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# Ligand and medium controlled photochemistry of iron and ruthenium mixed-ligand complexes: prospecting for versatile systems

Konrad Szaciłowski [a], Wojciech Macyk [a], Grażyna Stochel [a], Zofia Stasicka [a],*, Silvana Sostero [b], Orazio Traverso [b]

[a] *Department of Inorganic Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland*
[b] *Centro di Fotochimica del CNR, Dipartimento di Chimica, Universita di Ferrara, via Borsari 46, 44100 Ferrara, Italy*

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* Corresponding author. Tel./fax: +48-12-6335392.
*E-mail address:* stasicka@trurl.ch.uj.edu.pl (Z. Stasicka).

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## Abstract

Selected Fe and Ru systems, whose photochemical behaviour is sensitive to numerous parameters, are presented. These systems, containing multiple species in equilibrium, are versatile enough to be adapted to special tasks and may also be used to model the phenomena and mechanisms occurring in nature. The role of various parameters is analysed and principal emphasis is given to the ligand sphere influence on the nature of the excited state and thereby on the photochemical mode. This is crucial in the case of Fe(II) complexes of the type $[Fe(CN)_5L]^{n-}$, whereas in the carbolyl–cyclopentadienyl complexes, represented by $[cpRu(CO)_2]_2$, the nature of the excited state is of less importance than for pentacyanoferrates(II). The photochemistry of the carbonyl–cyclopentadienyl complexes is more susceptible to the impact of the medium and the role of the secondary processes is more significant.

*Keywords:* Iron; Ruthenium; Photochemistry; Environment; Bio-medicine

## 1. Introduction

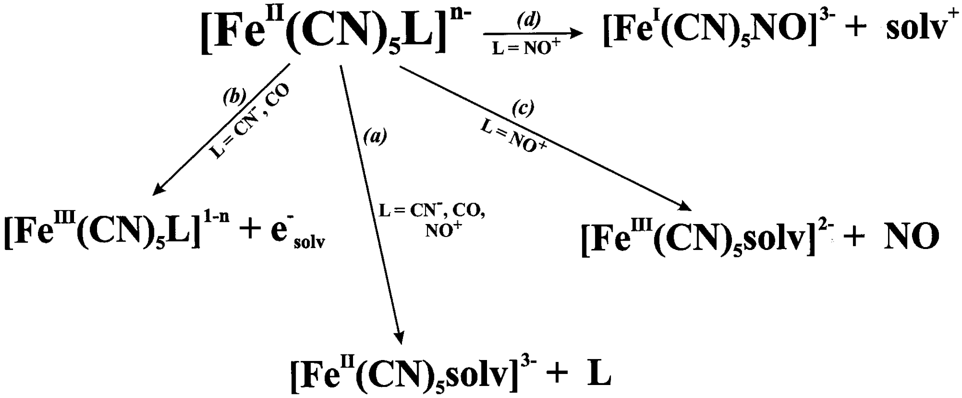
There has been growing interest in the application of the photochemistry of coordination compounds in environmental, biological and medical processes. To be useful for solar energy harvesting, organic synthesis, therapeutic and/or diagnostic purposes, the photocatalytic system must be flexible enough to meet different requirements imposed by these very often complex and subtle systems. The requirements mostly apply not only to the specific product(s), but also to the medium interactions, pH, limited light region, temperature and other reaction parameters.

Investigation of such versatile systems is especially important for the environmental research of both direct photolysis and indirect photoreactions. The processes often proceed in natural waters containing multiple species involved in rapid reversible equilibrium. Some of the most common components of these systems are the iron Fe(II)/Fe(III) compounds, which are easily converted into each other by thermal redox and/or photoredox processes and thus they play a role as either radical sources or their sinks [1]. The excited states of Fe(III) species are responsible for the oxidation of various organic species present in the environmental compartments. Especially effective are systems containing Fe(II)/Fe(III) accompanied by another redox couple, such as the Cu(I)/Cu(II) compounds [2–11] or the Cr(VI)/Cr(III) species [12].

Research in the area of medicinal chemistry concerns persistent questions of pharmaceutical (drugs and diagnostic species) resistance, toxicity and better targeting to the sites of action. Versatile photochemical systems are of great interest in designing molecular devices for biological delivery and targeting processes (e.g. search for NO photodonors [13–15]). The systems are also of importance in the photolabelling of biomolecules, in therapeutic and diagnostic processes (e.g. photodynamic therapy PDT) and in antitoxic protective processes [14,16–21]. In the latter case, the redox or photoredox reactions involving complexes of Cu(II/I), Co(II/III), Fe(II/III) can be used acting as redox scavengers for radicals photogenerated from drugs and biomolecules [18].

## 2. Ligand effects in the photochemistry of $[Fe^{II}(CN)_5L]^{n-}$ complexes

Looking for the prerequisites for constructing flexible systems, which could be adapted to different requirements, we consider the influence of the ligand nature on the excited state character, which, in consequence, affects the photochemical mode. A very good example to follow this influence is provided by the $[Fe^{II}(CN)_5L]^{n-}$ family whose photochemical reactivity has been studied extensively [22–48]. Photosubstitution proceeding from the MC excited state is the most common mode reported for hexacyanoferrate(II) and all its pentacyano-derivatives. In all cases when L is a singly bonded ligand, such as $NH_3$ or $H_2O$, it is the $CN^-$ ligand that undergoes substitution [23–27]. When the sixth ligand is replaced by a π-acceptor stronger than $CN^-$, such as the isoelectronic CO or $NO^+$, this ligand undergoes photosubstitution (path (a) in Scheme 1), consistent with the known photosubstitution rules [28–31]. Its quantum yield decreases, however, with increasing π-acceptance, and in the case of the $[Fe(CN)_5NO]^{2-}$ complex, the mode is only scarcely observed [30,31].



Scheme 1. Ligand-effect on the photochemical modes of the $[Fe(CN)_5L]^{n-}$ complexes, where L = $CN^-$, CO or $NO^+$. Adapted from Stasicka and Wasielewska [22].

The higher excited state, classified as MLCT or MSCT in character, is known to lead to the outer-sphere photooxidation of the $[Fe(CN)_6]^{4-}$ complex, accompanied by generation of the solvated electron with a relatively high quantum yield (path (b) in Scheme 1) [32–36]. A similar photoreaction was also observed in the case of $[Fe(CN)_5CO]^{3-}$, as a consequence of an LLCT excitation with a quantum yield somewhat lower than that of hexacyanoferrate(II) (path (b) in Scheme 1) [22,35]. Outer-sphere photooxidation was never found in the case of $[Fe(CN)_5NO]^{2-}$; instead the complex undergoes inner-sphere photooxidation, accompanied by substitution of the NO ligand in its reduced form (path (c) in Scheme 1) [15,30,31,37–41]. This mode is the main photochemical reaction of $[Fe(CN)_5NO]^{2-}$ proceeding within a wide range of irradiating wavelengths. Excitation of nitrosylpentacyanoferrate(II) to an even higher energy state, having LMCT + LLCT character, leads to photoreduction and generation of oxidised solvent cation radicals (path (d) in Scheme 1) [22,38–44]. This mode, unexpected in the $[Fe(CN)_5L]^{n-}$ family, is due to the unique properties of the $NO^+$ ligand, especially when it is bonded to the $[Fe(CN)_5]^{3-}$ moiety [22,45].

