

Spin trapping and some reactions of ruthenium-centred radicals

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Abstract

The generation of ruthenium-centred radicals by photolysis of dimeric ruthenium complex $[\text{Ru}(\text{CO})_2\text{Cp}]_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) has been studied by EPR and spin trapping. Mechanistic studies reveal that in toluene homolytic cleavage of both the Ru–Ru and Ru–CO bonds takes place yielding $\text{Ru}(\text{CO})_2\text{Cp}$ radicals and an intermediate dinuclear ruthenium complex which is CO-bridged. This reacts with $\text{P}[\text{OCH}(\text{CH}_3)_2]_3$ yielding the monosubstituted dinuclear compound $\{\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{P}[\text{COH}(\text{CH}_3)_2]_3\}$. The ruthenium-centred radicals react with dioxygen to form peroxy radicals which may abstract hydrogen from C–H bonds. The reactivity of the photogenerated ruthenium species with various substrates is reported.

Introduction

According to the principle of isolobal analogy [1], there is a close resemblance between many coordinatively unsaturated paramagnetic metal complexes and 'classical' organic free radicals. This analogy is also reflected by the behaviour of metal-centred radicals towards nitroso spin traps. Hudson *et al.* [2] first demonstrated that short-lived metal-centred radicals generated by the photoinduced homolysis of dinuclear organometallics form fairly persistent spin adducts with both aliphatic and aromatic nitroso compounds. Although many examples for spin trapping of metal-centred radicals can be found in the literature [3, 4], little is known about the behaviour of the heavier Group VIII transition metals.

Recently, report was made of the spin adducts of rhodium and platinum-centred radicals [5, 6] formed by photolysis of mononuclear complexes. Spin trapping of $\text{Ru}(\text{CO})_4\text{SiMe}_3$ radicals generated by thermolysis of the corresponding dinuclear complex has briefly been mentioned [7]. Apparently, spin adducts of these radicals to nitrosodurene are unstable, and no well-resolved EPR spectra could be recorded. Here we report EPR data of spin adducts of the radical $\text{Ru}(\text{CO})_2\text{Cp}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) generated by photolysis of the corresponding dinuclear complex in the presence of various nitroso spin traps (see Table 1). The behaviour of $\text{Ru}(\text{CO})_2\text{Cp}$

radicals towards some carbon halides and dioxygen was also studied and some comparisons with the corresponding $\text{Fe}(\text{CO})_2\text{Cp}$ radicals have been made.

Experimental

Spin trapping experiments were carried out in toluene and dichloromethane solutions. Unless otherwise stated, solutions containing 0.005 M spin trap and 0.01 M $[\text{Ru}(\text{CO})_2\text{Cp}]_2$ were used. Nitrosodurene (2,3,5,6-tetramethylnitrosobenzene, ND) and nitrosomesitylene (2,4,6-trimethylnitrosobenzene, NM) were prepared as described by Smith and Taylor [8, 9]. 2-Methyl-2-nitrosopropane (MNP) was synthesized according to the procedure published by Stowell [10]. The spin traps phenyl-*N*-*t*-butyl nitron (PBN), 2,3,6-tri-*t*-butylnitrosobenzene (BSB) and nitrosobenzene (NB) were commercially available (Aldrich). $[\text{Ru}(\text{CO})_2\text{Cp}]_2$ was purchased from Strem Chemicals.

All experiments were carried out at room temperature using a Bruker ER 200 D spectrometer operating in the X-band. Field calibration was made on the basis of the hyperfine splitting of di-*t*-butyl nitroxide generated *in situ* by photolysis in benzene ($a_N = 1.5404$ mT [11]). DPPH served as a standard for the measurement of g values ($g = 2.0036$). A quartz flat cell attached to an H-shaped mixing chamber was used as a sample cell. Dioxygen was removed from the sample by purging with purified dinitrogen for at least 20 min prior to EPR measurement.

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A computer program published by Oehler and Janzen [12] was used for simulation of complex EPR spectra. Photolysis was carried out directly inside the cavity of the EPR spectrometer using a high pressure mercury lamp mounted on an optical bench and fitted with suitable cut-off and band-pass filters in order to eliminate undesired light frequencies. A Bruker FT-IR spectrometer was used for recording IR spectra.

