

Homogeneous photo catalysis by transition metal complexes

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Contents

Abstract	101
1. Introduction	102
2. Photocatalysis	104
2.1. Examples of photocatalytic reactions	107
2.2. Spectral sensitization of photocatalytic systems	114
3. Conclusions	118
Acknowledgements	119
References	120

Abstract

The photochemistry of coordination compounds has become an increasingly popular technique for controlling and tuning the reactivity of transition metal complexes and organometallic compounds as well. Rather uncommon reaction pathways can be initiated by electronic excitation of diverse spectroscopic states of these compounds. Besides stoichiometric electron-transfer, dissociation, substitution as well as rearrangement reactions induced by light, photocatalytic processes and photoinduced chain reactions are of particular significance. Examples of photoinduced catalytic and photoassisted reactions as well as photoinduced chain processes will be reviewed to illustrate the advantages of such reaction pathways. Particular attention is given to the spectral sensitization of photocatalytic systems. A summarizing evaluation as well as perspectives for future developments are given. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

During the past decades photons have attracted increasing interest as uncommon physical reagents in coordination chemistry [1–10] and photocatalysis [11–31]. Among other things, this may find its explanation in the generation of electronically excited states of transition metal complexes under very moderate reaction conditions. Such electronically excited states are some 100 kJ higher in energy than the activation energy of usual chemical reactions of metal complexes.

Another reason for the renaissance of transition metal photochemistry has obviously to do with the greater diversity of the electronically excited states of metal complexes, particularly when compared with non-transition metal species or organic compounds. The course of electronic excitation and relaxation cascade of organic and coordination compounds differs considerably. Usually, in organic photochemistry the general features of the electronic excitation and the resulting photochemical reactions may be described satisfactorily by involving three electronic states: singlet ground state (1A), first singlet excited state ($^1A^*$), and corresponding longer-lived triplet excited state ($^3A^*$) formed by intersystem crossing.

Transition metal complexes distinguish themselves from organic compounds both by the number of accessible electronically excited states and their spin multiplicity. Consequently, depending on the wavelength (energy) of irradiation, various electronically excited states result, eventually leading to population of thexi states of different reactivity, as shown in Fig. 1. In some favorable instances this behavior allows the tuning of photochemical reactivity and switching between various pathways, such as electron-transfer (preferably due to the population of diverse CT states), dissociation/substitution/rearrangement reactions (caused by excited LF states), and ligand-centered reactivity due to the population of IL^* states (Fig. 1).

Thexi states of transition metal complexes may be regarded as isomers of the appropriate compound in its electronic ground state. In their dependence on the kind of populated thexi states such isomers are distinguished by changed complex geometry and electron distribution between central ion and ligands and, therefore, by different chemical reactivity, when compared with the same metal complex in the

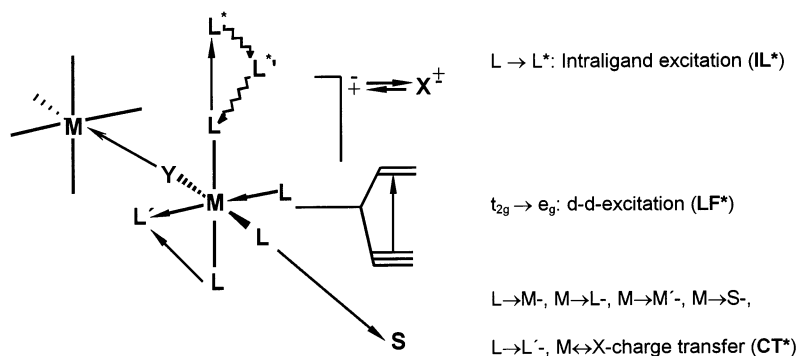


Fig. 1. Scheme of the various kinds of electronic excitation of transition metal complexes.

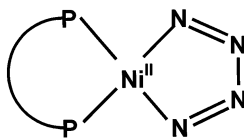
ground state. However, the chemistry of these isomers is limited because of their short life-time due to the high excess energy achieved by absorbing photonic energy. In addition, physical relaxation processes, such as radiationless and radiative (fluorescence, phosphorescence) deactivation compete strongly with the photochemical reaction path leading to photo products. Consequently, depending on both the life-time of the populated states (e.g. allowed, more or less weakly or strongly forbidden states) and physical relaxation processes the efficiency of photochemical primary reactions referring to the quantum yield value Φ is limited within an order of magnitude between 1 and 10^{-5} (or even lower).

Mixed-ligand azido complexes of transition metal ions like iron(III) [35], cobalt(III) [32,33,41–43,45], nickel(II) [44,47–49,44], palladium(II) and platinum(II) [34,36,37,40,46] are suitable candidates to demonstrate the tuning of photochemical reaction pathways by dependence on the kind of electronic excitation [38,39].

