

### Spin Trapping of a Rhodium-centred Radical in the Photolysis of $[(\eta^5\text{-CpMe}_5)\text{Rh}(\text{CO})_2]$

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Numerous papers report the photochemical generation of metal-centred radicals from metal–metal bonded organometallic dimers [1]. Using nitroso compounds as diamagnetic free-radical scavengers, the spin trapping technique [2] has been successfully applied to the ESR detection of a great variety of metal-centred radicals, including those of group VIII transition metals [3]. Although the formation of rhodium complexes with some nitroso compounds has been demonstrated [4, 5], spin adducts of nitroso compounds with short-lived Rh-centred radicals have not yet been described.

During our studies on the photocatalytic activity of organometallic radicals, we were interested in the behaviour of the complex  $[(\eta^5\text{-CpMe}_5)\text{Rh}(\text{CO})_2]$  (**I**).

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This compound is prepared from  $[(\eta^5\text{-CpMe}_5)\text{RhCl}_2]$  by reaction with carbon monoxide under reducing conditions [6].

The analogous complex  $[(\eta^5\text{-Cp})\text{Rh}(\text{CO})_2]$  was shown to form a dimer  $[(\eta^5\text{-Cp})_2\text{Rh}_2(\text{CO})_3]$  upon photolysis [7], whereas a dimer with two bridging carbonyl groups is formed on heating **I** under reduced pressure [8]. Briefly, previous experimental results may be interpreted in terms of Rh–CO bond cleavage rather than by homolysis of the Rh–Cp bond. In this communication we present evidence for the homolytic cleavage of the Rh–CpMe<sub>5</sub> bond occurring during photolysis with visible and near-UV light.

Thus, irradiation of **I** with either monochromatic ( $\lambda = 380$  nm) or polychromatic light ( $350 \text{ nm} \leq \lambda \leq 500 \text{ nm}$ ) in the presence of nitroso spin traps (see Table 1) led to the formation of spin adducts of radicals. As can be seen from the ESR shown in Fig. 1, two spin adducts are formed with nitrosodurene (ND): a triplet of triplets and a triplet of rather broad lines. The centre of the latter is shifted towards higher *g* values ( $g = 2.012 \pm 0.001$  in  $\text{CH}_2\text{Cl}_2$ ), whereas the triplet of triplets has a *g* value ( $g = 2.0061 \pm 0.005$ ) typical for spin adducts of carbon-centred free radicals. We observe similar spin adducts with other spin traps as well. The hyperfine splitting into three triplets of intensity 1:2:1 is due to the interaction of the unpaired electron with two equivalent nuclei having a nuclear spin  $I = 1/2$ . Therefore, this spin adduct is assigned to that of the radical  $\cdot\text{CH}_2\text{CpMe}_4^-$ . Other possible candidates for such a spin adduct would be radicals derived from the spin traps, e.g.  $\cdot\text{CH}_2\text{C}_6\text{H}(\text{CH}_3)_3\text{NO}$  for nitrosodurene.

TABLE 1. Spin adducts of radicals formed during photolysis of  $[(\eta^5\text{-CpMe}_5)\text{Rh}(\text{CO})_2]$  <sup>a</sup>

Spin trap	Solvent	Radical	$a_N$	$a_H$	$a_X$	<i>g</i>
MNP <sup>b</sup>	$\text{CH}_2\text{Cl}_2$	$\cdot\text{CH}_2\text{CpMe}_4^-$	1.595	1.271 (2H)		2.0061
ND	$\text{CH}_2\text{Cl}_2$	$\cdot\text{CH}_2\text{CpMe}_4^-$	1.417	0.815 (2H)	0.42 (1Rh)	2.0061
		$\cdot\text{Rh}(\text{CO})_2$	1.60 <sup>c</sup>			2.0012 <sup>c</sup>
	$\text{C}_6\text{H}_6$	$\cdot\text{CH}_2\text{CpMe}_4^-$	1.390	0.834 (2H)		2.0060
NM	$\text{CH}_2\text{Cl}_2$	$\cdot\text{CH}_2\text{CpMe}_4^-$	1.430	0.834 (2H)		2.0061
		$\cdot\text{Rh}(\text{CO})_2$	1.393	0.768 (2H)	d	2.012 <sup>c</sup>
	$\text{CH}_3\text{CN}$	$\cdot\text{CH}_2\text{CpMe}_4^-$	1.390	0.781 (2H)	d	2.012 <sup>c</sup>
PMNB	$\text{CH}_2\text{Cl}_2$	$\cdot\text{CH}_2\text{CpMe}_4^-$	1.401	0.854 (2H)		2.0060
		$\cdot\text{Rh}(\text{CO})_2$	1.59 <sup>c</sup>			2.011 <sup>c</sup>