Preparation of $\{Cp_2Ru_2(CO)_3P[OCH(CH_3)_2]_3\}$

$[Ru(CO)_2Cp]_2$ (0.266 g, 6 mmol) was dissolved in 100 ml of toluene containing 12 mmol of $P[OCH(CH_3)_2]_3$. The solution was purged with N_2 and irradiated with $\lambda > 335$ nm for 3 h. Chromatography, eluting with dichloromethane-hexane (4:1), then gave a brown band from which $\{Cp_2Ru_2(CO)_3P[OCH(CH_3)_2]_3\}$ was obtained. *Anal. Calc.* for $C_{22}H_{31}Ru_2PO_6$: C, 42.30; H, 5.00. Found: C, 42.18; H, 5.01%. IR absorption in KBr: ν (CO bridge) 1975s, 1940s; ν (CO term.) 1805 m, 1775s cm^{-1} .

Reaction of $[Ru(CO)_2Cp]_2$ in the presence of CCl_4 and $P[OCH(CH_3)_2]_3$

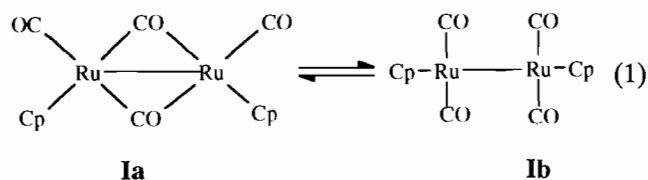
The reaction between $[Ru(CO)_2Cp]_2$ (6 mmol) and CCl_4 was carried out in toluene (100 ml) containing $P[OCH(CH_3)_2]_3$ (12 nmol) and 1 M CCl_4 . The solution was placed in an Erlenmeyer flask and purged with N_2 . After 3 h of irradiation ($\lambda > 335$ nm) the solution was rotary aspirated to dryness and the residue was chromatographed on alumina with CH_2Cl_2 . After removal of solvent $CpRu(CO)_2Cl$ was obtained. *Anal. Calc.* for $C_7H_5O_2ClRu$: C, 32.63; H, 1.96; Cl, 13.76. Found: C, 32.56; H, 1.99; Cl, 13.75%. IR absorption in KBr: 2055s and 2004s cm^{-1} .

Reaction of $[Ru(CO)_2Cp]_2$ in the presence of CH_3I and $P[OCH(CH_3)_2]_3$

Photoreaction was carried out with CH_3I (1 M), $[Ru(CO)_2Cp]_2$ and $P[OCH(CH_3)_2]_3$ in toluene as described for the photoreaction in the presence of CCl_4 . Chromatography was performed as above and evaporation of the solvent separated $CpRu(CO)_2I$. *Anal. Calc.* for $C_7H_5RuO_2I$: C, 24.08; H, 1.44. Found: C, 24.20; H, 1.42%. IR absorption in KBr: $\nu(CO)$ 2035s, 1990s cm^{-1} .

Results and discussion

It has been shown [13, 14] that both $[Ru(CO)_2Cp]_2$ and $[Fe(CO)_2Cp]_2$ have bridged dinuclear structures in the solid state. However, unlike the iron complex, which exists mostly (> 99%) in its CO-bridged, dinuclear form in solution [15], the analogous ruthenium complex was found to be present in an equilibrium of bridged (**Ia**) and non-bridged dinuclear forms (**Ib**), eqn. (1) [16].



Equilibrium (1) is known to be both temperature and solvent dependent. As shown in Fig. 1, in dichloromethane and toluene, the IR spectra of $[Ru(CO)_2Cp]_2$ can be clearly distinguished from one another. Based on the assignments made by McArdle and Manning [16], it may be concluded that the non-bridged form **Ib** is more dominant in toluene than in dichloromethane.

Equilibrium (1) is also reflected by the electronic absorption spectrum since UV absorption bands at 38 000 and c. 30 500 cm^{-1} may be assigned to $\sigma_b \rightarrow \sigma^*$ transitions of the bridged and non-bridged complexes, respectively [17]. Although equilibrium (1) is strongly temperature and solvent-dependent, this behaviour is not reflected by photochemical quantum yields which do not depend on the ratio of bridged and non-bridged forms. It is generally proposed that the photochemistry of this compound proceeds via metal-centered radicals [18] although alternative pathways involving ligand expulsion have also been forwarded [19].