Ligand field excitation may lead to *cis/trans* isomerization and/or to photo substitution of azide or other ligands depending on the solvent used. *Cis/trans* isomerization can be monitored by means of time resolved IR spectroscopy [46]. As depicted in Fig. 3, *trans*-[Pt(PPh₃)₂(N₃)₂] forms the *cis* isomer after excitation with 308 nm pulses and decays in the ms time range.

CT excitation gives rise to redox reactions yielding nitrido complexes or short-lived metal(II)nitrene complexes as well as metal(I) intermediates and azidyl radicals. The photochemical reaction pathway depends both on the kind of the first coordination sphere and the central ion coordinated. Transition metal ions of the same group can differ considerably in their reactivity. Thus, the d⁸ ions Pd(II) and Pt(II) undergo photo redox reactions yielding primarily metal(I) species and azidyl radicals, whereas Ni(II) yields nitrene intermediates (Fig. 2). the generation of azidyl radicals is shown by means of EPR spin trapping [34,35,50–52] and the formation of nitrene intermediates with appropriate scavenging reactions [44,47]. Fig. 4 schematically summarizes the possible photochemical reaction pathways of *cis*-[Pt(PPh₃)₂(N₃)₂].

It is proposed that nitrene complexes formed photochemically with appropriate nickel(II)azido complexes lead to the intermediate generation of nickelatetrazole derivatives (**1**) [49]. This reaction pathway illustrates how photons can be used to search for unknown or unusual compounds like the metallatetrazoles.



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The great variety of available electronically excited states may be used for the photo-generation of coordinatively unsaturated species, transition metal compounds with changed formal oxidation number as well as of free ligands and ligand

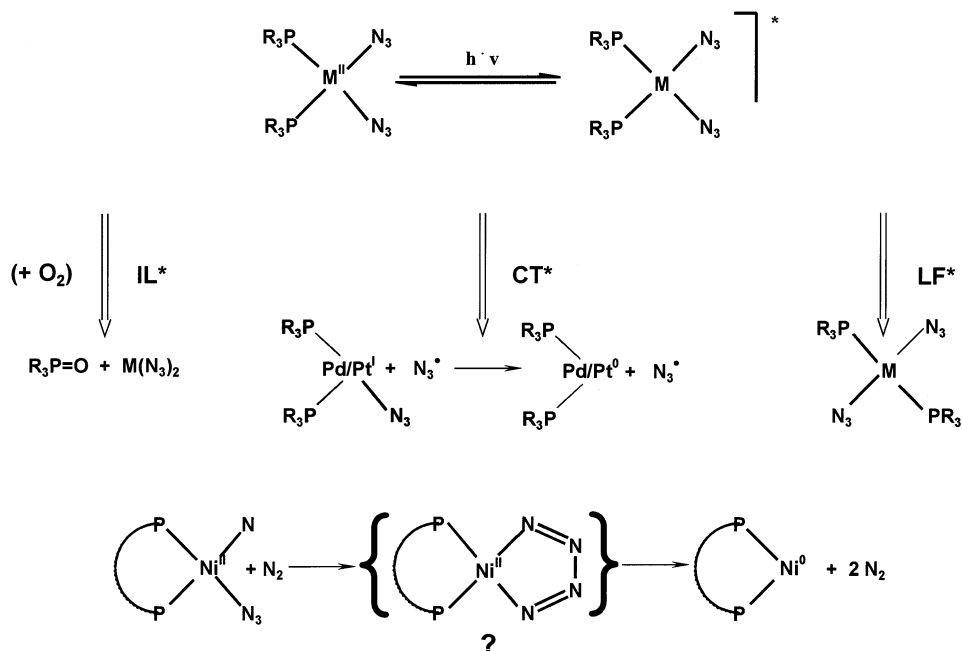


Fig. 2. Possible photochemical reaction pathways of transition metal azido complexes depending on the kind of electronic excitation (M: Ni(II), Pd(II), and Pt(II)).

redox products. Such species generated photochemically open new pathways into both light-induced catalytic reactions and chain processes.

Following the aim of this issue the review focuses preferably on some of our own results in photochemical reactions of transition metal complexes, photocatalysis, and the spectral sensitization of photocatalytic systems. It is not intended, therefore, to cover these subjects comprehensively. Instead, the reader is referred to numerous books and reviews dealing with the photochemistry of metal complexes [1–10] and photocatalysis [11–23]. Excellent overviews on the most recent results in this field are found in special conference reports [53]. Supramolecular photochemistry based on light-sensitive transition metal building blocks and its fascinating perspective [54] and applied aspects of photocatalysis in photoimaging processes [55], wastewater recycling and other environment-protecting processes [56], storage and conversion of solar energy [57], simulation and modelling of light-sensitive metallo-enzymes [58], and organic synthesis [20–31,59] have attracted particular interest, but will not be reviewed in detail.

