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Photochemistry of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ in polar and non-polar solvents

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Abstract

The photochemistry of bridged and non-bridged isomers of the title complex was studied in various solvents by flash photolysis and continuous irradiation at different wavelength regions. Reactive decay of the excited non-bridged isomer produced either a polymer (in neat non-polar solvents) or monomeric $[CpRu(CO)_2Cl]$ complex (in non-polar solvents containing CCl_4) via homolytic cleavage of the Ru-Ru bond. Polymerization was preceded by generation of a transient species (IP_1) with $\lambda_{max} \approx 470$ nm and $\tau_{1/2} \approx 4$ ms, which was tentatively formulated as a trimer $[CpRu(CO)_2]_3$. Photolysis of the bridged isomer generated another transient species, IP_2, characterized by the solvent-dependent absorption at 315–330 nm, assigned to the mono-bridged dimer with coordinated solvent L, $[Cp(CO)_2Ru(\mu\text{-}CO)Ru(CO)LCp]$. The IP_2 properties and reactivity led to conclusion that photocleavage of the CO-bridge is the mode for the bridged isomer. © 1997 Elsevier Science S.A.

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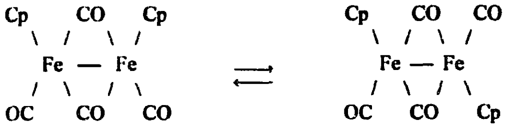
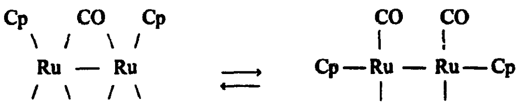
1. Introduction

$[CpM(CO)_2]_2$ complexes, where $Cp = \eta^5\text{-}C_5H_5$ and $M = Fe$ or Ru, have been the subject of interest for many years because of solvent-dependent equilibria between their different forms [1–7]. The equilibria make the photochemistry of the dimers more complicated. Of the two above complexes, more is known about the iron compound, for which major forms are *cis* and *trans* isomers of the double bridged compound, $[Cp(CO)Fe(\mu\text{-}CO)_2Fe(CO)Cp]$



(1)

Two following primary photochemical pathways were found for the iron complex: (a) homolysis of the Fe–Fe bond producing a short living species defined as $[CpFe(CO)_2]^{\cdot}$ radicals [7–18], and (b) a loss of one of the CO ligands as a result of which a longer living dinuclear intermediate formulated as triply bridged $[CpFe(\mu\text{-}CO)_3FeCp]$ is generated [10,17–25]. Recently it has been proposed that also a double bridged, $[Cp(CO)Fe(\mu\text{-}CO)_2FeCpL]$, or a single bridged, $[Cp(CO)Fe(\mu\text{-}CO)Fe(CO)Cp]$, transient species are produced (L = solvent) [26].



(2)

In ruthenium dimer solutions, a non-bridged form comes into importance due to the equilibrium [1] which is solvent, temperature and pressure-dependent [2,7,27]. Nevertheless, the photochemical pathways found thus far resemble those of the iron complex, namely either homolytical cleavage of the M–M bond accompanied by generation of the $[CpRu(CO)_2]^{\cdot}$ radicals [7,17,28] or CO dissociation leading to a dimeric species $[Cp_2Ru_2(CO)_3]$ [7,17,28]. The problem which needs further elucidation is selectivity in photolysis of bridged and non-bridged forms existing in the equilibrium (2). In ealier studies [7] the photochemical mode was assumed to be essentially wavelength independent, whereas in more recent investigations

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different pathways following irradiation of alternative forms were suggested [17].

In this study, an attempt was made to solve the above problem by product analysis for varied ratios of bridged and non-bridged forms, using different irradiation wavelengths and detection time scale: flash photolysis (μs–ms), continuous irradiation with UV/Vis detection (s–min) and IR spectroscopy (for stable products).

2. Experimental

$[CpRu(CO)_2]_2$ was purchased from Strem Chemicals and used as received. The solvents used were of spectrophotometric or reagent grade (from Aldrich and POCh, Poland). Concentrations of solutions varied from 5×10^{-6} M in flash photolysis experiments, through 2×10^{-4} M in continuous photolysis experiments to 10^{-3} M in IR product analysis. When CCl_4 was used, its concentration was ca. 1 M. Solutions were deaerated by argon which was bubbled for at least 0.5 h. All experiments were carried out under deaerated conditions.

