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Photochemical and thermal disproportionation of $[(\text{CO})_4\text{CoM}(\text{CO})_3(\text{LL})]$ ($\text{M} = \text{Mn}, \text{Re}$; $\text{LL} = 2,2'$ -bipyridine, 2-pyridinecarbaldehyde *N*-isopropylimine) complexes

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Abstract

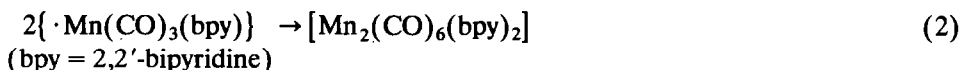
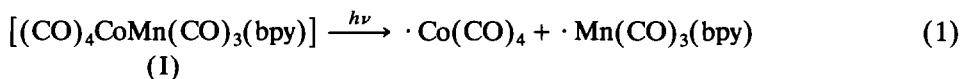
A study has been made of the secondary thermal reactions occurring after MLCT photolysis of $[(\text{CO})_4\text{CoRe}(\text{CO})_3(\text{LL})]$ ($\text{LL} = 2,2'$ -bipyridine, 2-pyridinecarbaldehyde *N*-isopropylimine). Contact ion pairs $\{[\text{Re}(\text{CO})_3(\text{LL})]^+[\text{Co}(\text{CO})_4]^- \}$ have been detected as final products upon irradiation into the MLCT band of the Re complexes in toluene. The initial quantum yield of the 476.5 nm photolysis of the 2,2'-bipyridine complex in toluene at 223 K is independent of the concentration and light intensity, implying that the contact ion pairs are formed by radical–radical interaction without involvement of any other donor molecule. The quantum yields increase with temperature. At initial concentrations of $10^{-2} \text{ mol l}^{-1}$ with toluene as the solvent the photodisproportionation into contact ion pairs is strongly retarded at about 50% conversion; this effect seems to depend on the concentration of the contact ion pair. The complexes under study disproportionate thermally into ion pairs when their solutions in CH_3CN or THF are left in the dark. In 2-MeTHF at $T \leq 243 \text{ K}$ only $[(\text{CO})_4\text{CoMn}(\text{CO})_3(2,2'$ -bipyridine)] undergoes disproportionation.

Introduction

Metal–metal-bonded carbonyl complexes with two carbonyls substituted by an α -diimine ligand show a metal-to-ligand charge-transfer (MLCT) band at low energy ($\lambda_{\text{max}} = 450\text{--}600 \text{ nm}$). Irradiation into this band causes CO loss, homolytic splitting of the metal–metal bond or both [1,2]. The photochemical properties of $[(\text{CO})_4\text{CoM}(\text{CO})_3(2,2'$ -bipyridine)] (I for $\text{M} = \text{Mn}$, II for $\text{M} = \text{Re}$) have recently been described for the first time [3]. All the experiments indicate that the primary photoprocess for these complexes is homolytic cleavage of the metal–metal bond.

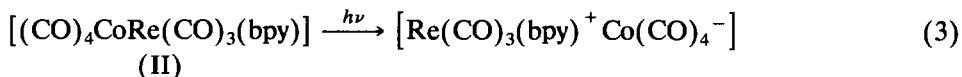
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Under no circumstances was release of CO observed upon irradiation into the MLCT band. In toluene, and in 2-MeTHF at room temperature the Mn complex reacted as shown in eqs. 1 and 2, with the fate of the $\text{Co}(\text{CO})_4$ radical unclear.



In the presence of phosphines or in a coordinating solvent (S) ionic photoproducts $[\text{M}(\text{CO})_3(\text{bpy})\text{L}][\text{Co}(\text{CO})_4]$ (L = PR_3 , S) were formed. Photolysis of the Mn complex in the presence of PR_3 appeared to be photocatalytic, with quantum yields varying from 7 to 60. From this it was concluded that intermediates of this reaction interacted with the parent complex in the course of the ion formation.

A remarkable reaction of the Re complex is its photodisproportionation in toluene at 230 K into a contact ion pair, reaction 3.