When c. 0.005 M toluene solutions of $[Ru(CO)_2Cp]_2$ are photolyzed in the presence of ND with filtered ($\lambda > 335$ nm) light at room temperature, fairly intense EPR signals of a spin adduct, **IIa**, exhibiting additional coupling by two ruthenium isotopes ($^{99}Ru: I=5/2, 12.7\%$ natural abundance; $^{101}Ru: I=5/2, 17\%$ natural abundance) were recorded (Fig. 2). The g value ($g = 2.0078 \pm 0.0005$) was found to be significantly higher than usually observed for spin adducts of organic radicals [20]. Therefore, this EPR signal is assigned to the spin adduct of the radical $\cdot Ru(CO)_2Cp$ to nitrosodurene.

Similar results were obtained with other aromatic nitroso compounds (Table 1). However, unlike aromatic nitroso compounds, two different EPR signals of spin adducts of Ru-centred radicals were recorded upon irradiation ($400 < \lambda < 500$ nm) in the presence of the spin trap MNP. While one signal, **IIe** ($g = 2.0073 \pm 0.0005, a_N = 1.731 \pm 0.008$ mT), resembles those obtained with aromatic nitroso compounds, the other signal, **III** ($g = 2.0038 \pm 0.0008, a_N = 1.680 \pm 0.008$ mT, $a_{101-Ru} = 0.560 \pm 0.008$ mT, $a_{99-Ru} = 0.531 \pm 0.008$ mT) is characterized by an unusually low g value which is typical of spin adducts formed by radical addition at the oxygen, rather than the nitrogen atom of a nitroso compound [21]. In addition, EPR signals of di-*t*-butyl nitroxide ($Bu_2NO, a_N = 1.528 \pm 0.005$ mT, $g = 2.0061 \pm 0.0005$) were also observed, although photolysis of MNP did not give rise to the formation of this nitroxide under the conditions employed ($400 < \lambda < 500$ nm). Ap-

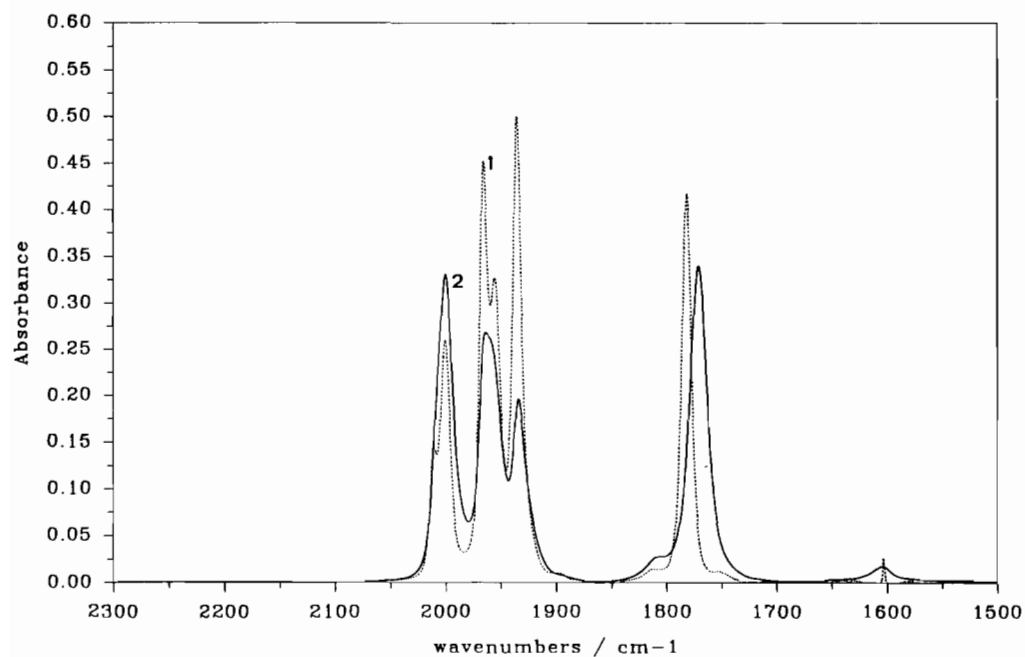


Fig. 1. Comparison of IR spectra of $[\text{Ru}(\text{CO})_2\text{Cp}]_2$ in toluene (1) and in dichloromethane (2) at 298 K in 1.00 mm path cells.