Differences in the photochemical modes of the $[Fe(CN)_5L]^{n-}$ complexes with $L = CN^-$, CO or $NO^+$, still wait for comprehensive theoretical interpretation, but even semi-empirical INDO type calculations allow one to justify some of this behaviour [22,45,47,48]. Comparison of the frontier orbital energies substantiates the differences in redox character of $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5NO]^{2-}$ (Fig. 1). The ground state characteristic is consistent with the expected increase in the π-bonding order along the series $CN^- < CO < NO^+$. There is also a strong influence of the outer charge on the $CN^-$ ligand charges, which are really high for hexacyano and very low for the nitrosyl complex (cf. Fig. 1) [45,47,48].

Interesting conclusions could be drawn from changes in charges, σ and π-bond orders and two-centre contribution to the total energy accompanying transitions,

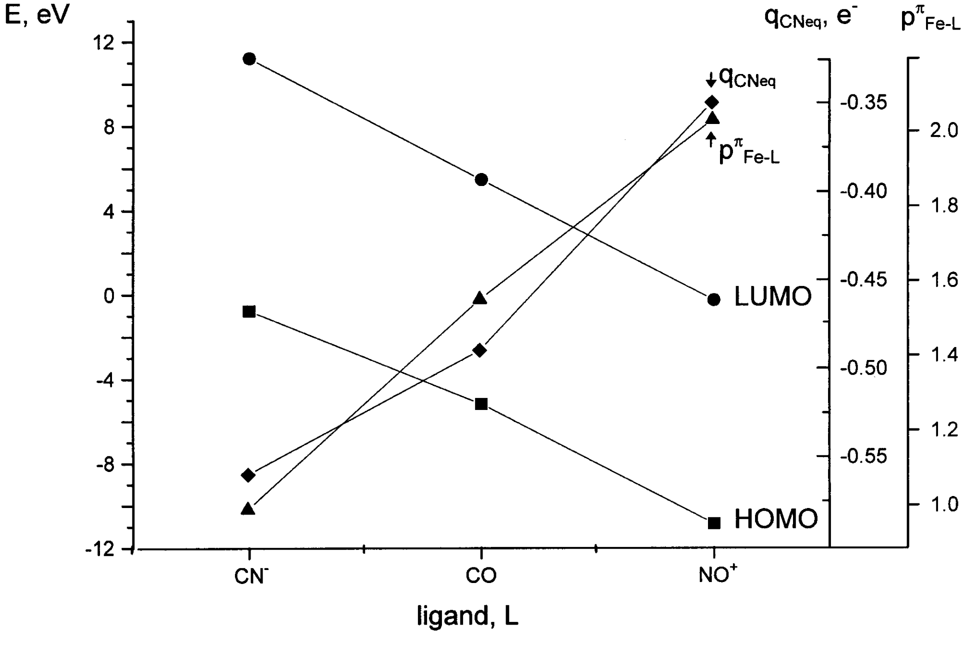


Fig. 1. Effect of the nature of the ligand on the ground state characteristics of the $[Fe(CN)_5L]^{n-}$ complexes for $L = CN^-$, CO, $NO^+$: energy of the frontier orbitals (HOMO and LUMO), π bond orders ($p^\pi_{Fe-L}$) and net charges on the $CN^-$ ligands in *cis* position to the L ligand ($q_{CNeq}$). Based on the SINDO calculations of Wasielewska and co-workers [46–48].

calculated by the same semi-empirical method [45,46]. The MC transition in $[Fe(CN)_6]^{4-}$ mostly affects the Fe–CN bond by a decrease its $\sigma$-bond order, whereas in $[Fe(CN)_5CO]^{3-}$ and $[Fe(CN)_5NO]^{2-}$ the weakening of the Fe–CO and Fe–NO bonds, respectively, is caused by a decrease in the $\pi$-bond order [22,45].

MLCT excitation in $[Fe(CN)_6]^{4-}$ does not lead to any weakening of the Fe–CN bond, but results in a considerable charge shift towards the $CN^-$ ligands (Fig. 2), which can be transferred to the solvent as shown in path (b) of Scheme 1. Similar consequences of the MLCT and LLCT excitations are expected for $[Fe(CN)_5CO]^{3-}$, but in this case negative charge is transferred from equatorial $CN^-$ ligands to the axial CO and $CN^-$ ligands (Fig. 2), which thus would be a source of solvated electron production ((b) in Scheme 1) [22,45].

The results obtained for $[Fe(CN)_5NO]^{2-}$ differ considerably from those presented for $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5CO]^{3-}$: the $8e \rightarrow 9e$ transition has MC + LC instead of MLCT character. The excitation leads to a considerable weakening of the Fe–NO $\pi$-bond order and the $O \rightarrow N$ charge shift within the NO ligand [45]. The change results in the inner sphere photooxidation followed by substitution of the oxidised NO ligand (by $OH^-$ in alkaline medium, path (c) in Scheme 1) [22,46]. The even higher energy $1a_2 \rightarrow 9e$ transition, LMCT + LLCT in character, induces a strong charge shift from the equatorial $CN^-$ ligands to the central Fe atom and axial $CN^-$ and $NO^+$ ligands, without any weakening of Fe–ligand bond. In consequence, the charge of the axial $CN^-$ ligand decreases, but not to a very low

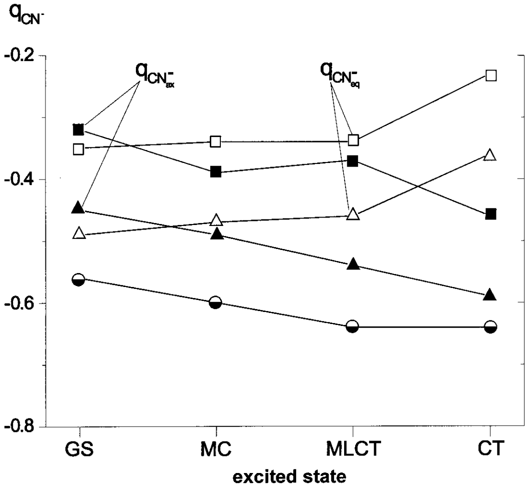


Fig. 2. Changes in net charges on the $CN^-$ ligands in *cis* and *trans* position to the L ligand ($q_{CNeq}$ and $q_{CNax}$, respectively) accompanying transitions in the $[Fe(CN)_5L]^{n-}$ complexes for L = $CN^-$ (–◒–), CO (–△– and –▲–) and $NO^+$ (–□– and –■–); the symbols on the *x* axis are: GS, ground state, whereas MC, LMCT and CT refer to the first, second and third transitions, respectively, assigned for $[Fe(CN)_6]^{4-}$ as $2t_{2g} \rightarrow 4e_g$, $2t_{2g} \rightarrow 2t_{2u}$, and $2t_{2g} \rightarrow 5t_{1u}$; and for $[Fe(CN)_5CO]^{3-}$ and $[Fe(CN)_5NO]^{2-}$ as: $2b_2 \rightarrow 9e$, $8e \rightarrow 9e$, $1a_2 \rightarrow 9e$, respectively. Based on the results presented by Wasielewska and co-workers [46–48].

level, whereas those of the equatorial $CN^-$ ligands increase approaching a really small negative value (CT in Fig. 2). The latter change may be effective in oxidising the solvent molecule and may also substantiate the outer sphere photoreduction mode (path (d) in Scheme 1) [22,45].