As a quantum yield of clearly < 1 was obtained, various mechanisms would be in accordance with this result. In order to provide information about this mechanism the dependence of the quantum yields on the light intensity, initial concentration and temperature was studied. In connection with recent studies on ion-pair charge-transfer photochemistry of ion pairs containing the tetracarbonylcobaltate anion [4,5] we also searched for a possible photoreaction of the $\{[\text{Re}(\text{CO})_3(\text{bpy})]^+[\text{Co}(\text{CO})_4]^- \}$ contact ion pair.

In order to study the influence of the ligand on the photochemical behaviour of these complexes we prepared $[(\text{CO})_4\text{CoRe}(\text{CO})_3(^i\text{Pr-Pyca})]$ ($^i\text{Pr-Pyca}$ = 2-pyridinecarbaldehyde *N*-isopropylimine) (III) by reaction of the ionic precursors $[\text{Re}(\text{CO})_3(^i\text{Pr-Pyca})]\text{OTf}$ (OTf = trifluoromethanesulfonate) and $\text{Na}[\text{Co}(\text{CO})_4]$ in toluene at room temperature. In the case of the ligand $^t\text{Bu-DAB}$ (= glyoxal-bis-(tert-butyl)imine) the reaction between $[\text{Re}(\text{CO})_3(^t\text{Bu-DAB})]\text{OTf}$ and $\text{Na}[\text{Co}(\text{CO})_4]$ led instead to the formation of $[\text{ReCo}(\text{CO})_5(\mu^2\text{-CO})(^t\text{Bu-DAB})]$, in agreement with the results obtained by Staal *et al.* [6]. During this study we also observed a purely thermal disproportionation of the complexes at room temperature in polar coordinating solvents and the formation of $[\text{M}(\text{CO})_3(\text{LL})\text{Br}]$ in the presence of an excess of CBr_4 .

Experimental

Materials and preparations

The solvents, particularly toluene (Merck, Uvasol) were carefully dried, purified by distillation and kept under nitrogen. All manipulations were carried out under an inert atmosphere. I and II were prepared as previously described [3].

For the preparation of III a suspension of 53 mg (0.5 mmol) of $[\text{Re}(\text{CO})_3(^i\text{Pr-Pyca})]\text{OTf}$ and 19.5 mg (0.5 mmol) of $\text{Na}[\text{Co}(\text{CO})_4]$ in 10 ml of toluene was stirred overnight in the dark at room temperature. The dark red solution was either used

as prepared ($\lambda_{\max} = 493 \text{ nm}$, $\nu(\text{CO})$ frequencies, see Table 3) or diluted if necessary.

Spectroscopic measurements

IR spectra were recorded on a Nicolet 7199 B FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 5 UV/VIS spectrometer connected to a Model 3600 data station. For low temperature UV/VIS and IR measurements an Oxford Instruments DN 1704/54 liquid-nitrogen cryostat was used.

Photochemistry

An SP 2025 argon-ion laser was used as light source in the photochemical experiments. The 476.5 nm line was selected for excitation of II, and the 514.5 nm line in the case of III. Photon fluxes for the quantum yield determinations were measured with Coherent Model 210 and 212 power meters.

Results

Photochemical reactions

II: Initially a series of experiments was carried out with II in toluene at low temperatures ($T \leq 248 \text{ K}$) and at concentrations $\leq 10^{-3} \text{ mol l}^{-1}$. The photoreactions were monitored by UV/VIS spectroscopy. The dependence of the quantum yields for the initial part of the reaction on the laser intensity, the concentration and the temperature was studied by monitoring the decrease in the intensity of the 470 nm band. The results, summarized in Tables 1 and 2, show that there is no significant difference between the quantum yields at various concentrations ($10^{-4} < c < 10^{-3} \text{ mol l}^{-1}$) and intensities (laserpower 5–80 mW). The quantum yield increases with temperature. Whereas the partially or completely photolyzed complex gave stable solutions in the dark at 223 K, a slow thermal back reaction was observed at 248 K. With the low laser light intensities (laser power $\leq 15 \text{ mW}$) and corresponding longer irradiation times that are normally applied for quantum yield determinations in this concentration range, no permanent change was observed at

Table 1

Dependence of initial quantum yields ($\times 10^2$) of photodisproportionation of II at 223 K on the light intensity and substrate concentration ($\lambda_{\text{irr}} = 476.5 \text{ nm}$)^a

Concentration ($10^{-3} \text{ mol l}^{-1}$)	Irradiation power (mW)					
	1	4	10	15	45	80
0.1	10+5	11+2	8+2	8+1	6+3	10+4
0.2		9+1				
0.8		10+4		9+1		
4				10+1		
10				7+2 ^b		

^a Error limits are standard deviations for successive quantum yield determinations within the first 30% of conversion of one run. ^b Quantum yield during the first 10% of conversion; it falls to 2% at 40% conversion.