2. Photocatalysis

Fig. 5 displays schematically the generally accepted principles of homogeneous photocatalysis induced by light-sensitive transition metal complexes and

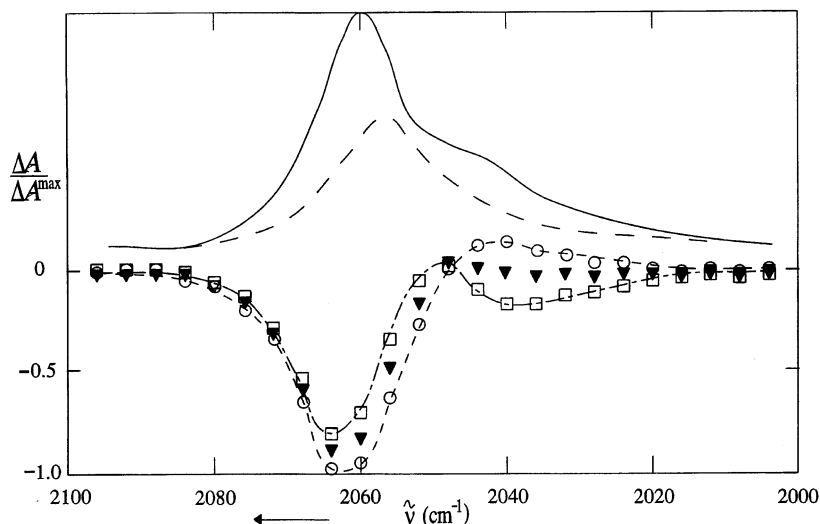


Fig. 3. Time-resolved IR spectra ($\Delta A^{\max} \approx -0.06$) of *cis*-[Pt(PPh₃)₂(N₃)₂] at 0.05 ms (○), 0.3 ms (▼), and 2 ms (□) after 388 nm laser pulse excitation. The upper curves refer to the starting complex (—) and to the spectra after 30 pulses (---).

organometallic compounds. This scheme sums up our contributions to the general features of photocatalysis [4,6,17,20–31]. However, it is not the aim of this paper to reflect on fundamental contributions offered by other authors [11–14,18,19,60,61,162] as summarized recently by Chanon [59].

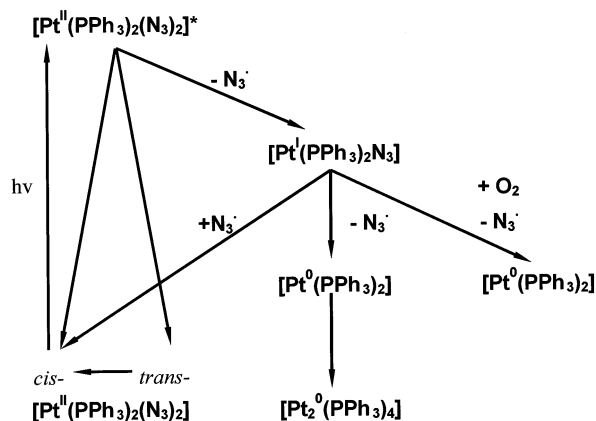


Fig. 4. Scheme the photochemical reaction pathway of *cis*-[Pt(PPh₃)₂(N₃)₂].

Considering the applications it is advantageous to distinguish between two limiting cases of photocatalysis, *photoinduced catalytic* and *photoassisted reactions*. Photoinduced catalysis means the photogeneration of a catalyst that subsequently promotes a catalyzed reaction. Photons are required to generate the catalyst only.

