared according to literature methods [24], were used as spin traps: 2-methyl-2-nitrosopropane (MNP), nitrosodurene (ND) and pentamethylnitrosobenzene (PMNB). 5,5-Dimethyl-pyrroline-1-oxide (DMPO) was purchased from Aldrich.

Results and discussion

Photolysis of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$

Solutions of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in toluene were photolyzed at ambient temperature using either monochromatic ($\lambda = 401$ nm) or polychromatic (350 nm $< \lambda <$ 600 nm) light. In the absence of spin traps, no EPR signals were detected. In the presence of spin traps, however, spin adducts of the $^{\bullet}Fe(CO)_2(C_5H_5)$ radical were observed (see Table 1). With PMNB a triplet of doublets ($a_N = 1.350$ mT, $a_H = 0.556$ mT) was also detected, which corresponds to the radical found by Carlton *et al.* [18], and is assigned to the cyclopentadienyl radical adduct.

In the presence of traces of oxygen, additional spin adducts have been detected which are caused by hydrogen abstraction from toluene. The coupling constants of the spin adducts to PMNB ($a_N = 1.350$ mT, $a_H = 0.794$ mT (2H)) and ND ($a_N = 1.360$ mT, $a_H = 0.800$ mT (2H)) are consistent with the data previously reported [25, 26] for the benzyl spin adduct.

When the concentration of the spin trap is increased, the intensity of the benzyl spin adduct is reduced. This may be explained by assuming hydrogen abstraction by the $^{\bullet}OOFe(CO)_2(C_5H_5)$ radical. Since a high spin trap concentration prevents the formation of this radical, hydrogen abstraction from toluene is diminished. However, if an oxygen-saturated solution is used, a sufficient number of $^{\bullet}Fe(CO)_2(C_5H_5)$ radicals may escape from spin trapping by reacting with dioxygen. The peroxyl radical $^{\bullet}OOFe(CO)_2(C_5H_5)$, which has been detected directly by EPR at lower temperatures [18], could not be detected in our experiments which were carried out at ambient temperature.

Photolysis of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$

Under anaerobic conditions photolysis ($\lambda \pm 401$ nm) of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ in the presence of nitroso spin traps led to spin adducts with $a_N \simeq 1.7$–1.8 mT (see Table 2). These nitroxides may be assigned to spin adducts of the $^{\bullet}Fe(CO)_2(C_5Me_5)$ radical.

The ^{14}N-hyperfine splitting constants resemble those found for the corresponding $^{\bullet}Fe(CO)_2(C_5H_5)$ spin adducts (see Table 1). The g values are, however,

TABLE 1. Spin adducts of the $^{\bullet}Fe(CO)_2(C_5H_5)$ radical to nitroso spin traps (in mT: ±0.008 mT; g value: ±0.0005; solvent toluene)

Spin trap	a_N	g
ND	1.787	2.0052
PMNB	1.774	2.0051
MNP	1.748	2.0048

TABLE 2. Spin adducts of radicals formed by photolysis of the complex $[(\eta^5C_5Me_5)Fe(CO)_2]_2$ under anaerobic conditions[a]

Sample	Radical	a_N	g
MNP + toluene (401 nm)	$^{\cdot}Fe(CO)_2(C_5Me_5)$	1.721	2.0067
	$^{\cdot}C(CH_3)_3$	1.523	2.0060
	$^{\cdot}$COL; COL′	0.986	2.0068
	$^{\cdot}COC(CH_3)_3$[b]	0.741	2.0069
	$(MNP^{\cdot -})$	1.467	2.0061
MNP + benzene (401 nm)	$^{\cdot}Fe(CO)_2(C_5Me_5)$	1.731	2.0064
	$^{\cdot}C(CH_3)_3$	1.536	2.0060
	$^{\cdot}$COL; COL′	0.993	2.0068
	$^{\cdot}COC(CH_3)_3$[b]	0.752	2.0068
	$(MNP^{\cdot -})$	1.403	2.0060
ND + benzene (401 nm)	$^{\cdot}Fe(CO)_2(C_5Me_5)$	1.708	2.0064
	$^{\cdot}H$	1.44 $(a_H = 1.38)$	2.0058
	$(ND^{\cdot -})$	1.337	2.0061
MNP + cyclohexane + PPh_3 (401 nm)	$^{\cdot}Fe(CO)_2(C_5Me_5)$	1.721	2.0069
	$^{\cdot}$COL, $^{\cdot}$COL′	0.973	2.0068
	$(MNP^{\cdot -})$	1.403	2.0060

[a] Coupling constants in mT (±0.008 mT); g values: ±0.0005. [b] Polychromatic irradiation ($350\ nm \leqslant \lambda \leqslant 600\ nm$).

significantly higher than those for the unsubstitued cylopentadienyl complex. We attribute these changes in the g value to the different energies of the frontier orbitals of the C_5Me_5 ligand.