The different photochemical modes of the $[Fe(CN)_5L]^{n-}$ complexes, described above, are a consequence of the replacement of only one ligand within the isoelectronic series. The change sufficiently affects the excited state character to switch the photochemical mode. This leads to the conclusion that the photochemical modes in adaptable systems can be steered by changing the reactive excited state via modification of the ligand sphere.

A system sensitive enough to respond photochemically to the subtle changes in ligand nature could be found within the same $[Fe(CN)_5L]^{n-}$ family, when ligand L is not changed, but only slightly modified. The concept could be also verified and extended by considering another versatile system, based on the $[cpRu(CO)_2]_2$ dimer.

## 3. $[Fe(CN)_5NO]^{2-}$– $[Fe(CN)_5N(O)SR]^{3-}$ system

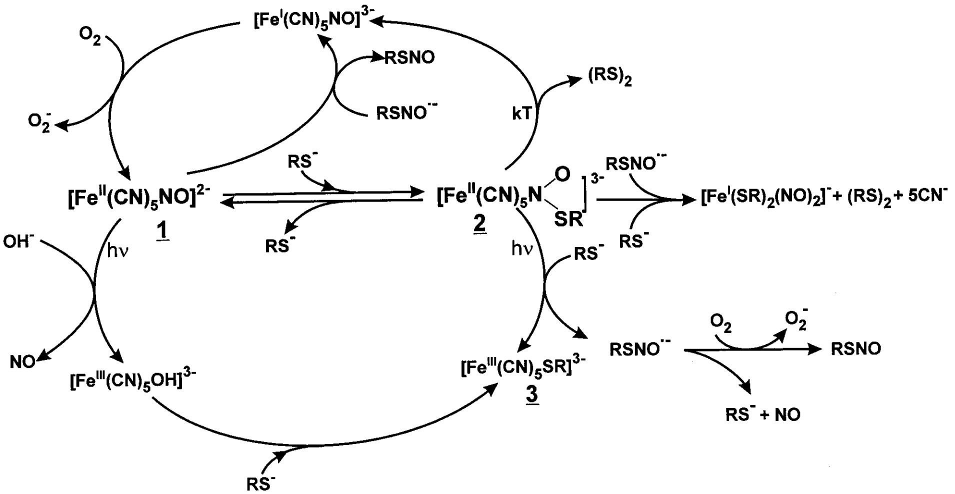
Fine modification of the coordination sphere can be achieved by addition of a molecule or ion to one of the ligands. The $[Fe(CN)_5NO]^{2-}$ complex (**1**) can be modified because it undergoes a nucleophilic attack on the N atom of the $NO^+$ ligand yielding the $[Fe(CN)_5N(O)Nucl]^{(2+n)-}$ complexes:

$$[Fe(CN)_5NO]^{2-} + Nucl^{n-} \rightleftarrows [Fe(CN)_5N(O)Nucl]^{(2+n)-} \tag{1}$$

A large variety of O-, N-, C- and S-nucleophiles are effective in reaction (1) including the $OH^-$ ions, which leads to formation of the $[Fe(CN)_5NO_2]^{4-}$ complex [49–53]. Many $[Fe(CN)_5N(O)Nucl]^{(2+n)-}$ complexes were obtained among which, those with S-nucleophiles are the most interesting due to their potential physiological importance [49,50,52,53]. In this case, as for other $[Fe(CN)_5N(O)Nucl]^{(2+n)-}$ complexes, the adducts are formed by a fast reversible reaction and both complexes remain in equilibrium (1). Moreover, the complexes with S-nucleophiles ($RS^-$) are susceptible to a spontaneous redox reaction:

$$[Fe^{II}(CN)_5N(O)SR]^{3-} \rightarrow [Fe^{I}(CN)_5NO]^{3-} + 1/2(RS)_2 \tag{2}$$

yielding the Fe(I) complex and oxidised thiol molecule [49,50,52,53]. For a long time, this thermal instability made the photochemical investigation of the $[Fe^{II}(CN)_5N(O)SR]^{3-}$ complexes impossible. Recent study [53] has shown, however, that the proneness to Fe reduction (Eq. (2)) depends strongly on the thiolate redox potential, which is related to the thiolate structure. Especially effective in inhibition of the reduction are carboxylic groups located in β or, better, in α positions. Proper thiolate selection enables one to obtain $[Fe^{II}(CN)_5N(O)SR]^{3-}$ complexes which are stable thermally within this time of the photochemical investigations. During the study, the reversibility of the addition reaction (Eq. (1)) and the presence of **1** as well as $[Fe^{II}(CN)_5N(O)SR]^{3-}$ in the irradiated solutions must always be taken into account.



Scheme 2. Photooxidation reactions and secondary thermal processes detected in alkaline solutions containing $[Fe(CN)_5NO]^{2-}$, $[Fe(CN)_5N(O)SR]^{3-}$ and thiolate, $SR^-$. Based on the results presented by Szaciłowski et al. for $RS^- =$ mercaptosuccinate [43,53,54].

For model photochemical studies the mercaptosuccinate as the S-nucleophile, $RS^-$, was chosen for which the $[Fe^{II}(CN)_5N(O)SR]^{3-}$ complex (**2**) is stable in the dark for hours ($t_{1/2} > 35$ h) and is characterised by an intense MLCT band with a maximum at 526 nm ($\varepsilon \sim 6000$ $M^{-1}$ $cm^{-1}$) [53]. These spectral features created the possibility for photochemical generation of a NO species by irradiation within a long wavelength region (Scheme 2). According to expectation, the inner sphere photooxidation accompanied by substitution of the reduced RSNO ligand is induced by the MLCT excitation [43,54]:

$$[Fe^{II}(CN)_5N(O)SR]^{3-} + SR^- \xrightarrow{h\nu} [Fe^{III}(CN)_5SR]^{3-} + RSNO^{\bullet -} \tag{3}$$

The general reaction mode is thus similar to that of **1** ((c) in Scheme 1), but in the case of **2**, the $RSNO^{\bullet -}$ radical, instead of NO, and $[Fe(CN)_5SR]^{3-}$ (**3**) instead of $[Fe(CN)_5OH]^{3-}$, are generated. The latter in the presence of $RS^-$ is, in any case, easily transformed into **3**. In the $[Fe(CN)_5NO]^{2-}$ – $[Fe(CN)_5N(O)SR]^{3-}$ system there are also different secondary processes, especially those leading to decay of the $RSNO^{\bullet -}$ radical (Scheme 2). These depend on the presence of molecular oxygen: in deoxygenated solutions two Fe(I) complexes, RSNO, NO and $(RS)_2$ were found to be produced, whereas the presence of $O_2$ also results in the formation of reduced forms of oxygen and, partially, the regeneration of **1** from $[Fe^{I}(CN)_5NO]^{3-}$ [53,54].

The two photochemical and several secondary thermal reactions proceeding in the $[Fe(CN)_5NO]^{2-}$ – $[Fe(CN)_5N(O)SR]^{3-}$ system (Scheme 2) generate a variety of possible products. However, the system is adaptable enough to be manipulated so that only the selected pathways can proceed and the chosen products can be formed. To the ‘steering committee’ belong many parameters, among which the most important are: irradiation region, concentration of **1**, **2**, $RS^-$, pH, oxygen presence, temperature, etc.