Continuous irradiations were performed in 1-cm quartz cuvettes using a high pressure mercury lamp HBO 200 F (Narva) and a medium pressure mercury lamp ASH 400. The desired spectral region was selected using the 265, 333 and 436-nm filters. UV-Vis spectra were recorded on a Shimadzu UV-2100 spectrophotometer.

The equipment and procedure used for quantum yield determinations were the same as described previously [29]. In all the cases irradiations were limited to less than 10% conversion.

Solutions for IR product analysis were irradiated directly in 1 mm NaCl or CaF_2 cells. Spectra were recorded on a Bruker IFS 48 spectrometer.

Flash photolysis experiments were performed in a 16 cm quartz cell using full spectrum of a xenon lamp with or without a glass filter cutting off the wavelengths below 340 nm. Flashes were of 400 J energy per pulse and of 25 μs duration. The flash photolysis equipment was described in details elsewhere [30].

3. Results

Photochemistry of $[CpRu(CO)_2]_2$ was studied under ambient temperature and pressure conditions, which is why, in order to obtain one isomer predominating in solution, non-polar and polar solvents were used. In non-polar solvents (isooctane, toluene and carbon tetrachloride) the non-bridged form prevailed, whereas in polar solvents (acetonitrile, isopropanol, DMSO or DMF) the equilibrium (2) was shifted towards the bridged isomer [2,7,27]. The UV/Vis analysis was based on the known spectral characteristics of the isomers: the intense band at 265 nm was assigned to the $\sigma_{\mathrm{bridge}}\rightarrow\sigma^*_{\mathrm{bridge}}$ excitation in the bridged form, whereas the one at 330 nm was assigned to the $\sigma_{\mathrm{nonbridge}}\rightarrow\sigma^*_{\mathrm{nonbridge}}$ transition in the non-bridged form, respectively [2,4,7,31]. In some of these solvents (acetonitrile, DMSO or DMF) the $\sigma_{\mathrm{nonbridge}}\rightarrow\sigma^*_{\mathrm{nonbridge}}$ band was shifted to 345–347 nm, and the minor absorption in visible region was moved from 430 to ~450–460 nm. The band at 265 nm characteristic of the bridged isomer was not solvent-dependent thus showing that in solutions of $[CpRu(CO)_2]_2$, a specific solvent effect is observed that exerts only on the non-bridged isomer.

3.1. Continuous irradiation

Continuous irradiation by 334 nm or 436 nm of the non-bridged isomer in neat isooctane or toluene was found to generate a turbidity followed by precipitation, which proceeded faster with increasing initial concentration. This was no longer observed in very dilute solutions ($c<10^{-5}$ M) or when CCl_4 was present in the system. In moderately dilute solutions the turbidity was preceded by an increase in absorbance at 265 nm at the expense of the band at 330 nm with an isosbestic point at ~310 nm (Fig. 1a) thus demonstrating the shift of the equilibrium (2) towards the bridged form. The same conclusion could be drawn from the flash experiments (Fig. 2).