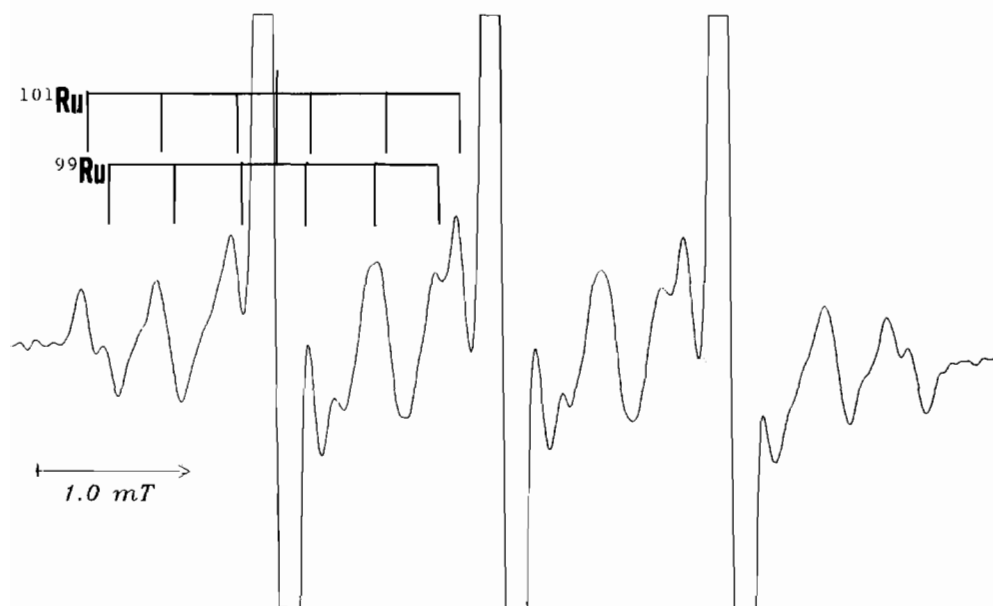


Fig. 2. EPR spectrum of spin adducts formed during irradiation ($\lambda = 335 \text{ nm}$) of a toluene solution of $[\text{Ru}(\text{CO})_2\text{Cp}]_2$ in the presence of ND.

parently, formation of di-*t*-butyl nitroxide results from the decomposition of another spin adduct. Both Ru-containing nitroxides may serve as precursors for di-*t*-butyl nitroxide since the EPR intensity of the latter signal increases after turning off the light, whereas the EPR signals **IIe** and **III** are rapidly decaying; **IIe** faster than **III**.

A possible route for the formation of di-*t*-butyl nitroxide is given in eqn. (2).

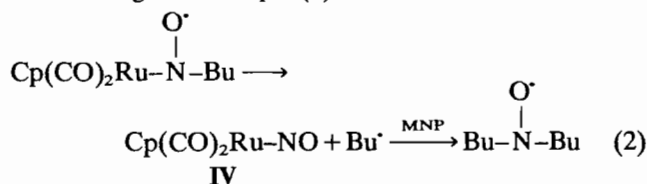
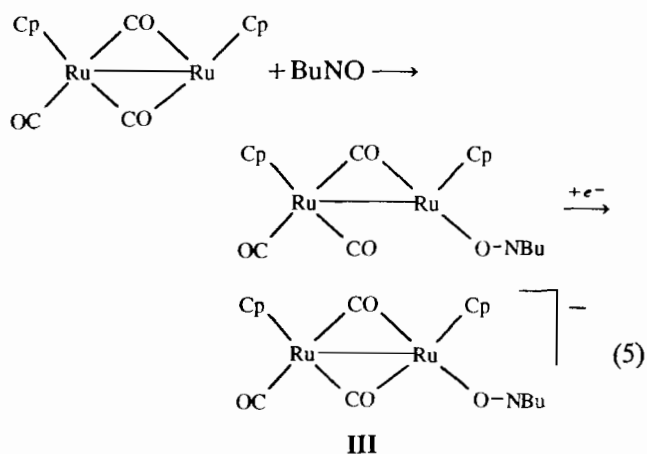
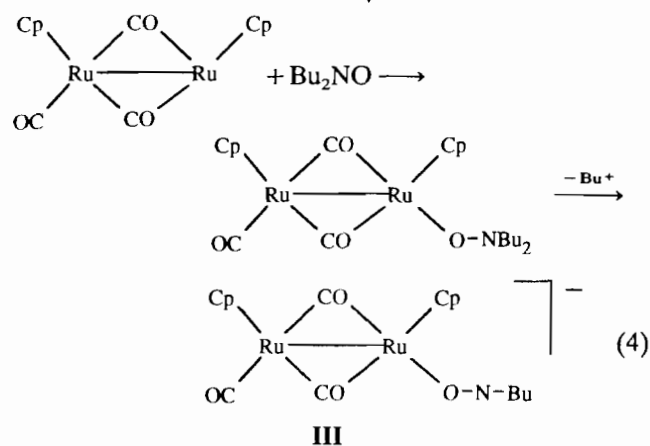
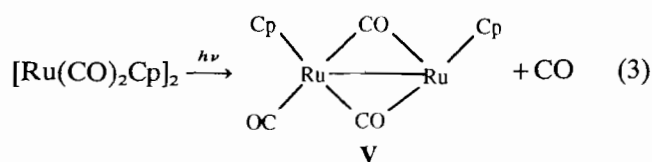