(i) The first tool which may be used to manipulate the system is irradiation wavelength: **1** is characterised by a very strong absorption between 200 and 300 nm, which decreases successively in the visible, approaching 0 at $\sim 500$ nm; while on the contrary, **2** absorbs strongly between 450 and 600 nm, with a somewhat weaker absorption at $\lambda < 450$ nm and much weaker at $\lambda > 600$ nm [53]. Thus, visible light exclusively activates the pathways characteristic of **2**; near UV generates the products of both **1** and **2**, in amounts proportional to their concentrations and quantum yields; whereas more energetic light ($\lambda \leq \sim 313$ nm) initiates photoreduction modes which compete with the photooxidation ones (path (d) in Scheme 1) [38,43,54].

Thus, to generate nitric oxide in the system containing **1** and **2**, irradiation within the near UV is needed, where the absorption of **2** is lower and its photooxidation quantum yield is smaller than that of **1** [43]. The nitrosothiol production needs the much lower energy of the visible light, which is able to induce photooxidation of **2** only (Eq. (3)) [43]. For example, in the case of mercaptosuccinate the photosensitivity limit overlaps almost the 'phototherapeutic window' (650–850 nm). Similar behaviour to the mercaptosuccinate may be expected for other thiolates, especially those which are present in biochemical systems. There is also the possibility of generating both NO and RSNO and their ratio can be regulated by tuning the irradiation wavelength.

(ii) Another very important parameter useful for the manipulation of this versatile system (Scheme 2) is to shift the equilibrium (Eq. (1)) to obtain more **1** or **2**. There are many parameters effectively influencing the equilibrium; to those recognised in more detail belong: temperature, pH, concentrations of **1**, of $RS^-$ and their ratio, concentration and nature (ionic radius, redox potential, viscosity etc.) of cations [49,53].

When the equilibrium (1) is shifted to the left, NO, $[Fe^{III}(CN)_5OH]^{3-}$ and/or $[Fe^{III}(CN)_5SR]^{3-}$ (depending on the $RS^-$ to **1** ratio) are the major products; whereas when **2** is prevailing, RSNO is the main NO species produced in the system together with oxidised and reduced iron complexes, such as: $[Fe^{III}(CN)_5SR]^{3-}$, $[Fe^{I}(CN)_5NO]^{3-}$ and $[Fe(SR)_2(NO)_2]^-$. Generation of the last two complexes also depends on the presence of oxygen and the $RS^-$ to **1** ratio.

(iii) The $RS^-$ concentration influences not only the equilibrium (1), but also sets the trends for the secondary processes. $[Fe^{III}(CN)_5OH]^{3-}$ and NO are the only major products when there is a lack of or a very low $RS^-$ concentration. Increased $RS^-$ concentration induces generation of $[Fe^{III}(CN)_5SR]^{3-}$, RSNO and $[Fe^{I}(CN)_5NO]^{3-}$. Still higher $RS^-$ concentration, however, activates the reduction and decyanation reaction leading to formation of $[Fe(SR)_2(NO)_2]^-$, $(RS)_2$ and $CN^-$. At very high $RS^-$ to **1** ratio ($\geq 50$) the reaction also proceeds in the dark [54].

Thus, when there is a requirement to generate nitric oxide, the presence of a thiolate in the system should be avoided. While a nitrosothiolate is needed, the thiolate concentration has to be sufficient for conversion of **1** into **2**, although it should not exceed the level high enough to initiate the thermal release of $CN^-$.

(iv) The presence of oxygen can regenerate **1** from $[Fe^{I}(CN)_5NO]^{3-}$, which makes the system partly catalytic in character. Moreover, $O_2$ may contribute to the production of $[Fe^{III}(CN)_5SR]^{3-}$ by oxidation of other Fe complexes in lower oxidation states. The processes are accompanied by generation of the oxygen-reduced forms, which contribute to further redox reactions.

(v) There are also other parameters for disposal, which are as yet not fully recognised but they are known to influence the versatile system, such as: the nature and concentration of innocent cations, pH, temperature, pressure, etc. [49,53]. The system may also be modified by the choice of thiolate, and even by using another nucleophile instead of thiolate, an N-, O- or C-nucleophile.

In conclusion, the versatile system, presented above, consists of two reagents involved in fast equilibrium, which are somewhat different in their coordination sphere, and thereby in their photochemical reactivity. The photochemical reactions are followed by a variety of secondary processes sensitive to different parameters.

The basic conditions for such versatility can also be found among the carbonyl-cyclopentadienyl complexes of Fe and Ru.

## 4. Photochemistry of the $[cpRu(CO)_2]_2$ isomers

The $[cpM(CO)_2]_2$ complexes, where cp = $\eta^5$-$C_5H_5$ and M = Fe or Ru, have been known for a long time for solvent-dependent equilibria between their tautomeric forms [55–61]. In the solid phase, both dimers have a double-bridged structure; in solution, however, they behave differently: the Fe complex mostly occurs in the bridged structure existing in a *cis–trans* equilibrium [55,56,58,62]:

$$trans\text{-}[cp(CO)Fe(\mu\text{-}CO)_2Fe(CO)cp] \rightleftarrows cis\text{-}[cp(CO)Fe(\mu\text{-}CO)_2Fe(CO)cp] \quad (4)$$

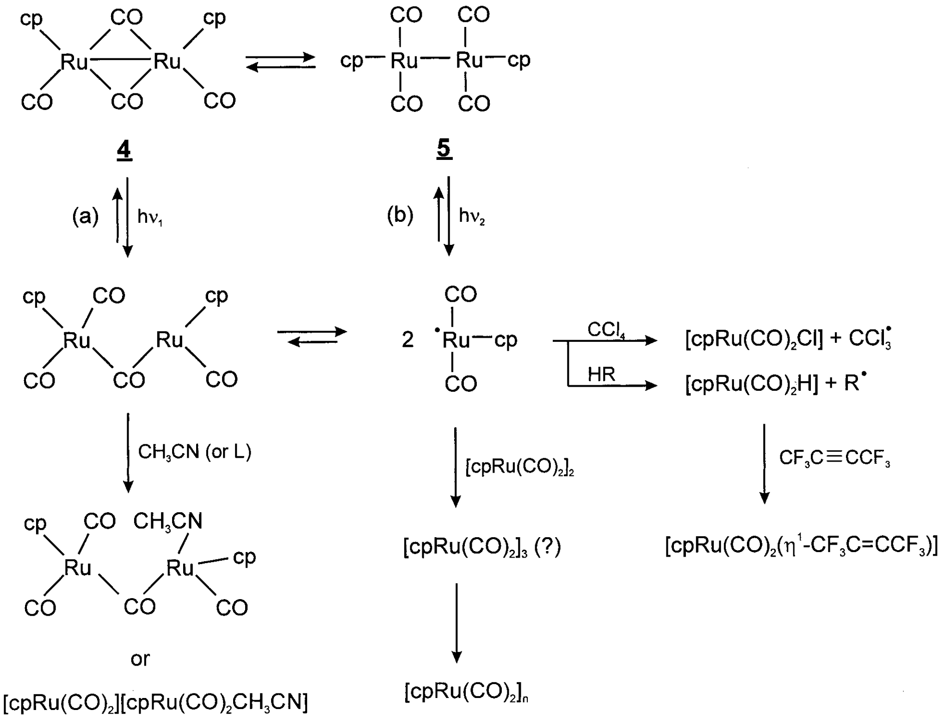
whereas in solutions of the ruthenium complex a non-bridged **5** form also exists beside the CO-bridged **4** [55,56,61,63]:

$$\underset{\mathbf{4}}{[cp(CO)Ru(\mu\text{-}CO)_2Ru(CO)cp]} \rightleftarrows \underset{\mathbf{5}}{[cp(CO)_2Ru\text{–}Ru(CO)_2cp]} \quad (5)$$

Both equilibria include isomers differing somewhat in their coordination spheres. The differences are more subtle in the Fe case, and more significant in the case of the Ru complexes, when two of the CO ligands change their role between bridged and terminal. This results in strengthening (form **4**) and weakening (form **5**) of the bond between the monomeric fragments of the dimer. The structural differences entail changes in the excited state energy and character: the $\sigma_{bridge} \rightarrow \sigma^*_{bridge}$ excitation needs higher energy ($\lambda_{max} = 265$ nm) than the $\sigma_{nonbridge} \rightarrow \sigma^*_{nonbridge}$ one ($\lambda_{max} = 330$ nm) [56,58,62]. In consequence, the two isomeric forms **4** and **5**, are characterised by different photochemical modes (Scheme 3) [64].