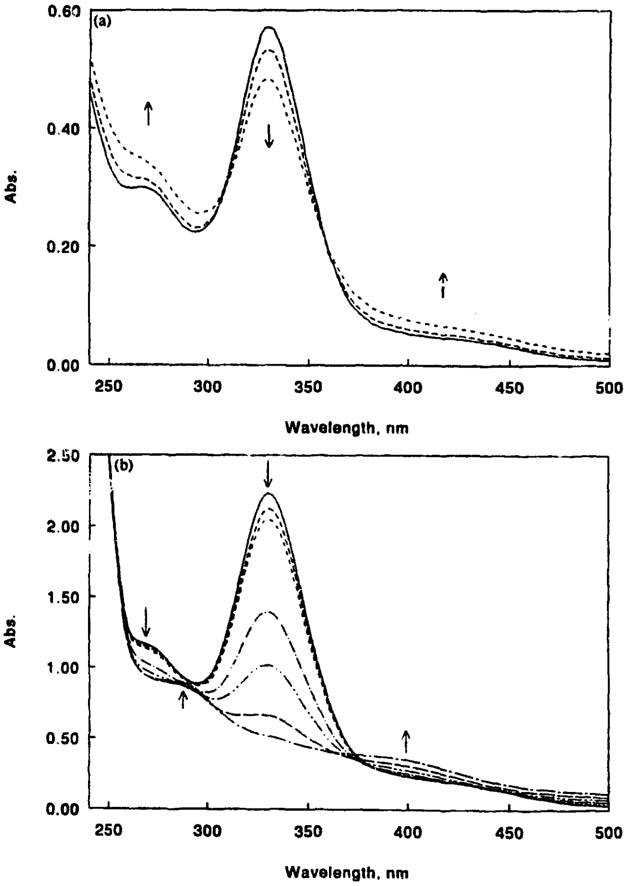


Fig. 1. UV-Vis spectral changes during $[CpRu(CO)_2]_2$ continuous photolysis ($\lambda_{irr}=334$ nm) in the neat isooctane (a) and in the presence of CCl_4 (b). Arrows show the direction of changes.

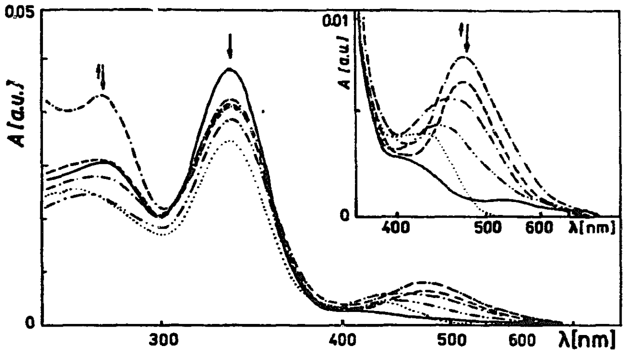


Fig. 2. UV-Vis spectral changes recorded in flash photolysis of $[CpRu(CO)_2]_2$ in isooctane: before flashing (———) and at t=40 μs (– – –), 100 μs (— · —), 1 ms (– · · –), 100 ms (– · · · –), 60 s (···) after initiation the flash, respectively.

In the presence of CCl_4 production of $[CpRu(CO)_2Cl]$ was observed by the increase in absorption at 285 nm [7] (Fig. 1b). The decay of the substrate was then more effective, which was demonstrated by a considerable increase in the quantum yield values (Table 1). Upon prolonged irradiation the conversion into $[CpRu(CO)_2Cl]$ was nearly 100%. Photolysis of the non-bridged form of $[CpRu(CO)_2]_2$ in toluene containing $CF_3C{\equiv}CCF_3$ resulted in formation of $[CpRu(CO)_2(\eta^1\text{-}CF_3C{=}CHCF_3)]$.

Continuous irradiation of solutions, in which the bridged isomer is the dominating form (acetonitrile, DMF or DMSO), resulted in a decrease of both the bands irrespective of the irradiation wavelength (265, 334 or 436 nm). The dimer concentration in the neat solvents decreased with the ratio between both the forms, characteristic of a given solvent, unchanged. The decrease led to nearly complete disappearance of absorbance within the visible and near UV region. In the presence of CCl_4 in the system, only absorption at 285 nm, characteristic of $[CpRu(CO)_2Cl]$ could be detected within UV-Vis region upon prolonged irradiation.

In 1-propanol or 2-propanol both the forms of $[CpRu(CO)_2]_2$ are present at comparable concentrations [27], and their behaviour at continuous irradiation was intermediate between the previously discussed cases. As in other polar solvents the decay of both the isomers was recorded during which the equilibrium (2) was maintained. As in non-polar solvents, however, the increase in turbidity with prolonged irradiation was observed. The turbidity was suppressed by addition of NPh_4CN or CCl_4. In the case of CCl_4, production of $[CpRu(CO)_2Cl]$ was easily detected.

The quantum yields values (Table 1) demonstrated their dependence on: wavelength of irradiation, solvent nature and presence of CCl_4. The last effect was predominant. The results with CCl_4 are comparable with those previously reported [7].