Table 2

Dependence of initial quantum yields ($\times 10^2$) for photodisproportionation of II and III on the temperature ($\lambda_{\text{irr}} = 476.5 \text{ nm}$)^a

T (K)	I	II
295	20 +6	21+3
248	16 +3	
223	9 +2 ^b	7+2
183	1.2+0.6	

^a Error limits are standard deviations for successive quantum yield determinations of one run. ^b Mean value of Table 1.

room temperature and so the occurrence of a fast thermal back reaction was assumed [3].

A $10^{-2} \text{ mol l}^{-1}$ solution of II in toluene in a 0.1 cm cuvette was irradiated for 20 s with 200 mW. A decrease in the MLCT band was observed, but the band was regenerated in the dark. The reaction mixture was shaken after irradiation in order to give a homogeneous solution. From the increase in absorbance of the MLCT band a first order rate constant of 0.2 min^{-1} was determined for the re-formation of the parent complex. IR spectra recorded after such intense irradiation showed the presence of vibrational bands belonging to the ion pair. At 223 K and for concentrations less than $10^{-3} \text{ mol l}^{-1}$ the MLCT band disappeared completely. However, at concentrations of about $10^{-2} \text{ mol l}^{-1}$, normally used for IR detection of the products, complete conversion could not be accomplished (compare Figs. 1 and 2). Under these conditions the photochemical reaction was strongly retarded at about 50% conversion and a mixture of II and the ion pair was obtained. This

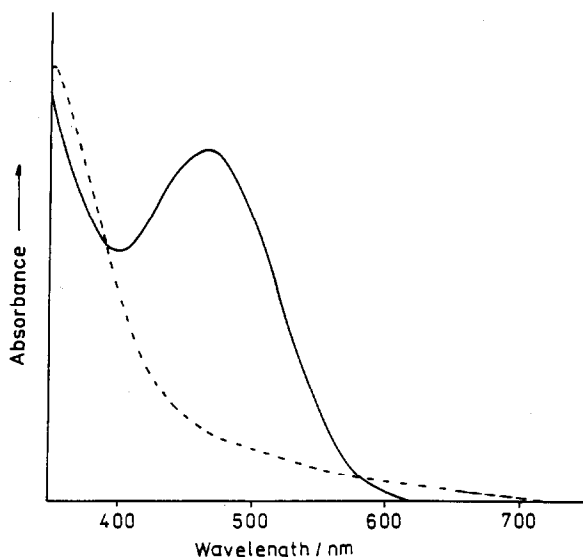


Fig. 1. UV/VIS spectra of II ($7 \cdot 10^{-4} \text{ mol l}^{-1}$) in toluene at 223 K, before (—) and after (---) irradiation with 476.5 nm, 1 cm cuvette.

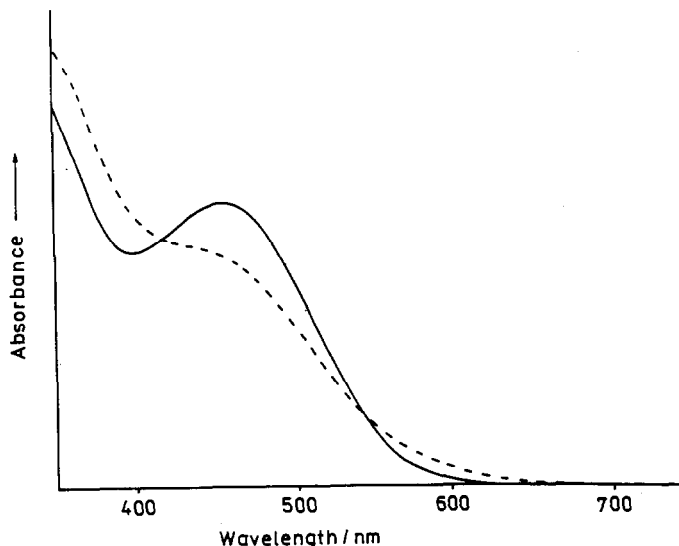


Fig. 2. UV/VIS spectra of II (10^{-2} mol l^{-1}) in toluene at 223 K, before (—) and after (---) irradiation with 476.5 nm, 0.2 mm IR cuvette.