Contrary to previous hints [61,65,66], in recent studies, no photochemical dissociation of the CO ligand was reported; instead the cleavage of Ru–$CO_{bridged}$ and Ru–Ru bonds was recognised to follow the $\sigma_{bridge} \rightarrow \sigma^*_{bridge}$ and $\sigma_{nonbridge} \rightarrow \sigma^*_{nonbridge}$ excitation of **4** and **5**, respectively (path (**a**) and (**b**) in Scheme 3) [63,64,66]. In the former case, the monobridged dimeric radical species, whereas in the latter - the monomeric $[\mathrm{cpRu(CO)_2}]^{\bullet}$ radicals, are generated photochemically. The radicals are interconvertible and undergo back and secondary processes, which can finally transform the dimer into a monomeric or polymeric form. The course of these pathways strongly depends on the nature of the solvent and the presence of a ligand or radical precursor in the system. The susceptibility to the medium makes the Ru system versatile, similar to $[\mathrm{Fe(CN)_5NO}]^{2-}$–$[\mathrm{Fe(CN)_5N(O)SR}]^{3-}$. There are, however, distinct differences between the two systems: in contrast to the Fe case, in the Ru system the nature of the excited state is of less importance and the role of secondary processes is more important.

(i) Compounds **4** and **5** differ spectrally and the effect of irradiation energy on the photochemical mode can be easily recorded using the flash technique with a microsecond resolution. In continuous photolysis, however, the final products of the (a) pathway are observed only under specific conditions. Due to the radicals evolving into each other with different kinetics (cf. Scheme 3), the yield of the monobridged radicals generated from recombination of $[\mathrm{cpRu(CO)_2}]^{\bullet}$ can be neglected in continuous photolysis, and the solvent coordination product, e.g. $[\mathrm{cp_2Ru_2(CO)_4CH_3CN}]$ or $[\mathrm{cpRu(CO)_2}]$ $[\mathrm{cpRu(CO)_2CH_3CN}]$, may be regarded as selectively produced by irradiation within the $\sigma_{\mathrm{bridge}} \rightarrow \sigma^{*}_{\mathrm{bridge}}$ band of **4** (path (a) in



Scheme 3. Ligand sphere effect and medium impact on photochemical modes and secondary pathways for bridged and non-bridged forms of $[\mathrm{cpRu(CO)_2}]_2$. Adapted from Macyk et al. [63,64].

Scheme 3) [64]. In contrast, the $[cpRu(CO)_2]^{\cdot}$ radicals and, in consequence, their addition products, e.g. $[cpRu(CO)_2Cl]$, are generated easily in both pathways. Light energy can thus be used for steering the reaction pathways, but only to a limited extent. It has also a small quantitative effect: somewhat increased quantum yields of the dimer decay were observed at shorter wavelengths [61,64].

(ii) Shifting the equilibrium (Eq. (5)) to obtain more **4** or **5** also plays a role and may be used for a limited manipulation of the system (Scheme 3). A decrease in temperature and increase in pressure can shift the equilibrium towards **4**, but the most crucial effect is exerted by the nature of the solvent. Increased solvent polarity is known to shift the equilibrium (5) towards formation of **4** [61,63], presumably due to the coordination of the solvent molecules to the non-bridged form. However, the interconversion of the radical photoproducts somewhat decreases the effect of the predominant concentration of one isomer. Similar to the effect of irradiation energy, the shift in equilibrium has only a small influence on generation of the addition products, whereas to obtain the ligand substituted complex, shift of the equilibrium (5) towards **4** is desirable.

(iii) The most important tool for manipulating the Ru system is, however, the choice of solvent. Its significance is not limited to a shift of the equilibrium (5) but, first of all, the nature of the solvent controls the secondary pathways. Depending on their role, the solvents may be divided into at least three groups: (a) non-polar and poor radical precursors (e.g. heptane, octane); (b) non-polar and good radical precursors (e.g. toluene, carbon tetrachloride); and (c) polar and ligand precursors (e.g. acetonitrile, DMSO).

(a) In non-polar and poor radical precursor solvents, polymerisation is the only reactive pathway of the photochemically generated radicals, irrespective of their origin from the bridged or non-bridged isomer [64].

(b) In non-polar, but good, radical precursors all photochemically generated radicals are transformed into the monomeric Ru(II) complexes, e.g. $[cpRu(CO)_2Cl]$ [61,63,64,66].

(c) In the presence of ligating solvents the Ru radicals can undergo complexation and/or disproportionation, similar to that observed in the case of the analogous iron compound, $[cpFe(CO)_2]_2$ [67].

There are also further cases possible, which are, however, not fully recognised, such as: (d) polar solvents which are ligands and good radical precursors (e.g. alcohols) and (e) polar solvents being neither radical nor ligand precursors (e.g. sulfolane). As yet, it is only known that the overall quantum yield in alcohols, e.g. 2-propanol, is higher than in other neat solvent [64].

Concluding, the $[cpRu(CO)_2]_2$ system (Scheme 3) is versatile enough to be manipulated to proceed by one of three main pathways, yielding different products:

(i) To obtain complexation and/or disproportionation products (path (a) in Scheme 4) the system should be irradiated by UV light within the 265 nm band, at low temperature, under increased pressure, and in a polar coordinating solvent (L) or in a polar solvent containing the requested ligand L.

(ii) Preparation of the $[cpRu(CO)_2]_n$ polymer needs the presence of a non-polar poor radical precursor solvent, whereas other parameters may almost be freely chosen.

(iii) In contrast to the previous compounds, addition products are formed under almost any conditions, provided that a good radical precursor is present in the system. To obtain them in higher yield, however, a non-polar solvent should be used which is, or contains, a good radical precursor. As yet, the highest quantum yields were obtained in the presence of $CCl_4$, which surpassed the yields in other neat solvents by as much as 3–5 times [64]. A somewhat higher temperature of the solutions is recommended (300–310 K) and irradiation can be carried out using longer UV or even visible light (within the 330 nm band and within the low intensive 430–460 nm band).

The latter pathway ((b) in Scheme 3) is of great importance due to its prospective use in the photocatalytic activation of the C–H bond. The system was tested using toluene as radical precursor and EPR spectroscopy was tried to detect the radical products: generation of the hydride Ru transient complex, $[cpRu(CO)_2H]$, and $C_6H_5CH_2^{\bullet}$ radicals were determined [63,66].