3.2. Flash photolysis

Both UV ($\lambda>250$ nm) and visible ($\lambda>340$ nm) flash photolysis of the dimer in isooctane or toluene led to a decrease in the substrate absorption at 330 nm and to formation of a transient absorption with the maximum at ~470 nm, IP_1 (Fig. 2). The substrate decay proceeded in two consecutive steps: photochemical, recorded immediately after the flash (40 μs), and secondary thermal, observed up to seconds after the flash (post-irradiation effect). Within hundreds of μs, the increase in absorption characteristic of the bridged form could be also detected. The transient absorption intensity at ~470 nm did not reach the maximum immediately upon flashing, but its intensity developed within hundreds of μs and decayed with $\tau_{1/2}\approx 4$ ms. In the presence of CCl_4 the immediate decay at 330 nm was more effective, whereas the absorption at ~470 nm was significantly suppressed; in neat CCl_4 solution the band was practically not observed.

Table 1
Quantum yields of the $[CpRu(CO)_2]_2$ decay at λ_{irr} = 334 and 436 nm

Conditions	λ_{irr}	
	334 nm	436 nm
Neat isooctane	0.10 ± 0.01	0.070 ± 0.005
Isooctane + CCl_4	0.39 ± 0.01	0.31 ± 0.02
Neat toluene	0.074 ± 0.007	
Toluene + CCL_4	0.22 ± 0.03	
Neat 2-propanol	0.143 ± 0.015	
Neat acetonitrile	0.088 ± 0.006	0.065 ± 0.001
Acetonitrile + CCL_4	0.433 ± 0.005	0.34 ± 0.01

Note: $c=2\cdot10^{-4}$ M; ϵ^0_{330} = 13 750 $dm^3\,cm^{-1}\,mol^{-1}$, ϵ^0_{333} = 11 200 $dm^3\,cm^{-1}\,mol^{-1}$, ϵ^0_{330} = 5100 $dm^3\,cm^{-1}\,mol^{-1}$, ϵ^0_{341} = 5040 $dm^3\,cm^{-1}\,mol^{-1}$ in isooctane, toluene, 2-propanol and acetonitrile, respectively; $[CCl_4]$ = 1 M; error calculated as a mean standard deviation).

In acetonitrile and in 1- or 2-propanol the transient spectra depended on the spectral characteristics of the flash: when cut-off filter was used ($\lambda>340$ nm) nearly the same results as by flashing of the non-bridged form in a non-polar solvent were recorded (Fig. 3). UV-flash photolysis led to generation of IP_1 at much lower concentration than in the photolysis in non-polar solvents. In addition to IP_1, a new intensive transient absorption (IP_2) with maximum at ~330 nm and ~315 nm in acetonitrile and propanol, respectively, was developed within μs. The bathochromic shift of the maximum resem-

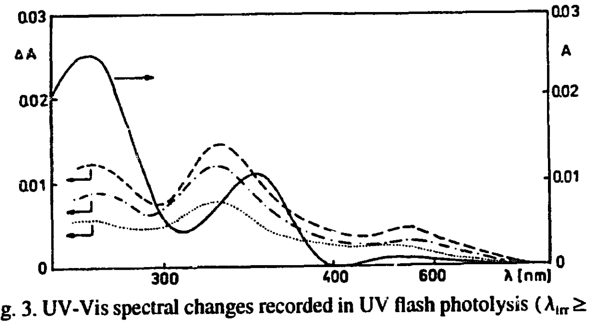


Fig. 3. UV-Vis spectral changes recorded in UV flash photolysis ($\lambda_{irr}\geq 250$ nm) of $[CpRu(CO)_2]_2$ in acetonitrile. The transient absorption is presented as difference spectra, ΔA is the absorbance change observed from before the flash (———) to t=40 μs (– – –), 100 μs (– · –) and 400 μs (···) after flashing, respectively.