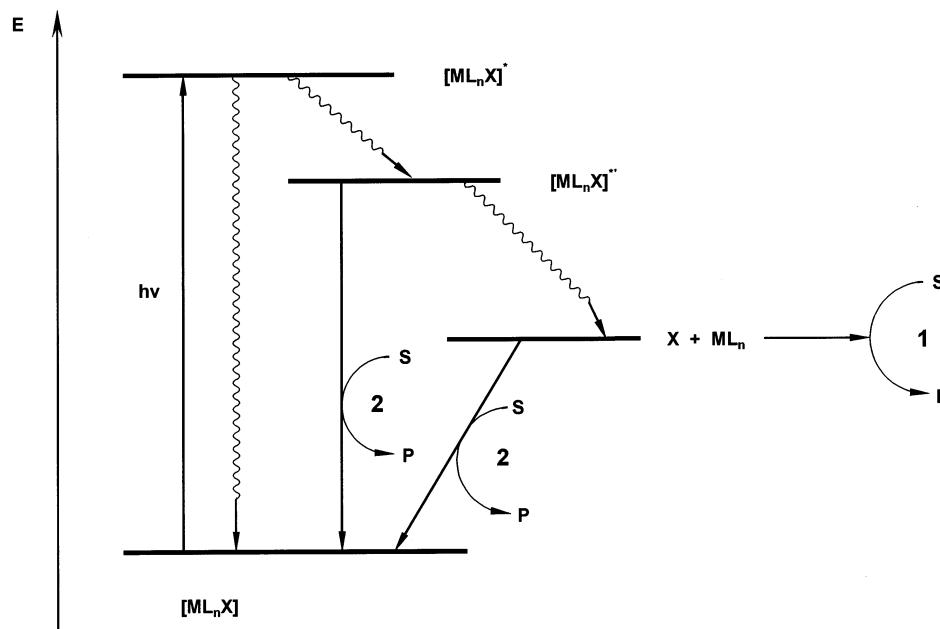


Fig. 5. Simplified Jablonski diagram of photocatalytic reactions based on light-sensitive coordination compounds $[ML_nX]$ (1, photoinduced catalytic reaction; 2, photoassisted reaction; S, substrate; P, product).

Thus, the efficiency of such processes depends only on the activity of the catalyst produced photochemically. Therefore, high turnovers of the photochemically produced catalyst are one of the main criteria concerning efficient photocatalytic processes. Quantum yields (here, ratio of moles of product formed to the number of photons absorbed) greater than 1 may occur. The same is true for photoinduced chain reactions.

Photoassisted reactions include interactions between electronically excited states or short-lived intermediates and substrate molecules leading to product formation under the concomitant regeneration of the starting complex in its electronic ground state. Product quantum yields greater than 1 are impossible, because one photon may not initiate more than one catalytic cycle. In contrast to photoinduced catalytic processes photoassisted reactions can be thermodynamically uphill, thus allowing the possibility for light energy conversion.

Photoinduced chain processes in some way resemble photocatalytic ones. Such reactions offer considerable potential for light-induced polymerizations, but also for the synthesis of fine chemicals, and, therefore, they will be considered here.

Fig. 6 displays the more convenient photocatalytic reaction pathways using light-sensitive transition metal complexes or organometallic compounds. The scheme (Fig. 6) contains for instance the photochemical generation of coordinative unsaturation (O), the activation of small molecules (Z) to be inserted into C–H–,

$C=C-$, or $C\equiv C-$ bonds, the generation of free ligands or ligand redox products behaving as catalysts (A), or the activation of coordinated ligands (X).

Fig. 6 may serve as a guide throughout this article to illustrate how photocatalysis can be initiated using different kinds of Werner-type complexes.

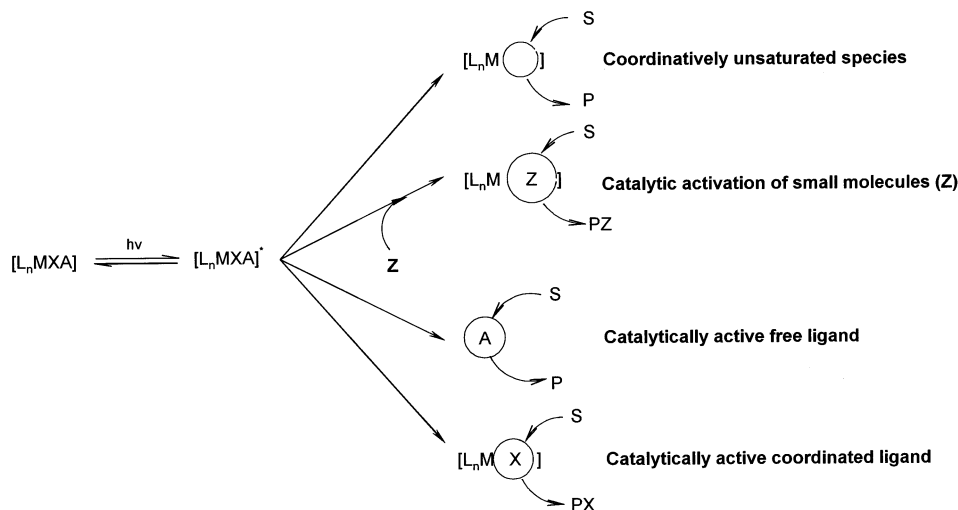


Fig. 6. General scheme of the photocatalytic activation of substrates (S) yielding products (P, PX and PZ, respectively) due to the presence of light-sensitive transition metal complexes or organometallic compounds ($[L_nMX(A)]$).