## 5. Other systems in prospect

There are numerous other systems, which are versatile enough to be adapted to different tasks, also amongst the iron and ruthenium complexes. To discuss all of them is beyond the capacity of this article, but it is useful to provide some selected examples which are, or can be, of industrial, environmental or biomedical importance.

### *5.1. Photocatalytic systems of conceivable use in organic synthesis*

#### *5.1.1. $[cpFe(CO)_2]_2$ dimer*

In the case of $[cpFe(CO)_2]_2$ (**6**) unlike its ruthenium analogue, the equilibrium between bridged and non-bridged forms is shifted greatly towards the bridged form ($>99\%$ at room temperature) [56,58,62] and is not affected either by solvent polarity nor by temperature [61]. Instead, the equilibrium (4) between the *cis–trans* tautomers is observed which, however, are spectrally indistinguishable and their excited states and photochemical modes should behave similarly. As a result, in the $[cpFe(CO)_2]_2$ system there are fewer factors influencing photochemical behaviour. Two photochemical modes of **6** were observed:

(i) Splitting of the metal–metal bond with generation of the $17e^-$ $[cpFe(CO)_2]^{\bullet}$ radicals. The radicals undergo secondary reactions producing mononuclear $[cpFe(CO)_2X]$ complexes (X = Cl, Br, I) in the presence of radical precursors RX [61,68,69]. Phosphites, however, can substitute one of the carbonyl groups in $[cpFe(CO)_2]^{\bullet}$ yielding $[cpFe(CO)P(OR)_3]^{\bullet}$ radicals [70]. Generation of highly reductive $19e^-$ adducts $[cpFe(CO)_2L]^{\bullet}$ (where L = neutral ligand) is followed by disproportionation of **6**, producing $[cpFe(CO)_2]^-$ and $[cpFe(CO)_{3-n}L_n]^+$ [67].

$$[cpFe(CO)_2]_2 + L \xrightarrow{h\nu} [cpFe(CO)_2]^- + [cpFe(CO)_{3-n}L_n]^+ \qquad (6)$$

Finally, the $[\mathrm{cpFe(CO)_2}]^{\bullet}$ radicals can dimerise or couple with $[\mathrm{cpFe(CO)P(OR)_3}]^{\bullet}$ [70].

(ii) Cleavage of one of the terminal CO groups. The formed unsaturated complex can coordinate a ligand like $PR_3$, $P(OR)_3$ [68,71] or a molecule of coordinating solvent, e.g. THF [70] or acetonitrile [71]. The alkyne coordination, leading to formation of a transient $[\mathrm{cp_2Fe_2(CO)_3(RC{\equiv}CR)}]$ species, followed by intramolecular transformations, was also reported [72]. The nature of the $[\mathrm{cp_2Fe_2(CO)_3}]$ intermediate has been discussed in the literature and was postulated to be triply [65,73–78], doubly [79] or singly CO-bridged [79].

Since tautomers of **6** do not differ spectrally and additionally the *cis*-tautomer prevails in solution [55], excitation of an individual isomer is difficult to accomplish by changing irradiation energy or shifting the equilibrium, as in the Ru analogue case. The photochemical reactions appeared to be sensitive to the geometry of **6** only in inert gas matrices at 12 K [65]. However, there are still some factors, which can influence the photoreactivity pathway:

(i) Similar to the ruthenium system, a crucial factor governing the photochemistry of **6** is the nature of the solvent. In non-polar and good radical precursors the mononuclear products, $[\mathrm{cpFe(CO)_2X}]$, are formed. In polar and ligand precursors (THF, acetonitrile) formation of the binuclear $[\mathrm{cp_2Fe_2(CO)_3L}]$ compound is favoured. In non-polar and poor radical precursor solvents, the photochemical pathways depend on other factors and moieties present in the system.

(ii) The nature of the entering ligand also drives the reaction. In the presence of $PPh_3$, $PR_3$, THF, acetonitrile etc., the CO-substitution reaction with preserved binuclear structure of a product is the main process. Phosphites, e.g. $P(OMe)_3$, undergo a similar reaction, but additionally they are able to substitute the carbonyl group in the $[\mathrm{cpFe(CO)_2}]^{\bullet}$ radical and, in consequence, to form the $[\mathrm{cpFe(CO)P(OMe)_3}]_2$ dimer [70]. Finally, in the presence of $R_2PC_2H_4PR_2$ in benzene or acetone solution, photoinitiated disproportionation of the parent complex **6** takes place (Eq. (6)) [67]:

(iii) Secondary thermal and/or photochemical reactions should also be taken into consideration. An example can be the formation of ferrocene upon prolonged irradiation of $[\mathrm{cpFe(CO)_2X}]$ ($X = Cl$, Br) [69]. On the other hand, the ligated halogen can be photochemically substituted by the N-donor ligands forming $[\mathrm{cpFe(CO)_2NR_2}]$ [17,80–82].

(iv) Exchange of CO groups can be more efficiently performed by an inert gas bubbling during irradiation. This procedure decreases the rate of the back re-coordination of CO molecule.

In conclusion, the versatility of the $[\mathrm{cpFe(CO)_2}]_2$ complex allows one to drive its photochemical reactions towards various products:

(i) Formation of monomeric addition product $[\mathrm{cpFe(CO)_2X}]$ requires irradiation in the presence of good radical precursors. Prolonged irradiation in $CHCl_3$ leads, however, to ferrocene formation, while in the presence of some N-donor ligands formation of $[\mathrm{cpFe(CO)_2X}]$ can be followed by photochemical substitution of X with N-donor.

(ii) Single or double substitution of CO ligands with preserved dinuclear structure, $[\mathrm{cp_2Fe_2(CO)_3L}]$ or $[\mathrm{cp_2Fe_2(CO)_2L_2}]$, proceeds upon irradiation in the presence of coordinating solvents, phoshines (single substitution) or phosphites (single and double substitution).

(iii) Photoinduced disproportionation of **6** (Eq. (6)) requires an inert solvent and the presence of 1,2-bis(dialkylphosphino)ethane.

### 5.1.2. [$Ru_3(CO)_{12}$] cluster

Among many other photochemically active ruthenium complexes, the [$Ru_3(CO)_{12}$] cluster exemplifies another versatile system with various possible pathways [83]. Three main processes take place upon UV-irradiation, depending on the reaction conditions:

(i) Photofragmentation is the main reaction, when [$Ru_3(CO)_{12}$] is irradiated in non-coordinating solvents, such as methylene dichloride and in the presence of phosphine, [$Ru(CO)_4(PR_3)$] and [$Ru(CO)_3(PR_3)_2$] fragments are formed [84].

(ii) Photosubstitution leading to formation of [$Ru_3(CO)_{11}L$] is favoured in coordinating solvents (L = diethyl ether, acetonitrile, THF, etc.). In acetonitrile and/or in the presence of phosphines, mono-, di- and tri- substituted products were detected after irradiation [83]; in THF also a red polymer, formulated as [$Ru(CO)_4$]$_n$, is produced [85].

(iii) In the presence of thiols, photosubstitution results in the formation of the cluster with a thiolato bridge, [$HRu_3(\mu\text{-}SR)(CO)_{10}$]. After prolonged irradiation, the sulfido cluster [$Ru_3(\mu_3\text{-}S)(CO)_{10}$] is produced [100].