The deviation of the g value from the free-electron value is the result of mixing higher electronic states with the ground state. According to eqn. (1) this g shift depends on both the spin–orbit coupling constant ζ, the geometry and the bonding of the complex (which is reflected by the factor c), and by the energy separation Δ between the singly occupied orbital (SOMO) and the orbital which interacts via spin–orbit coupling [27, 28].

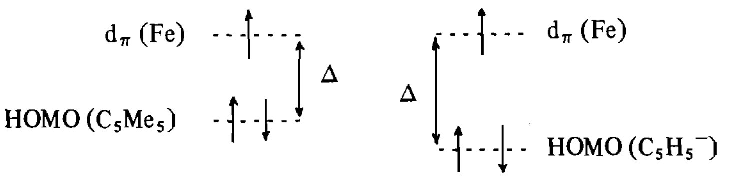
$$g = g_e \pm \frac{c\zeta}{\Delta} \qquad (1)$$

Although an exact MO scheme for the radicals $^{\cdot}Fe(CO)_2L(ArNO)$ ($L = C_5H_5$, C_5Me_5) is unknown, one should expect that, because of the electron-donating methyl groups, both the HOMO and the LUMO of the ligand $C_5Me_5^-$ are higher in energy than those for the unsubstituted $C_5M_5^-$ (see Scheme 1). Since ζ should be negative for a d^7 Fe(I) ion, mixing between the HOMO of the $C_5Me_5^-$ moiety and the iron SOMO is responsible for the positive g shift.

During the photolysis of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$, anion radicals of the nitroso spin traps are also detected (Table 2). Their formation is more pronounced for C_5Me_5 complexes than for unsubstituted cyclopentadienyl complexes. This may reflect the stronger reducing capability of the former complexes.

It should be noted that no spin adducts were observed when exposure to light was carefully avoided.

When $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ is photolyzed with monochromatic light ($\lambda = 401$ nm) in the presence of nitrosodurene in benzene, a single EPR line at $g = 1.9824$ is detected in addition to the $^{\cdot}Fe(CO)_2(C_5Me_5)$ spin adduct and nitrosodurene anion radical. Because of the lack of any hyperfine splitting, correct assignment of this species is difficult. However, the low g value excludes the presence of a carbon radical. It is reasonable to assume that this radical is an iron-containing species. Since the g shift is negative, the presence of a low-energy unoccupied



Scheme 1.

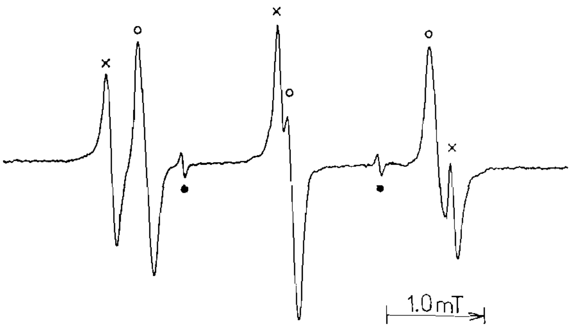


Fig. 1. ESR spectrum of spin adducts formed during monochromatic irradiation ($\lambda = 401$ nm) of a toluene solution of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ in the presence of MNP (spin adducts: $^{\bullet}Fe(CO)_2(C_5Me_5)$ (×), $^{\bullet}$COL or $^{\bullet}$COL′ (●), in addition $MNP^{\bar{\bullet}}$ (○).

orbital is indicated. The most likely candidate for the assignment of this species is the cation $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2^{\dot{+}}$.

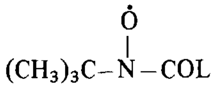
With the spin trap MNP, the EPR signals of at least five species are observed (see Table 2) upon photolysis. In addition to the spin adduct of the radicals $^{\bullet}Fe(CO)_2(C_5Me_5)$ and the radical anion $MNP^{\bar{\bullet}}$, three different three-line EPR signals are detectable.