In addition to these reaction pathways *catalyzed photolysis* might also be considered [4,20]. However, because this pathway may be described as the normal catalysis of photochemical reactions it will not be considered. Although *heterogeneous photocatalysis* has developed very rapidly during the last decade this special field will not be discussed. Instead, the reader is referred to some excellent papers reviewing the application of such processes [12,62].

2.1. Examples of photocatalytic reactions

Photoinduced catalytic reactions due to the photogeneration of coordinatively unsaturated species (Fig. 6) connect photochemistry with homogeneous complex catalysis. The photochemical activation of catalyst precursors emphasizes the advantages of photocatalytic reaction pathways due to the very moderate reaction temperature and pressure upon which this occurs. From the mechanistic point of view the photochemical generation of catalysts and their structural identification opens new approaches to the better understanding of the primary steps of complex catalytic cycles.

One path way for the photogeneration of coordinatively unsaturated species which behave as catalysts, is based on electron-transfer processes with reducible or oxidizable sacrificial ligands such as azide or oxalate, and dithioxalate.

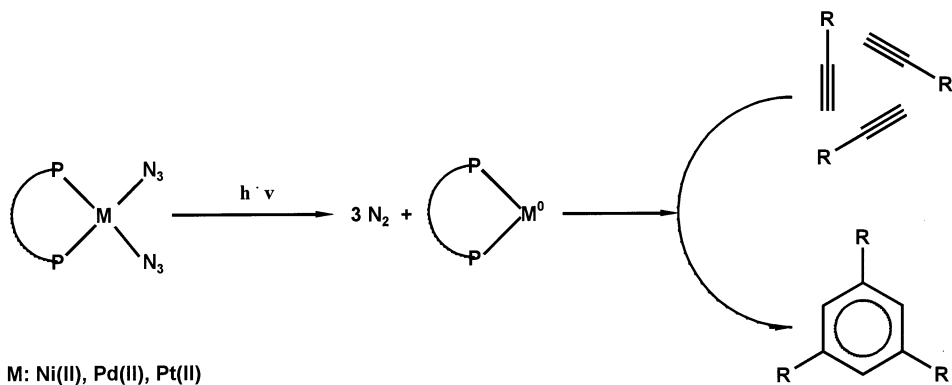


Fig. 7. Scheme of the photoinduced catalytic cyclotrimerization of alkynes to the corresponding benzene derivatives.

Azido complexes with Ni(II), Pd(II), and Pt(II) behave as very efficient sources for the photochemical generation of the corresponding coordinatively unsaturated metal(0) fragments (Fig. 2). Photoinduced catalytic cycles for the cyclization of diverse alkynes to the corresponding benzene derivatives are due to photo redox reactions of mixed-ligand complexes of the type $[\text{MP}_2(\text{N}_3)_2]$, where P_2 corresponds to mono- or diphosphine ligands. Fig. 7 depicts the general scheme for such cycles.

However, in the presence of alkenes or cyclohexane the photochemical activation of the nickel(II) complexes $[\text{NiP}_2(\text{N}_3)_2]$, leads to N-insertion into C=C double bonds or CH bonds due to the formation of nickel(II)nitrene intermediates (Fig. 2). CO and CS_2 , behave similarly where the corresponding isocyanato or isothiocyanato complexes form, as shown in Fig. 8 [44,47].

The photolysis of $[\text{N}_3\text{Co}(\text{chelate})\text{B}]$ complexes (chelate = dimethylglyoxime, dmg; *N,N'*-*o*-phenylene-bis(salicylideneimine), salpen; *N,N'*-ethylene-bis(salicylideneimine), salen; B = pyridine) leads upon the homolytic cleavage of the Co– N_3 bond both to coordinatively unsaturated cobalt(II) chelates ($[\text{Co}(\text{chelate})\text{B}]$) and free N_3^\bullet radicals that undergo fast decay to dinitrogen. In the presence of thiophenole and other thioles the photolysis of these cobalt(III) complexes runs down catalytically yielding the corresponding disulphides and hydrogen. The mechanism of the photocatalytic generation of hydrogen is due to the catalytic activity of the coordinatively unsaturated cobalt(II) species formed photochemically as displayed in Fig. 9 [41–43,45].