### 5.1.3. Ruthenocenes

The photochemistry of other ruthenium compounds also shows sensitivity towards their molecular environment. Thus, while $(C_5H_5)_2Ru$ photolysis in $CCl_4$ leads to formation of $(C_5H_5)_2RuCl$ [86], the photolysis of $(C_6Me_6)_2Ru$ results in the cleavage of one of the $C_6Me_6$–Ru bonds generating the complex with a coordinated solvent molecule, $(C_6Me_6)Ru(Solv)$ [87]. The bis(hexamethylbenzene)ruthenium(0) as an axially symmetrical sandwich complex would be a 20 VE system. When, however, only one of the rings is coordinated, the 18 VE configuration is attained. The complex is fluxional in solution and photolysis in $C_6H_6$ gives the oxidative addition complex [$\eta^6\text{-}(C_6H_6)RuH(C_6H_5)$] as the final product. Another interesting ruthenium system is the photolabile cation [$(C_5H_5)Ru(C_6H_6]^+$. The photoreaction is here strongly dependent upon the nature of the solvent forming solvates [$(C_5H_5)Ru(Solv)_3]^+$, which can transfer the $(C_5H_5)Ru^+$ fragment to other arenes. This renders possible the synthesis of mixed benzene–cyclopentadienyl complexes. Moreover, the photolysis of [$(C_5H_5)Ru(C_6H_6)]^+$ is a versatile entry point into the organometallic chemistry of the [$(C_5H_5)Ru]^+$ fragment and can be used to produce efficiently complexes of the type [$(C_5H_5)RuL]^+$ (L = CO, $PR_3$) [87].

## 5.2. Environmentally versatile systems

### 5.2.1. Fe(III)/Fe(II)–Cu(II)/Cu(I)

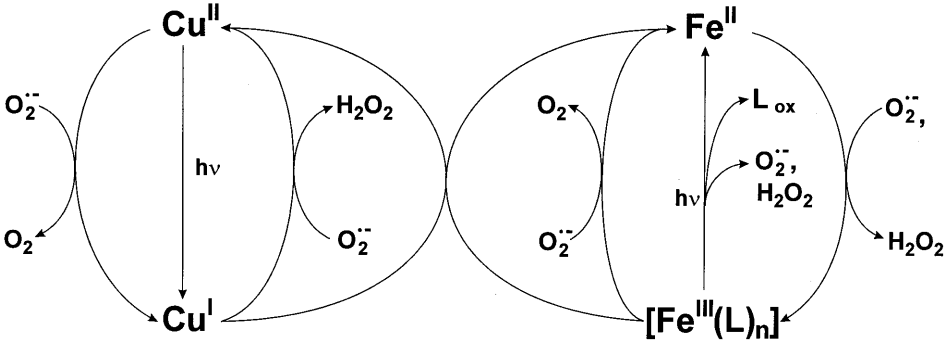
In atmospheric and surface waters, different complexes of Cu(I/II) and Fe(II/III) are involved in the formation and decay of the $OH^\bullet$, $OOH^\bullet$ and $O_2^{\bullet -}$ radicals [1].

Complexes of Cu(II) and Fe(III) with different naturally occurring inorganic and organic ligands [3–6] undergo photoreduction yielding Cu(I) or Fe(II), respectively, and oxygen radicals ($OH^{\bullet}$, $OOH^{\bullet}$, $O_2^{\bullet -}$), hydrogen peroxide or oxidised ligand, depending on the exposure wavelength, ligand nature, the complex structure and the impact of the medium [2,7–9]. Moreover, Fe(II/III) species play a crucial role in the photodecomposition of numerous organic compounds [2], e.g.:

$$Fe^{III}(RCOO)_n \xrightarrow{h\nu} O_2^{\bullet -} + Fe^{II} + \text{organic oxidation products} \tag{7}$$

$$Fe^{III}(RCOO)_n \xrightarrow{h\nu} H_2O_2 + Fe^{II} + \text{organic oxidation products} \tag{8}$$

Reduced complexes and radicals formed in these reactions are substrates for secondary redox reactions, which are also coordination-dependent.



Scheme 4. Environmental cycle of oxidation and/or photooxidation of the organic substances (L) coordinated to Fe(III), in the presence of copper complexes.

In competition with direct photoreduction, Cu(II) and Fe(III) complexes can also be reduced by photochemically generated $O_2^{\bullet -}$. In the case of copper, the indirect photoreduction dominates over the direct, whereas in the case of iron, direct photoreduction is much faster. However, some naturally occurring complexes of copper do not react with $O_2^{\bullet -}$, but they readily undergo photoreduction [3,10]. As Fe(II) and Cu(I) are also easily oxidised by $O_2$, $O_2^{\bullet -}$, $OOH^{\bullet}$ and $H_2O_2$ photocatalytic cycles are formed. Thanks to a redox reaction between Cu(I) and Fe(III) the two cycles can be coupled [8,11] and the system shown formally in Scheme 4 is very often responsible for degradation and/or photodegradation of organic pollutants. To the parameters, which can be used to manipulate the system, belong: exposure, temperature, substrate and oxygen concentrations, pH and other medium parameters, but the complex structure and the nature of the ligand are of crucial importance.

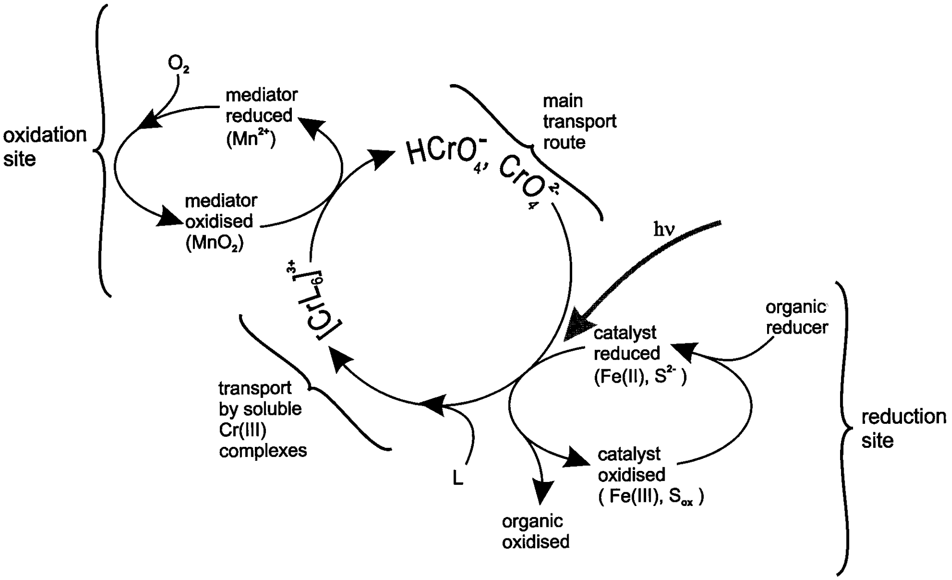
### 5.2.2. Fe(III)/Fe(II)–Cr(VI)/Cr(III)

Chromium is known to circulate in the environment through relatively easy interconversion between Cr(III) and Cr(VI), whereas the $HCrO_4^-$ and $CrO_4^{2-}$ ions and some soluble complexes of Cr(III) with organic ligands provide transport

(Scheme 5) [12,88–99]. The redox processes depend on many parameters, such as pH, oxygen concentration, as well as the presence and concentration of appropriate ligands, reducers and catalysts. Among others, photochemical processes are also engaged in the circulation. One of the important pathways of Cr(VI) reduction in soil, waste and natural waters is photoreduction in the system containing Fe(III)/Fe(II) compounds and some organic reducers. Recently, such a system with oxalate and citrate was studied by Hug and Laubcher [100] and a mechanism was proposed, in which Fe(III) is photoreduced and re-oxidised thermally by $O_2^{\bullet -}$, $CO_2^{\bullet -}$ and $H_2O_2$ generated by oxidation of the organic ligand. The overall photocatalytic reaction leads to Cr(VI) reduction with oxalate oxidation in the presence of Fe(III)/Fe(II):

$$HCrO_4^- + 3C_2O_4^{2-} + 14H^+ + h\nu \xrightarrow{Fe(III)/Fe(II)} 2Cr(III) + 6CO_2 + 8H_2O \tag{9}$$

The Cr(VI) reduction in the environment, sometimes called 'dechromification' [95] is a very important process because it changes the mobile and strongly toxic $CrO_4^{2-}$ or $HCrO_4^-$ into less toxic and much less mobile Cr(III) forms, mostly hydrated $Cr(OH)_3$.