Table 2
IR spectra of $[CpRu(CO)_2]_2$ and its final photoproducts in isooctane and acetonitrile (λ_{irr} = 334 nm, values in cm^{-1})

Conditions\band assignment	$\nu_{\mu\text{-CO}}$ [a]	$\nu_{CO\text{-}t}$ [a]	$\nu_{CO\text{-}t}$ [a]	$\nu_{CO\text{-}t}$ [a]	$\nu_{CO\text{-}t}$ [a]	$\nu_{CO\text{-}t}$ [b]	$\nu_{CO\text{-}t}$ [a]	$\nu_{CO\text{-}t}$ [b]
$[CpRu(CO)_2]_2$ in isooctane [c]	1793	1944	1965	1974	2010	2021		
Photoproducts:								
in isooctane + CCl_4						2010		2057
in neat isooctane:								
(a) solution						~2015		
(b) solid state	1790	~1950					2020	
$[CpRu(CO)_2]_2$ in acetonitrile [d]	1772	1934	1957	1965	1996			
Photoproducts:								
in acetonitrile + CCl_4				1965 [e]		1998		2055
in neat acetonitrile				1965 [e]				

[a] Bands characteristic of both the isomers of the $[CpRu(CO)_2]_2$ dimer [1,2] $\nu_{\mu\text{-CO}}$ denotes CO-bridged stretching; $\nu_{CO\text{-}t}$ denotes stretchings of the terminal CO.

[b] Bands characteristic of $[CpRu(CO)_2Cl]$ according to [7].

[c] Bands: 1794, 1944, 1965, 1973, 2010 and 2020 cm^{-1} were reported in [2] for $[CpRu(CO)_2]_2$ in heptane.

[d] Bands: 1778, 1935, 1954, 1962 and 1995 cm^{-1} were also reported in [2] for $[CpRu(CO)_2]_2$ in acetonitrile.

[e] The band of the photoproduct of $[CpRu(CO)_2]_2$ in acetonitrile, assigned to $[CpRu(CO)_2(CH_3CN)]$.

bled the specific solvent effect on the non-bridged form in acetonitrile. The transient species decayed within tens of ms, and after 1 min only the reactant absorption at reduced concentration was recorded. In the presence of CCl_4, the IP_1 was not observed, whereas the IP_2 was suppressed and decayed much faster than in the neat solvent.

3.3. IR product analysis

IR spectrum of $[CpRu(CO)_2]_2$ was already reported in several papers [1,2,7]. The recorded bands and their changes during irradiation of the dimer in isooctane/CCl_4, acetonitrile/CCl_4 mixtures and neat solvents are summarized in Table 2. When $[CpRu(CO)_2]_2$ was irradiated in isooctane/CCl_4 mixture the bands characteristic of the dimer decreased and the new bands (2010 and 2057 cm^{-1}) increased (Fig. 4). According to Wrighton et al. [7] the formed bands are characteristic of the $[CpRu(CO)_2Cl]$ complex. The analogous bands (1998, 2055 cm^{-1}) appeared when $[CpRu(CO)_2]_2$ was irradiated in acetonitrile/CCl_4 mixture. In this case also, formation of another band, at 1965 cm^{-1} was observed (Table 2, Fig. 5). When similar experiments were performed in the absence of CCl_4, the only increasing band was 1965 cm^{-1}. These results suggest that in the presence of CCl_4, $[CpRu(CO)_2Cl]$ is the main final product for each studied solvent except acetonitrile, for which competition between CCl_4 and solvent had to be taken into consideration.

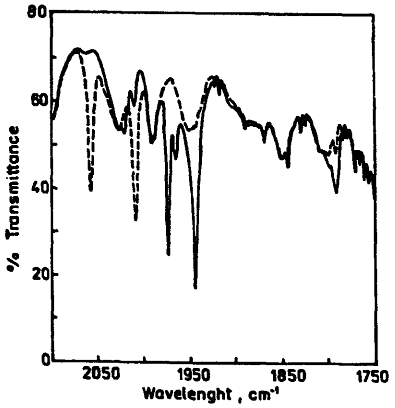


Fig. 4. IR spectra of $[CpRu(CO)_2]_2$ in isooctane/CCl_4 before (———) and after 25 min of irradiation with 334 nm (- - -).