Under monochromatic irradiation ($\lambda = 401$ nm), a nitroxide exhibiting a ^{14}N-hyperfine splitting of only $\simeq 0.99$ mT is detected (see Fig. 1). This hyperfine splitting is unusually small for an alkyl spin adduct and points to the presence of an electron-withdrawing functional group. The most likely candidate is a carbonyl function. However, acyl spin adducts to MNP have an even smaller ^{14}N-hyperfine coupling, e.g. for the $^{\bullet}COC(CH_3)_3$ spin adduct a coupling constant $a_N = 0.796$ mT has been reported in benzene solution [29].

After prolonged irradiation, the EPR signal of the di-tert-butyl nitroxide ($a_N \simeq 1.5$ mT), which is formed by decomposition of other spin adducts (most probably the spin adduct of the $^{\bullet}Fe(CO)_2(C_5Me_5)$ radical) and subsequent trapping of the tert-butyl radical rather than by decomposition of MNP itself, is recorded. Blank experiments with MNP alone did not give di-tert-butyl nitroxide under our experimental conditions.

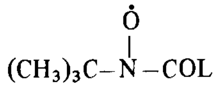
When the sample is photolyzed with polychromatic light, a third signal with $a_N = 0.741$ mT and $g = 2.0070$ is found. This spin adduct can be assigned to the pivaloyl radical.

As regards the 0.99 mT triplet, it is tentatively assigned to a spin adduct of an iron radical bound to the spin trap through a carbonyl group (type I or type II) for example



$$(CH_3)_3C-\overset{\overset{\bullet}{O}}{\overset{|}{N}}-COL$$

(Type I)



$$(CH_3)_3C-\overset{\overset{\bullet}{O}}{\overset{|}{N}}-COL'$$

(Type II)

However, it cannot be said whether a monomeric iron radical (type I, $L = (CO)Fe(C_5Me_5)$) or a cation radical containing two iron atoms (type II, $L' = FeC_5Me_5(CO)Fe(C_5Me_5(CO)_2{}^+$ is trapped. Spin trapping at the CO function has also been observed for $^{\bullet}Mn(CO)_5$ [30].

A possible route leading to radical cation of type II could be an electron transfer between photoexcited $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ and MNP (eqn. (2)).

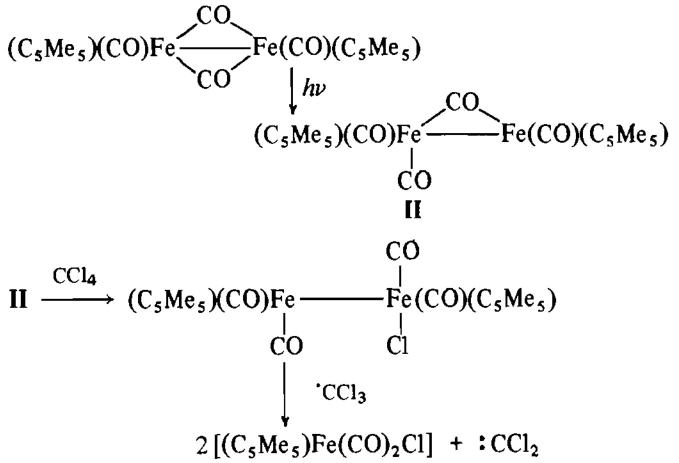
$$[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2^* + MNP \longrightarrow MNP^{\bar{\bullet}} + {}^{\dot{+}}COFe(\eta^5\text{-}C_5Me_5)(CO)Fe(\eta^5\text{-}C_5Me_5)(CO)_2 \quad (2)$$

However, CO insertion into the N–Fe bond or rearrangement of the $^{\bullet}Fe(CO)_2C(_5Me_5)$ spin adduct to MNP could also lead to the 0.99 mT triplet.

On the other hand, the formation of the spin adduct of $^{\bullet}COC(CH_3)_3$ is very probably the result of $^{\bullet}C(CH_3)_3$ radical attack on the iron complex. The tert-butyl radicals are formed by the photodecomposition of MNP under polychromatic photolysis. The stationary concentration of $^{\bullet}COC(CH_3)_3$ spin adducts is, however, very low since acyl nitroxides are known to undergo photoreduction. Interestingly, neither the 0.99 mT triplet nor the $^{\bullet}COC(CH_3)_3$ spin adduct was observed when the corresponding iron complex of unsubstituted cyclopentadienyl was photolyzed.