Mixed-ligand iron(III) [63–65] and cobalt(III) complexes [66–73] with oxalate or dithiooxalate [74] as sacrificial ligands may also serve as sources for photogeneration of coordinatively unsaturated complex fragments, particularly when α -diimines are used as stabilizing ligands. This kind of ligands influences the spectroscopic properties and the electron-transfer behavior of $[\text{Co}(\text{diimine})_2\text{ox}]\text{X}$ complexes (ox = oxalate) [75–79]. Oxalate or formate radicals formed during the photolysis of such complexes can advantageously be used to initiate photo-polymerization processes.

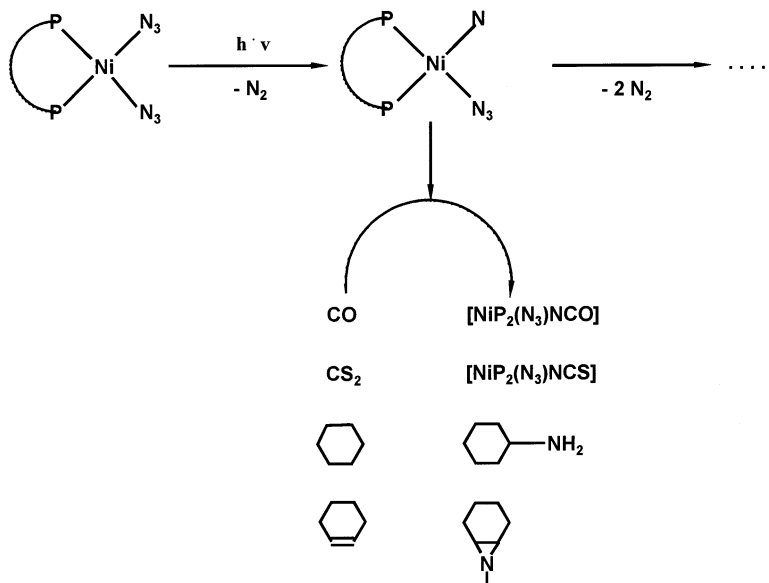


Fig. 8. Photoinduced N-insertion reactions with CO, CS₂, cyclohexene, and cyclohexane in the presence of [NiP₂(N₃)₂] complexes.

The photocatalytic activation of small molecules such as dioxygen also requires the light-induced generation of coordinatively unsaturated species able to coordinate O₂. The photocatalytic oxygenation of hydrocarbons in the presence of metal

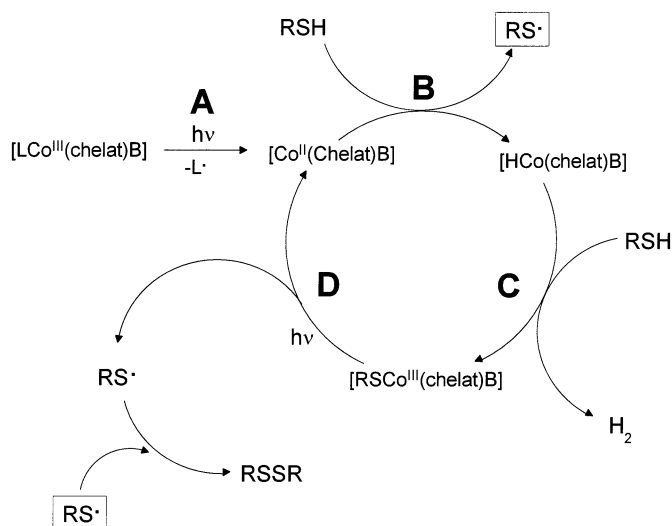


Fig. 9. Scheme of the photoinduced catalytic (A) hydrogen generation (C) from thioles (B, D) in the presence of [N₃Co(chelat)B] complexes.

porphyrins may illustrate the general reaction pathway for this direct activation of oxygen [58,80–92].

The catalytic oxygenation of various substrates in the presence of metal porphyrins has been investigated heavily. However, instead of direct activation of O₂, oxygen donors like iodosylbenzene or peracids are often used [93]. Oxygenation reactions using dioxygen require additional reductants [94,95]. Oxometal(IV) porphyrin π cation radicals ($[(P^+ \bullet)M^{IV} = O]$) are assumed to be the catalytically reactive species when iron or manganese porphyrins are used. This radical is also considered as the catalytically active species of cytochrome P-450 or other metalloenzymes in biological oxygenation cycles, as detailed mechanistic investigations propose [96].

Higher-valent transition metal porphyrins with sacrificial axial ligands are distinguished by extremely low photo-sensitivity upon irradiation in inert solvents such as benzene. However, if coordinating solvents like pyridine or CH-active solvents as toluene are used, the light-sensitivity increases. The same effect happens in the presence of numerous alkenes, particularly cycloalkenes like α -pinene [82–91].