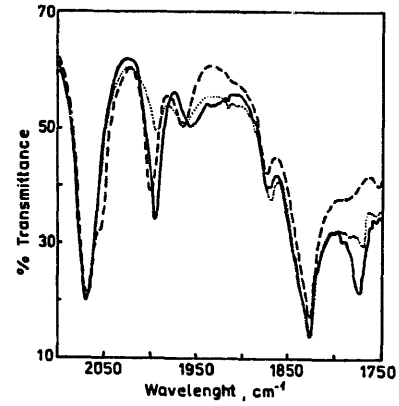
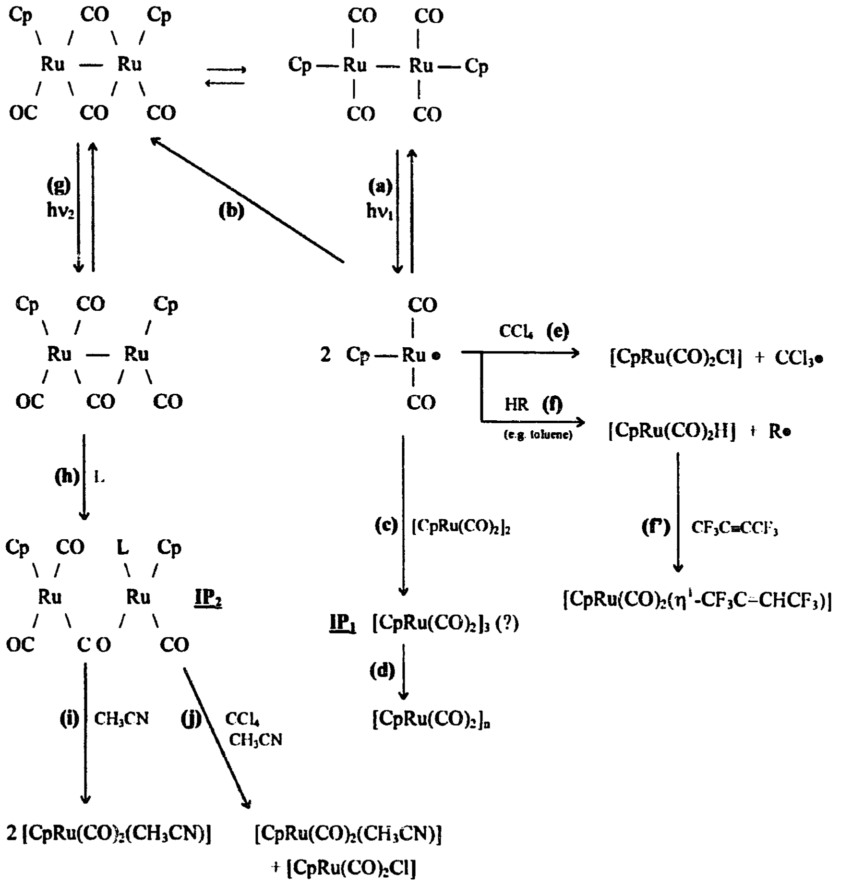


Fig. 5. IR spectra of $[CpRu(CO)_2]_2$ in acetonitrile before (———) and after 25 min of irradiation with 334 nm in neat acetonitrile (···) and after 1 h of irradiation in the presence of 1 M CCl_4 (- - -).

This hypothesis was supported by estimated yields of conversion of $[CpRu(CO)_2]_2$ into $[CpRu(CO)_2Cl]$ in continuous photolysis experiments performed in various solvents containing CCl_4. Basing on molar extinction coefficient of $[CpRu(CO)_2Cl]$ [7], the estimated degree of dimer conversion was ca. 100% in DMF, 2-propanol, toluene, isooctane and CCl_4, while in acetonitrile the yield was much lower (ca. 50–60%).

The IR spectra of the photoproducts obtained in neat isooctane (both turbid solution and solid phase, Table 2) demonstrated the presence of both CO-bridged and CO-terminal stretching vibrations in the polymeric photoproduct.



Scheme 1. Photoreactivity pathways of bridged and non-bridged forms of $[CpRu(CO)_2]_2$ concluded from the spectral studies ($h\nu_1$: $\lambda_{irr} \geq 330$ nm; $h\nu_2$: $\lambda_{irr} \geq 250$ nm; L = acetonitrile, 1- or 2-propanol).

4. Discussion

The overall photochemical reaction of the $[CpRu(CO)_2]_2$ dimer under studied conditions was a conversion of the dimer to a monomeric or polymeric form. This conversion could be achieved by different pathways depending both on the isomer which undergoes excitation and on the presence of a ligand or radical precursor in the system.