outcome was independent of the cuvette used (0.2 mm IR cuvette or 1 cm UV/VIS cuvette with a light path reduced to 0.1 cm for analysis). The initial quantum yield was 0.07 but it decreased to 0.02 at about 40% conversion (see Table 1). The conversion could only be increased to a significant extent by a drastic increase in the laser intensity. This rules out a photochemical equilibrium. We carefully examined the mixture of the parent complex and the ion pair product between 10^{-3} and 10^{-2} mol l^{-1} of the initial concentration of II but could not find significant changes in the IR band shapes of the product ion pair; thus there was no evidence for association of $[Re(CO)_3(bpy)^+Co(CO)_4^-]$ with the starting complex or with itself to form a dimer. Variation of the irradiation wavelength between 457.5 and 514.5 nm also caused no significant differences.

Irradiation in 2-MeTHF at $T = 223$ K resulted, however, in complete conversion of II into $[Re(CO)_3(bpy)(2-MeTHF)]Co(CO)_4$ (see Ref. 3). Addition of a small amount of 2-MeTHF to an established stationary state of about 50% conversion of II in toluene (initial concentration 10^{-2} mol l^{-1}) resulted in complete conversion upon further irradiation. The IR product bands of the ion pair formed were then in accord with those observed in neat 2-MeTHF. This shows that the presence of the high concentration of the contact ion pair is responsible for the retardation of the photochemical disproportionation.

Evidently the contact ion pair exhibits no IPCT absorption, since neither Fig. 1 nor Fig. 2 shows a significant product band except for that of the cation at 360 nm. The photolysis mixture was irradiated with 351-363 or 600 nm, *i.e.* away from the isosbestic points, where the products absorb more strongly than the parent complex. No significant change in the UV/VIS spectra was observed, and thus no evidence for ion pair charge transfer photoreactivity.

III: The solution of complex was used as prepared (see Experimental). For the quantum yield determination the solution was diluted to a concentration of

Table 3

Infrared $\nu(\text{CO})$ frequencies of the $[(\text{CO})_4\text{CoM}(\text{CO})_3(\text{LL})]$ complexes, their precursors and the thermal and photochemical products ^a

Complex	Solvent, <i>T</i> (K)	$\nu(\text{CO})$ (cm^{-1})		
		Mn(bpy)	Re(bpy)	Re(ⁱ Pr-Pyca)
$[(\text{CO})_4\text{CoM}(\text{CO})_3(\text{LL})]$	toluene, RT	1911	1901	1904
		1938	1935	1933
		1952	1950	1957
		sh	sh	sh
		1998	2011	2012
		2046	2048	2050
$[\text{M}(\text{CO})_3(\text{LL})\text{OTf}]$	toluene, RT		1918	1914
			1934	1940
			2037	2034
$[\text{M}(\text{CO})_3(\text{LL})\text{Cl}]$	CH_2Cl_2 , RT		1899	
			1921	
			2024	
$[\text{M}(\text{CO})_3(\text{LL})\text{Br}]$	toluene, RT	1914	1897	1897
		1939	1925	1927
		2024	2023	2024
$[\text{M}(\text{CO})_3(\text{LL})(\text{CH}_3\text{CN})]$ $[\text{Co}(\text{CO})_4]$	CH_3CN , RT	1893	1893	1891
		1956(br)	1937(br)	1933
				1948
		2048	2041	2041
$[\text{M}(\text{CO})_3(\text{LL})(\text{THF})]$	THF, RT	1886	1886	
			1924	
$[\text{Co}(\text{CO})_4]$		1946(br)	sh	
		2044	2036	
$[\text{M}(\text{CO})_3(\text{LL})(2\text{-MeTHF})]$ $[\text{Co}(\text{CO})_4]$	2-MeTHF, RT	1888		
		1937(br)		
		2044		
$[\text{M}(\text{CO})_3(\text{LL})^+ \text{Co}(\text{CO})_4^-]$	toluene, 223	not formed	1887	1887
			1920	1921
			1928	1929
			2034	2035

^a sh: shoulder attached to the band with the maximum given in the line above; br: broad band enveloping two bands.