TABLE 1. EPR data for spin adducts of Ru-centred radicals to nitroso compounds^a

Spin trap	Radical	Spin adduct		In toluene		In CH ₂ Cl ₂	
		a_N	$a_{99\text{-Ru}}$	g	$a_{101\text{-Ru}}$	g	a_N
ND	$\text{Ru}(\text{CO})_2\text{Cp}$	1.706	0.504	2.0078	0.570	2.0070	1.598
NM	$\text{Ru}(\text{CO})_2\text{Cp}$	1.673	0.484	2.0082	0.538	2.0073	1.595
BNB	$\text{Ru}(\text{CO})_2\text{Cp}$	1.222	0.362 ^b	2.0057	0.441 ^c	2.0053	1.190
NB	$\text{Ru}(\text{CO})_2\text{Cp}$	1.170	0.398	2.0073	0.457	2.0070	1.139
MNP	$\text{Ru}(\text{CO})_2\text{Cp}$	1.731	0.407	2.0073	0.631	2.0064	1.642
MNP	$\text{Ru}(\text{CO})_2\text{Cp}$	1.680	0.560	2.0038			not observed

^aRoom temperature; all coupling constants in mT (± 0.008 mT); g value ± 0.0005 . ^b⁹⁹Ru hyperfine splitting not resolved; $a_H = 0.148$ mT. ^c $a_H = 0.309$ mT ($3H^{\text{op}}$), $a_H = 0.108$ mT ($2H^{\text{m}}$). ^dStructure see eqns. (4) and (5), respectively. ^e⁹⁹Ru hyperfine splitting not resolved; $a_H = 0.140$ mT. ^f $a_H = 0.300$ mT ($3H^{\text{op}}$), $a_H = 0.097$ mT ($2H^{\text{m}}$).

The nitrosyl complex **IV** is expected to be EPR silent. However, oxidation or reduction of **IV** could produce a paramagnetic species with EPR parameters similar to those found for **III**. On the other hand, photolysis of $[\text{Ru}(\text{CO})_2\text{Cp}]_2$ in the presence of dissolved NO did not lead to enhanced formation of **III**. Therefore, it should be unlikely that **III** is a nitrosyl ruthenium complex. An alternative assignment of **III** is based on the assumption that besides the homolytic cleavage of the Ru–Ru bond, a photoinduced Ru–CO bond cleavage occurs producing a coordinatively unsaturated dinuclear complex **V**, eqn. (3). In the intermediate **V** one of the Ru atoms is a 16-electron center. The coordinatively unsaturated Ru can add a di-*t*-butyl nitroxide or MNP to give the O-coordinated aminyl radical ion **III**, eqns. (4) and (5).



Two pieces of evidence may be given in support of eqns. (3)–(5).

(1) Irradiation of $[\text{Ru}(\text{CO})_2\text{Cp}]_2$ in the presence of $\text{P}[\text{COH}(\text{CH}_3)_2]_3$ in toluene solutions leads to formation

of the monosubstituted dinuclear species $\{\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{P}[\text{PCH}(\text{CH}_3)_2]_3\}$. This strongly supports the formation of the coordinatively unsaturated intermediate **V**.

(2) Irradiation of toluene solutions of **1**, containing MNP and increasing amounts of $\text{P}[\text{OCH}(\text{CH}_3)_2]_3$ results in a progressive decrease in the EPR signal **III**. In these photoreactions, signal **IIe** is formed to the extent that formation of signal **III** is suppressed.

To our knowledge there is only one example of this type of MNP spin adduct [21]. The low g value is in accordance with the proposed MNP bonding mode. Generally, the formation of this type of spin adduct is preferred in the case of bulky radicals [22]. Steric hindrance may also be the reason why no spin adducts of dinuclear paramagnetic species are formed with *ortho*-substituted aromatic nitroso compounds.