<sup>a</sup>The following acronyms are used: MNP = 2-methyl-2-nitrosopropane, ND = nitrosodurene (2,4,5,6-tetramethylnitrosobenzene), NM = nitrosomesitylene (2,4,6-trimethylnitrosobenzene), PMNB = pentamethylnitrosobenzene; all coupling constants are given in mT ( $\pm 0.008$  mT), *g* values:  $\pm 0.0005$ ;  $T = 298$  K. <sup>b</sup>The radical di-tert-butyl nitroxide ( $a_N = 1.562$  mT) has been detected as well. <sup>c</sup>Coupling constants:  $\pm 0.02$  mT; *g*-values:  $\pm 0.001$ . <sup>d</sup>Not resolved.

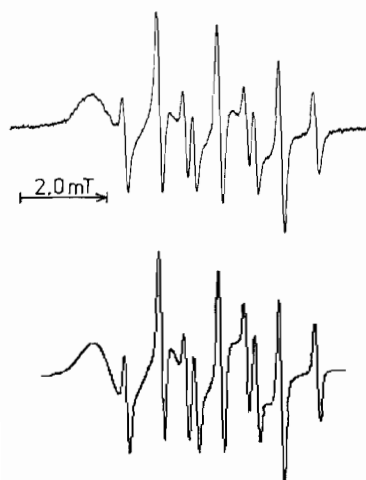


Fig. 1. ESR spectrum (top) of the spin adducts of the Rh-centred radical (broad lines) and  ${}^{\bullet}\text{CH}_2\text{CpMe}_5^-$  (triplet of triplets), respectively, formed during the photolysis (380 nm) of 0.01 M  $[(\eta^5\text{-CpMe}_5)\text{Rh}(\text{CO})_2]$  in the presence of 0.005 M nitrosodurene in dichloromethane; computer simulation (bottom).

However, the hyperfine splitting of the duryl radical produced by hydrogen abstraction from durene ( $a_{\text{N}} = 1.396 \pm 0.010$  mT,  $a_{\text{H}} = 0.935 \pm 0.010$  mT (2H);  $\text{CH}_2\text{Cl}_2$ ) is clearly different from that observed during the photolysis of the rhodium complex I.

As regards the assignment of the broad triplet, the considerable  $g$  shift suggests a Rh-centred radical. This assignment is also supported by the computer simulation of the ESR spectrum [9]. Satisfactory simulations were obtained only by taking into account an additional hyperfine splitting by one  ${}^{103}\text{Rh}$  nucleus ( $I = 1/2$ , 100% natural abundance). Since the carbon-centred and the Rh-centred radicals are formed simultaneously in a ratio of approximately 1:1, a structure  ${}^{\bullet}\text{Rh}(\text{CO})_2$  appears to be in accordance with the trapped Rh-centred radical. It is assumed that these radicals are formed by homolysis of the Rh–CpMe<sub>5</sub> bond, see eqn. (1).

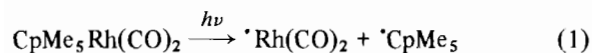
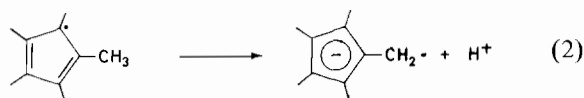


Photo-induced metal–Cp bond cleavage has been observed for the dimeric  $[\text{CpFe}(\text{CO})_2]_2$  as a side-reaction of minor importance [10], whereas the analogous iron complex of CpMe<sub>5</sub>, in contrast to the rhodium complex studied here, did not yield detec-

table amounts of  ${}^{\bullet}\text{CpMe}_5$  radicals [11]. The  ${}^{\bullet}\text{CpMe}_5$  radicals formed in eqn. (1) undergo fast rearrangement leading to  ${}^{\bullet}\text{CH}_2\text{CpMe}_4^-$  radicals, see eqn. (2).



Apparently, spin trapping of primary  ${}^{\bullet}\text{CpMe}_5$  radicals cannot compete with rearrangement of these radicals. An increase of spin trap concentration leads, however, to further complications in so far as electron transfer between nitroso spin traps and the rhodium complex may occur.

## Experimental

All experiments were carried out at room temperature. The ESR spectra were recorded using a Bruker ESR spectrometer, Model ER 200 tt operating at the X-band. A high-pressure mercury lamp (100 W, Hanovia) mounted on an optical bench and equipped either with a 380 nm Balzer or a band-pass filter (350 nm  $\leq \lambda \leq$  500 nm) served as the source of radiation.

For the simulation of the ESR spectra a computer program first described by Oehler and Janzen [9] was used.

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