$5 \cdot 10^{-4}$ mol l^{-1} . At room temperature the MLCT band disappeared much more rapidly than in the case of II, indicating a slower rate of the thermal back reaction, which can be observed in the dark. At 223 K this back reaction was not observed. The quantum yields were similar to those obtained upon irradiation of II (see Table 1). At concentrations of 10^{-2} mol l^{-1} there was up to 50% conversion as in the case of II. The wavenumbers of the product bands of II and III appeared to be nearly identical (see Table 3). From the similarity of all of the results we conclude that in the case of III also the photoproduct in toluene is a contact ion pair $[\text{Re}(\text{CO})_3(^i\text{Pr-Pyca})^+ \text{Co}(\text{CO})_4^-]$.

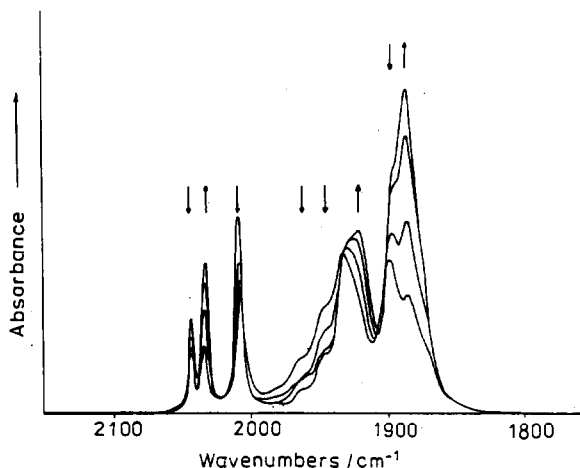


Fig. 3. IR spectra of II (10^{-2} mol l^{-1}) in THF at 333, 298, 273, 253 K. The arrows indicate the change with decreasing temperature.

Thermal disproportionation

The contact ion pairs derived from II and III were formed only in the nonpolar and noncoordinating solvent toluene. An attempt to prepare these ion pairs directly from precursors such as $[Re(CO)_3(bpy)]OTf$ and $Na[Co(CO)_4]$ or PPN $[Co(CO)_4]^-$ at 223 K failed. These salts showed a low solubility at 223 K in toluene and the temperature seemed to be too low to overcome the activation energy for the ion-scrambling needed to form the much more soluble $[Re(CO)_3(bpy)]^+Co(CO)_4^-$.

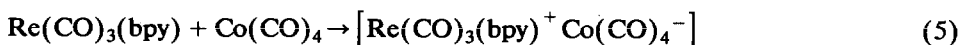
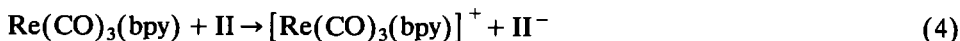
During our experiments we also used other solvents for complexes I, II and III. In CH_3CN the formation of the ions $[M(CO)_3(LL)(CH_3CN)]^+$ and $[Co(CO)_4]^-$, probably with one solvent molecule coordinated to the cation, was indicated by the IR spectra. In THF the IR spectra showed an equilibrium between $[M(CO)_3(LL)(THF)][Co(CO)_4]$ and the parent complex, with the position of equilibrium varying with temperature. An increase of temperature favoured the formation of the complex and a decrease raised the concentrations of the ions increased (see Fig. 3). For complex I the equilibrium for the disproportionation lies far over to the side of the ions.

For reactions in 2-MeTHF a remarkable difference between reactions of I and II was observed. At room temperature both complexes are present completely as metal-metal-bonded species. When the temperature was lowered slowly to 253 K only I underwent a disproportionation into its ions, and this process continued to almost complete conversion at *ca.* 193 K. These experiments were carried out with the exclusion of light. The IR spectra of a solution formed from II in CH_2Cl_2 showed the bands of $[Re(CO)_3(bpy)Cl]$ after 15 h, as similar to those from the equivalent mixture of $[Re(CO)_3(bpy)]OTf$ and $Na[Co(CO)_4]$ or PPN $[Co(CO)_4]^-$. Toluene solutions of I, II and III containing an excess of CBr_4 gave $[M(CO)_3(LL)Br]$ at room temperature in the dark.