Scheme 5. Environmental chromium circulation in soil, waste and natural waters. Adapted from Kotaś and Stasicka [12].

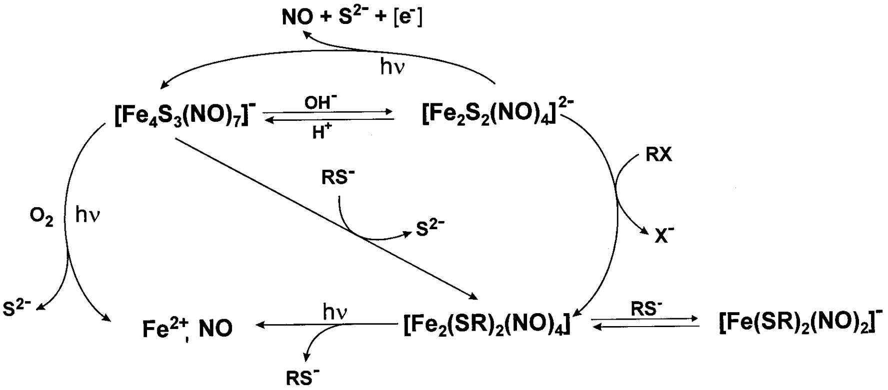
Both systems with Fe(III)/Fe(II) compounds, described in Section 5.2 contribute to environmental oxidation of organic substances, and thus to photodegradation of organic pollutants. At the same time, however, they exemplify wasting of energy accumulated by photosynthesis and from the aspect of solar energy harvesting may be treated as being disadvantageous [12].

### *5.3. Systems of biomedical importance*

#### *5.3.1. Roussin's salts*

Biologically occurring iron-sulfur clusters are active sites of many enzymes [101,102]. Some of them contain coordinated nitric oxide and are photoactive [103]. Others react with NO yielding nitrosylated iron–sulfur clusters [104]. These complexes exhibit extensive biological activity: they are potent nitrovasodilators [105–108], antimicrobials [109] and are involved in immune system activation and signalling [110,111], but can also be mutagenic and carcinoogenic [112]. Black and red Roussin's salts and esters are photochemically active and the systems are versatile enough to meet different requirements.

Roussin's black salt, containing the $[Fe_4S_3(NO)_7]^-$ ion, is thermally stable, but when irradiated within 313–546 nm undergoes photodecomposition, which is effective only in the presence of oxidants (with an average quantum yield of $\sim 10^{-3}$), whereas in deoxygenated aqueous solution no effective photoreactivity was observed. The only detected products were $Fe^{2+}$, $S^{2-}$ and NO (Scheme 6) [15,113]. Recent laser photolysis studies showed, that the first step in the photodecomposition is NO dissociation followed by redox processes leading to the complete cluster destruction [114].



Scheme 6. Photochemistry and secondary processes of Roussin's salts and esters. Based on the results presented by Ford and co-workers [15,113,114] and Butler et al. [112,115].

Similarly to black salt, the red salt, containing the $[Fe_2S_2(NO)_4]^{2-}$ ion, undergoes photodecomposition with the NO release within $\lambda_{irr}$ 313–546 nm [15,113]. In this case, however, the cluster rearrangement and generation of the $[Fe_4S_3(NO)_7]^-$ salt follow NO release (Scheme 6). The red salt also undergoes photolysis under anaerobic conditions, but with a quantum yield $\sim 50$ times smaller than in the presence of oxygen [15,113].

The Roussin's red 'esters', $[Fe_2(SR)_2(NO)_4]$, were also found to undergo photodecomposition yielding $Fe^{2+}$, thiolate anion and NO carried out with the relatively high quantum yield ($\Phi \sim 0.2$) [15]. An excess of thiolate, and also other nucleophiles, transforms the clusters into the monomeric $[Fe(SR)_2(NO)_2]^-$ ion whose photochemical behaviour is as yet not recognised (Scheme 6) [112,115].

Easy interconversion between $[Fe_4S_3(NO)_7]^-$, $[Fe_2S_2(NO)_4]^{2-}$, $[Fe_2(SR)_2(NO)_4]$ and $[Fe(SR)_2(NO)_2]^-$ makes the system susceptible to ligand-controlled NO photogeneration. The strong dependence of the quantum yield on oxygen concentration and ligand-controlled solubility of the $[Fe_2(SR)_2(NO)_4]$ clusters (hydrophilic versus lipophillic effect of the R group polarity) can lead to tissue-selective NO photogeneration, which is an important prospective application for these complexes in photomedicine.

### *5.3.2. Other NO donors*

Nitrosylmetalloporphyrins are another group of nitrosyl adducts, which are known from their versatile photochemical behaviour and have been extensively studied as potential NO donors [14,15,21]. Nitrosylmetalloporphyrins can release NO upon excitation within their macrocyclic π-system [14,15]. Research into nitrosyl porphyrin complexes of the first row transition metals indicated, however, that these compounds are too labile and/or too reactive with oxygen to be used in practice. In this respect, the main attention was turned to more stable compounds with heavier metals, for example the ruthenium analogues. Synthesis, structural characterisation and photoreactivity of several ruthenium porphyrin nitrosyl complexes are now under investigation and these compounds seem to be promising for practical application in photochemical NO delivery to specific targets in biological systems [14,15,21].

## 6. Concluding remarks

There are numerous other systems, containing different transition metals, which are flexible enough to drive their photochemistry towards the desired direction. The aim of this study, dealing with some iron and ruthenium complexes, was to demonstrate that knowledge of this behaviour is useful for a better understanding of the natural photochemical systems. Besides modelling the environmental phenomena and mechanisms, the systems are of importance in designing various molecular devices of bio-medical importance. In order to meet all these requirements very flexible systems, which could be tuned in the controlled way, are needed.

In designing such systems, different strategies are undertaken such as ligand modification, coordination to various metal ions or change of medium. The versatile systems consist of multiple species involved in rapid reversible equilibrium, with at least one photochemically active complex. The complexes differ somewhat in their coordination sphere, which influences their excited state character and thereby their photochemical reactivity. The results of this study show that the most important role in such systems is played by ligands of π-acceptor character. Then, even a subtle modification of the ligand sphere may result in the generation of another product. The manipulatable systems are also characterised by a variety of secondary processes, following the photochemical stage, which are sensitive to the nature of the medium impact.

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