Unlike the photolysis of $[Re_2(CO)_{10}]$ [31, 32], irradiation of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ in the presence of triphenylphosphine did not lead to spin trapping of phosphorous-containing iron radicals. This is in accordance with the results found by Tyler and coworkers [33, 34] who provided evidence for a photoinduced disproportionation of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ in the presence of phosphines. Although it is known that $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ forms $[\eta^5\text{-}C_5H_5Fe(CO)_2X]$ (X = halide) when it is photolyzed in halocarbon solutions [7], neither $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ nor $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ gives rise to solvent-derived radical spin adducts when irradiated in CCl_4 and $CFCl_3$, respectively, in the presence of ND.

On the other hand, photolysis (401 nm) of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ in the presence of ethyl iodide led to ethyl radicals which could be trapped, e.g. by MNP ($a_N = 1.505$ mT, $A_H = 1.012$ mT (2H) in cyclohexane/C_2H_5I (5:1 vol./vol.)). No ethyl radicals were detected in blank experiments i.e. with no iron complex present and in experiments where n-butyl chloride was used instead of ethyl iodide. This result



Scheme 2..

TABLE 3. Spin adducts to MNP of solvent-derived radicals formed by photolysis (401 nm) of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ in the presence of dioxygen[a]

Solvent	Spin trap	Radical	a_N	a_H	g
Pentane	MNP	$^{\cdot}CH(C_2H_5)_2$ or $^{\cdot}CH(CH_3)C_3H_7$	1.443	0.172	
		$^{\cdot}OCH(C_2H_5)_2$ or $^{\cdot}OCH(CH_3)C_3H_7$	2.926		
Toluene	MNP	$^{\cdot}OCH_2C_6H_5$	2.953	0.106 (2H)	2.0052
Benzene	MNP	$^{\cdot}OC(CH_3)_3$ $^{\cdot}OOL$, $^{\cdot}OOL'$	2.714 2.827		
Cyclohexane	MNP	$^{\cdot}OC_6H_{11}$	2.880		

[a]Coupling constants in mT (±0.008 mT); g values: ±0.0005.

is quite surprising since one would expect CCl_4 or $CFCl_3$ to react more readily than ethyl iodide. It supports, however, the assumption first made by Gray *et al.* [13] that the rearrangement of the dimer, rather than the homolysis, is the primary step in the photolysis of the iron complex dimer in the presence of perhalocarbons. Halogen abstraction by the intermediate II (see Scheme 2) leads to a perhalocarbon radical ($^{\cdot}CCl_3$, $^{\cdot}CFCl_2$) in close proximity with another Fe(I) center. Subsequent halogen transfer finally leads to $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2X]_2$, Scheme 2.

Ethyl radicals, however, cannot react in this way and may escape into the bulk solution where they are spin-trapped. Upon photolysis, $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ also reacts with dioxygen. However, at ambient temperature no free peroxyl iron complexes were detectable by EPR spectroscopy. On the other hand, photolysis (401 nm) of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ in the presence of 5,5-dimethyl-pyrroline-1-oxide (DMPO) led to $O_2^{\cdot-}$ spin adducts ($a_N = 1.284$ mT, $a_H^1 = 0.768$ mT, $a_H^2 = 0.204$ mT, $g = 2.0061$; benzene). After prolonged photolysis a second (as yet unidentified nitroxide ($a_N = 1.483$ mT, $A_H = 2.039$ mT) was observed.

In toluene and alkane solutions (pentane, cyclohexane) alkoxy radicals, together with the corresponding alkyl radicals, were spin-trapped by MNP (see Table 3).

The observation of alkyl and alkoxy radicals, respectively, clearly demonstrates the activation of dioxygen by the photoexcited iron complex. None of these radicals was observed when MNP was photolyzed in the absence of the iron complex or when the samples were kept in the dark.

In benzene, two different oxygen-centred radicals were detected. One of them could be assigned to the tert-butoxy radical which is formed by reaction of tert-butyl radicals (from the decomposition of the $^{\cdot}OOL$ spin adduct to MNP). The other signal is tentatively assigned to the $^{\cdot}OOL$ or $\bullet OOL'$ spin adducts ($L = [Fe(CO)_2C_5Me_5]$; $L' = [Fe(CO)_2C_5Me_5]_2^{+}$).

The assumed formation of tert-butyl and tert-butoxy radicals is in agreement with the findings by Howard and Tait [35] who observed the EPR spectra of both di-tert-butyl aminoxyl and tert-butyl tert-butoxyl aminoxyl radicals during thermal decomposition of tert-butylperoxyl spin adducts to MNP. These authors have also shown that tert-butylperoxyl spin adducts to MNP are too unstable to be detected by ESR.

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