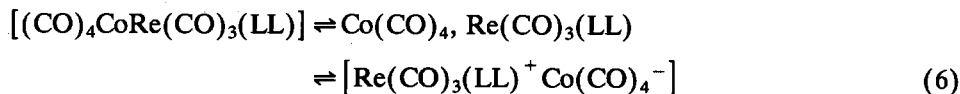
Discussion

With a few exceptions photodisproportionation of binuclear metal carbonyls has only been shown to occur in coordinating solvents or in the presence of nucleophiles [7,8]. Such an exception is provided, for example by $[(\eta^5\text{C}_5\text{H}_5)(\text{CO})_2\text{-FeCo}(\text{CO})_4]$, which is converted into $[\eta^5\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]^+$ and $[\text{Co}(\text{CO})_4]^-$ in a CO-doped matrix at 10 K; for this photoreaction a heterolytic splitting of the metal-metal bond was postulated [9]. The suppression of the ion-pair formation upon irradiation of II and III in the presence of added CBr_4 at 230 K is evidence that homolysis of the metal-metal bond is the primary photolysis step [3]. The temperature-dependence of the quantum yield of photolysis of II and III observed in this work supports the view that the electron transfer step is a thermal process. If the temperature-dependence of the quantum yield of the complex ion-pair formation had been due to the observed back reaction, then a decrease in the quantum yield with temperature would have been observed instead.

Following the primary homolysis reaction of II, both reactions 4 and 5 have to be considered as possible thermal electron transfer steps. Reaction 4 is a possible alternative, since irradiation of I in the presence of excess PR_3 has been shown to lead to a catalytic disproportionation of this complex by electron transfer from the intermediate $\text{Mn}(\text{CO})_3(\text{bpy})\text{PR}_3$ radical [3]. It is evident from the data in Table 1 that the initial quantum yield upon irradiation of II at 223 K does not change



with a 20-fold increase of light intensity. This means that the radicals formed in the primary photolytic step do not enter further secondary photoreactions. The constancy of the quantum yield over the 100-fold increase of concentration of the parent complex definitely rules out reaction 4. The disproportionation of the radicals in reaction 5 can occur either within the original solvent cage of the geminate radical pair or after cage escape and new approach of the radicals. Both the observation of higher initial quantum yields at higher temperatures and faster rates of the thermal back reaction to give the metal-metal-bonded complex at room temperature can be attributed to a different mutual orientation of the fragment-radicals or -ions in the recombination and disproportionation reaction. The mutual orientations exchange more rapidly, and so the rate of conversion of the radical pair into the ion pair and vice versa is increased relative to the rate of recombination in sequence 6.



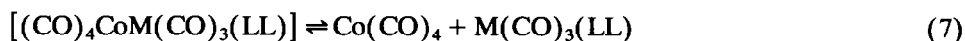
Since the $\text{M}(\text{CO})_3(\text{LL})$ radicals are in fact 16-electron bipolar species $^+\text{M}(\text{CO})_3(\text{LL}^-)$ [2], electron transfer will be more probable when the $\text{Co}(\text{CO})_4$ radical lies near the ligand. In contrast recombination of the radicals will be favoured when the cobalt is nearest to the Re atom.

Observation of disproportionation with $\text{Co}(\text{CO})_4$ radicals in particular is in accord with the higher reduction potential of this radical compared with that of

e.g. $\text{Mn}(\text{CO})_5$. In accordance with this, IPCT complexes with $\text{Co}(\text{CO})_4^-$ show IPCT bands at higher energy than those for $\text{Mn}(\text{CO})_5^-$ [4]. This may account for the fact that we observe no significant IPCT band in the visible region. However, if reorientation of the ions is in fact necessary for the recombination, IPCT absorption if it occurs at all would not be expected to lead to the formation of permanent products. All the experimental observations on the inhibition of ion-pair formation at higher initial complex concentration point to the conclusion that the contact ion pairs $[\text{Re}(\text{CO})_3(\text{LL})^+ \text{Co}(\text{CO})_4^-]$ themselves inhibit further ion-pair formation.