Photoedox reactions due to the electronic excitation of LMCT [97] or Soret states of chloro(tetraphenylporphyrinato)iron(III) (TPPFeCl) lead to the generation of TPPFe and Cl \bullet radicals. These radicals are trapped by H abstraction in the presence of CH active compounds. Such scavenging processes considerably improve the efficiency of photoredox reactions of appropriate metal porphyrins. Under aerobic conditions TPPFe or other low-valent transition metal porphyrins coordinate dioxygen and are converted photochemically to TPPFe^{IV}=O or other oxo complexes depending on the metal porphyrins used.

Oxo metal porphyrins such as TPPFe=O are both strong oxidants and efficient oxygen transfer reagents. In the presence of α -pinene and other cycloolefins three reaction pathways have been observed, as shown in Fig. 10. Path **A** represents undesired autoxidation reactions due to the escape of allyl radicals from the radical cage. **B** stands for the hydroxylation pathway due to the rebound mechanism induced by TPPFe^{III}–OH or other hydroxo(porphyrinato)metal complexes and **C** refers to the direct oxygen transfer yielding the corresponding epoxides.

The ratio of products formed by pathway **A**, **B**, or **C** depends strongly on the central ion coordinated with the porphyrin unit. Further, second axial ligand, preferably N-donor ligands or phosphines, as well as the variation of substituents at the porphyrin unit itself, may influence the product selectivity and the efficiency of the photocatalytic process considerably. The solvents used also affect the product ratio. Thus, with water-soluble metal porphyrin complexes path **C** is improved, and only traces of **B** and **A** products form [89].

It is possible to tune the photocatalytic reactivity towards stereoselective syntheses as shown for a scaled-up synthesis of *t*-verbenol from α -pinene. Further, it was shown that substitution of the porphyrin ligands by cyclodextrin units leads to enantioselective hydroxylation of α -pinene to *S*(–)*t*-verbenol with surprisingly high enantiomeric excess [86].

However, there are still unanswered questions concerning the mechanistic details of oxygen-transfer from porphyrin complex units to organic substrates and, there-

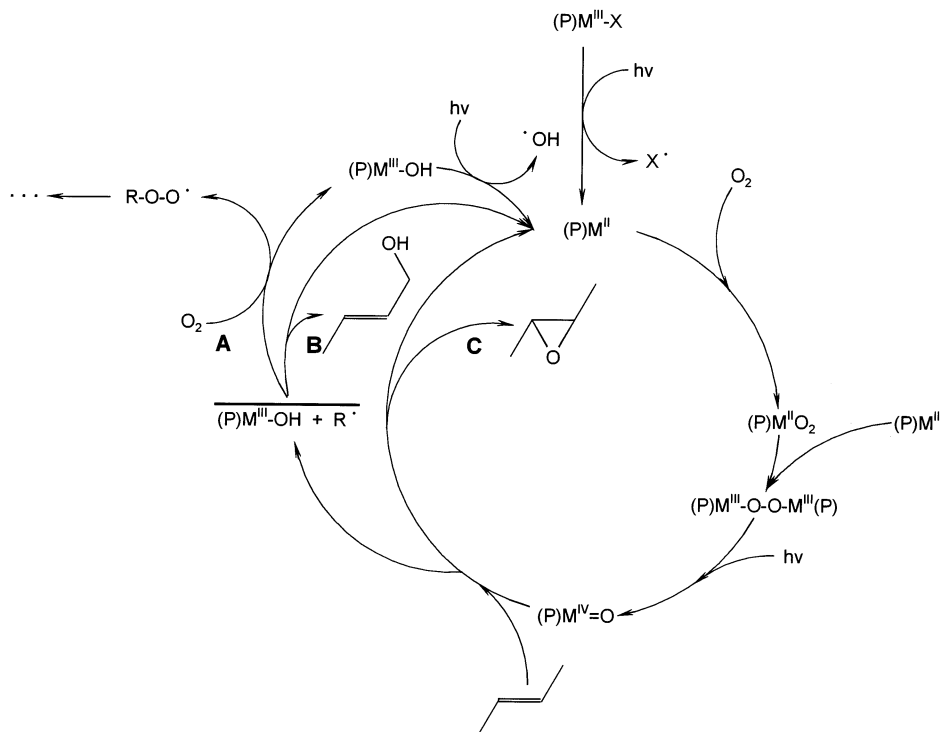


Fig. 10. Photocatalytic oxygenation of olefins to the corresponding oxygenation products (A, autoxidation; B, hydroxylation; C, epoxidation) due to the activation of molecular oxygen by photochemically formed, coordinatively unsaturated transition metal(II)porphyrins.

fore from porphyrin complex units to organic substrates and, therefore, there is no rule that allows prediction of the experimental conditions to be selected for controlled hydroxylation or epoxidation and how undesired radical escape processes can be successfully quenched.