Selective photolysis of the non-bridged isomer resulted in its homolytical cleavage [path (a) in Scheme 1] and generation of the $[CpRu(CO)_2]^{\bullet}$ radicals, which is consistent with earlier reports [7,17,28]. The radicals could not be observed directly but their reactivity was easily detected. The geminate recombination regenerated the dimer also in the bridged form [cf. Figs. 1 and 2, path (b) in Scheme 1]. The reaction between the radicals and the parent non-bridged form [(c) in Scheme 1] observed as the post-irradiation decay of the 330-nm band was assumed to initiate the polymerization going through the transient species IP_1 [(c) and (d) in Scheme 1]. The intermediate IP_1 characterized by a broad band round 470 nm and a lifetime of the order of milliseconds could be thus considered as a direct product of association of the radical to the parent dimer[1], formulated thus $[CpRu(CO)_2]_3$. The intermediate IP_1 was not generated in photolysis of the bridged form or in photolysis of the non-bridged isomer in neat CCl_4. In the latter case only the formation of monomeric $[CpRu(CO)_2Cl]$ was recorded at μs resolution time [(e) in Scheme 1]. The $[CpRu(CO)_2Cl]$ complex was also generated in other solvents when CCl_4 was present in the system, being the only or the main final product of the photolysis. In the presence of a compound prone to homolytic cleavage of a C–H bond e.g. toluene, the production of hydride intermediate, $[CpRu(CO)_2H]$, [(f) in Scheme 1] was detected by identification of the simultaneously generated $C_6H_5CH_2^{\bullet}$ radical [32]. The conclusion was confirmed by isolation of the insertion product $[CpRu(CO)_2(\eta^1\text{-}CF_3C{=}CHCF_3)]$ in the presence of $CF_3C{\equiv}CCF_3$ [(f') in Scheme 1].

Photolysis of the bridged isomer was found to generate another transient species, IP_2, which was characterized by high absorbance between the bands characteristic of $\sigma_{nonbridge} \rightarrow \sigma^*_{nonbridge}$ and $\sigma_{doublebridge} \rightarrow \sigma^*_{doublebridge}$. This is why the transient absorption was assigned to the monobridged dimer formed in the photocleavage of one of the CO-bridges [Fig. 3, path (g) in Scheme 1]. The maximum of the transient species was found to be solvent dependent: 315 nm in propanol and 330 nm in acetonitrile. This is in agreement with the specific solvent effect noticed for some solvents:

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[1] An alternative formulation of IP_1 as hydride, $[CpRu(CO)_2H]$ cannot be, however, excluded.

acetonitrile, DMSO and DMF demonstrated a specific interaction with the non-bridged form of $[CpRu(CO)_2]_2$, which could be observed as a well marked bathochromic shift of the $\sigma_{nonbridge} \rightarrow \sigma^*_{nonbridge}$ band. Because IP_2 intermediate showed the specific solvent effect similar to that of the non-bridged isomer, it was assumed that the photocleavage product coordinates a solvent molecule giving IP_2, $[Cp(CO)_2Ru(\mu\text{-}CO)Ru(CO)LCp]$ [path (h) in Scheme 1]. The IP_2 transient species decayed within milliseconds and in the presence of CCl_4, again the $[CpRu(CO)_2Cl]$ complex formation was detected [(j) in Scheme 1]. Some solvents could compete with CCl_4 in formation of a stable product. This was the case of acetonitrile, in which, besides the bands characteristic of ν_{CO} in $[CpRu(CO)_2Cl]$, another absorption in terminal CO stretching region was observed (1965 cm^{-1}, Table 2). This led us to conclude that it is the monomeric form containing acetonitrile instead of Cl, which was tentatively formulated as $[CpRu(CO)_2(CH_3CN)]$. In neat acetonitrile only this compound was identified as the stable product of the photolysis [(i) in Scheme 1]. The back reaction is in this case of major importance (cf. Table 1). The spectral results did not exclude other pathways of the IP_2 decay leading e.g. to double bridged substitution species [7,28].

The results lead to the conclusion that photoreactivity of the ruthenium dimer $[CpRu(CO)_2]_2$ differs considerably from the photochemical behaviour of the analogous iron complex. The differences emphasize the role of the non-bridged isomer in the photochemistry of the ruthenium complex, and the decreased stability of the CO-bridges in this case.

Acknowledgements

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