The lifetimes of electronically excited dinuclear metal carbonyl complexes eventually exceed 10 ns [10], so that maximum concentrations of $[\text{Re}(\text{CO})_3(\text{LL})^+ \text{Co}(\text{CO})_4^-]$ of $5\text{--}10^{-3} \text{ mol l}^{-1}$ might be sufficient to act as efficient quencher for electronically excited II or III.

Thermal reactions between the starting complex and reactants such as CBr_4 or solvent molecules generally complicate the elucidation of the mechanism of a photochemical reaction. Thermal reactions can, however, be prevented by applying low temperatures. Our observations concerning these thermal reactions can be interpreted as follows: the formation of $[\text{M}(\text{CO})_3(\text{LL})\text{Br}]$ in toluene containing an excess of CBr_4 at room temperature in the dark indicates that very small amounts of radicals are present. At 223 K this mixture underwent no chemical change in the dark, obviously because equilibrium 7 lies completely on the left-hand side.



The formation of $[\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}]$ from either II or in a mixture of $[\text{Re}(\text{CO})_3(\text{bpy})]\text{OTf}$ and $\text{Na}[\text{Co}(\text{CO})_4]$ or $\text{PPN}[\text{Co}(\text{CO})_4]$ in CH_2Cl_2 within 15 h at room temperature, indicates that radicals are intermediates in the ion-pair formation out of metal–metal-bonded complexes and in the reverse reaction 6. As the amount of $[\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}]$ formed is larger in the case of ionic precursors, the direct formation of II and the successive homolytic splitting is apparently of only minor importance.

The thermal disproportionation of the complexes probably also occurs via radical formation since thermal heterolytic splitting has never been observed. The differences in the extent of thermal disproportionation between the complexes I and II may thus be due to differences in the metal–metal bond strength and in the (unknown) reduction potentials of the radicals $\cdot\text{M}(\text{CO})_3(\text{bpy})$. In neat toluene only the Re radical reduces $\text{Co}(\text{CO})_4$. Assuming that the order of the reduction potential between the Re and the Mn radical does not change upon coordination of a solvent molecule, the higher extent of disproportionation of complex I in both THF and 2-MeTHF will be due to the lower metal–metal bond strength of I with respect to II. The decrease in the extent of disproportionation with increase in temperature shows that the decrease in coordination ability with increasing temperature is the dominant cause of the increased dissociation of the metal–metal bond.

Acknowledgements

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References

- 1 D.J. Stufkens, Steric and Electronic Effects on the Photochemical Reactions of Metal-Metal Bonded Carbonyls, in I. Bernal (Ed.), Stereochemistry of Organometallic and Inorganic Compounds. Elsevier, Amsterdam, 1989, Vol. 3, p. 226.
- 2 D.J. Stufkens, *Coord. Chem. Rev.*, 104 (1990) 34.
- 3 H.K. van Dijk, J. van der Haar, D.J. Stufkens and A. Oskam, *Inorg. Chem.*, 28 (1989) 75.
- 4 T.M. Bockman and K.J. Kochi, *J. Am. Chem. Soc.*, 111 (1989) 4669 and references therein.
- 5 H. Knoll, R. Billing, H. Hennig and D.J. Stufkens, *Inorg. Chem.*, 29 (1990) 3051.
- 6 L.H. Staal, J. Keijsper, G. van Koten, K. Vrieze, J.A. Cas and W.P. Bosman, *Inorg. Chem.*, 20 (1981) 555.
- 7 A.E. Stiegman and D.J. Tyler, *Coord. Chem. Rev.*, 63 (1985) 217.
- 8 A.E. Stiegman and D.J. Tyler, *Acc. Chem. Res.*, 17 (1984) 61.
- 9 S.G. Fletcher, M. Poliakoff and J.J. Turner, *J. Organomet. Chem.*, 268 (1984) 259.
- 10 M. Glezen, A.J. Lees and D.J. Stufkens, to be published.
- 11 T. van der Graaf, D.J. Stufkens, A. Oskam and K. Goubitz, *Inorg. Chem.*, 30 (1991) 599.