When oxygen is present in solution, no ruthenium-centred radicals could be spin trapped. This suggests a fast reaction between dioxygen and intermediate ruthenium-centred radicals. On the other hand, benzyl radicals ($\text{CH}_2\text{C}_6\text{H}_5$) were readily detectable by spin trapping by nitrosodurene in an oxygen-containing toluene solution ($a_{\text{N}} = 1.349 \pm 0.008$ mT, $a_{\text{H}} = 0.780 \pm 0.005$ mT (2H), $g = 2.0061 \pm 0.0005$). This assignment could be confirmed by using perdeuterated toluene which led to formation of $\text{CD}_2\text{C}_6\text{D}_5$ spin adducts ($a_{\text{N}} = 1.35 \pm 0.01$ mT, $a_{\text{D}} = 0.11 \pm 0.01$ mT, $g = 2.0061 \pm 0.0008$). When the light is turned off, an increase in benzyl spin adduct signal intensity could still be observed. Since no benzyl spin adducts could be detected when either a ruthenium complex or dioxygen or light were absent, intermediate coordinatively unsaturated ruthenium complexes are assumed to be photocatalysts for the generation of benzyl radicals, possibly via peroxo ruthenium species. Similar behaviour has been observed for the corresponding iron compound [6]. It is, however, worth noting that, unlike the corresponding dinuclear iron complex, $[\text{Ru}(\text{CO})_2\text{Cp}]_2$ leads to intense signals of CCl_3 spin adducts ($a_{\text{N}} = 1.063 \pm 0.005$ mT, $a_{\text{Cl}} = 0.132 \pm 0.005$ mT) upon irradiation in CCl_4 in the presence of nitrosodurene. The lack of CCl_3 radicals in the photolysis of $[\text{Fe}(\text{CO})_2\text{Cp}]_2$ has been attributed to a fast secondary process involving the bridged dinuclear iron complex [6, 23].

In view of the more preferred non-bridged structure of $[\text{Ru}(\text{CO})_2\text{Cp}]_2$, the formation of free CCl_3 radicals appears to be in accordance with what is known from other metal-centred radicals. Apparently, chlorine abstraction from CCl_4 by Ru-centred radicals is a very efficient process since no ruthenium spin adducts could be detected when 1 M CCl_4 was present in the solution.

In order to obtain information on the fate of the intermediate **V** (eqn. (3)) it was necessary to perform other photochemical experiments. In particular, irradiation of $[\text{Ru}(\text{CO})_2\text{Cp}]_2$ in a toluene solution containing

1 M $\text{P}[\text{OCH}(\text{CH}_3)_2]_3$ and 1 M CCl_4 yields $\text{CpRu}(\text{CO})\text{Cl}$ as the dominant product, without any evidence of the formation of $\{\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{P}[\text{OCH}(\text{CH}_3)_2]_3\}$. By using CH_3I instead of 1 M CCl_4 , the formation of the dinuclear bridged monosubstituted complex is suppressed, the dominant product being $\text{CpRu}(\text{CO})_2\text{I}$. Monitoring the photoreaction by EPR spin adducts of CH_3 radicals to ND were observed ($a_{\text{N}} = 1.370 \pm 0.08$ mT, $a_{\text{H}} = 1.236 \pm 0.080$ mT (3H)). The results strongly suggest that the presence of CCl_4 and CH_3I can quench the formation of monosubstituted dinuclear species, probably as a consequence of the cleavage of the Ru–Ru bond in **V**.

Irradiation of $[\text{Ru}(\text{CO})_2\text{Cp}]_2$ has also been carried out in different solvents. No solvent derived radicals were observed when CH_2Cl_2 was used as solvent. Spin adducts of Ru-centred radicals to nitroso spin traps were readily detectable in dichloromethane solutions (Table 1). In most cases their EPR parameters closely resemble those obtained in toluene solution. With MNP, however, only one type of Ru-centred radical could be detected in CH_2Cl_2 . Taking into account that the non-bridged structure of $[\text{Ru}(\text{CO})_2\text{Cp}]_2$ is more preferred in toluene solutions, this result is rather surprising as one would expect type **III** radicals to be more readily formed from bridged structures.

Taken together the above results suggest that the actual structure of the dimeric ruthenium compound $[\text{Ru}(\text{CO})_2\text{Cp}]_2$ is of little, if no importance for its photochemical behaviour in comparison with the role of the bridged, dinuclear intermediate **V**.

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