In the presence of tetrahedrally distorted copper(II) complexes of constitution $[\text{CuN}_2\text{S}_2]$ (Fig. 11) α -pinene rearranges to limonene upon anaerobic irradiation of μ -oxo(tetraphenylporphyrinato)iron(III) or manganese(III) complexes [98]. This rearrangement occurs by photoinduced electron-transfer between photochemically generated oxo(tetraphenylporphyrinato)iron(IV)/manganese(IV) with $[\text{CuN}_2\text{S}_2]$ complexes. The $[\text{CuN}_2\text{S}_2]$ complexes themselves are distinguished by uncommon photo oxidation and reduction processes [99–101].

Photoinduced catalytic reactions based on the generation of catalytically active free ligands are illustrated with the help of cyanometallates. The photo-sensitivity of cyanide complexes such as $[\text{Mo}(\text{CN})_8]^{4-}$ or $[\text{W}(\text{CN})_8]^{4-}$ has been known for a long time [102]. The mechanism of the very efficient light-induced CN^- release ($\phi > 1$) is described in some detail [102–106]. The very high efficiency of these photo reactions led to utilization of cyanide release to catalytic purposes as depicted in

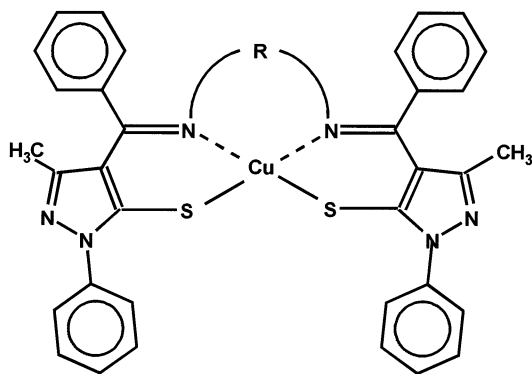


Fig. 11. Constitution of tetrahedrally distorted $[\text{CuN}_2\text{S}_2]$ complexes.

Fig. 12. In contrast to $[\text{Mo}(\text{CN})_8]^{4-}$ or $[\text{W}(\text{CN})_8]^{4-}$ themselves, free cyanide catalyzes the dimerization of heterocyclic carb-2-aldehydes to the corresponding endioles. Heterocyclic endioles are stabilized by intramolecular hydrogen bridges. They are distinguished from their parent aldehydes by much stronger reduction potentials, intense low-energy absorption, and chelate forming properties [107]. The photocatalytic system $[\text{M}(\text{CN})_n]^{4-}$ /heterocyclic aldehyde is also effective in solid layers and can be used, therefore, for photoimaging processes [108].

The search for photocatalytic reactions based on catalytically active coordinated ligands and ligand fragments, led to N-insertion reactions as discussed previously (see Fig. 8). However, no catalytic processes were found.

In addition to photoinduced catalytic reactions photoassisted cycles, based on transition metal compounds can be designed. Fig. 13 displays the photoassisted reduction of certain Fe(III), Co(III), and Cu(II) complexes in the presence of chromic acid esters or organometallic chromates, usually known as strong oxidants under both thermal and photochemical conditions. This rather surprising reaction

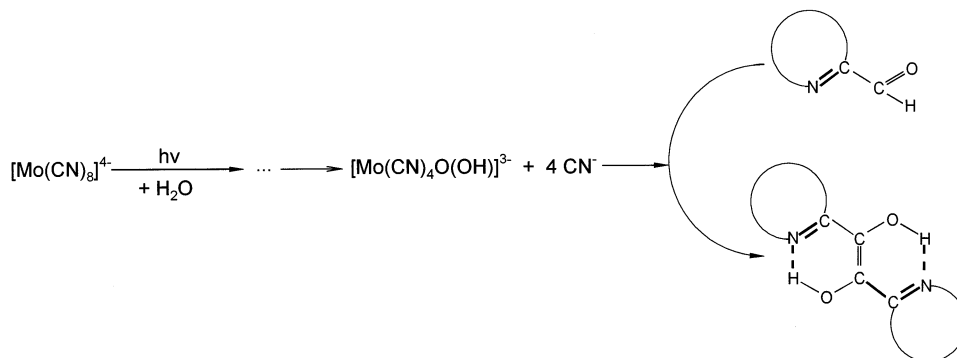


Fig. 12. Photoinduced catalytic formation of heterocyclic endioles from corresponding aldehydes by means of photochemical release of CN^- from cyanometallates.

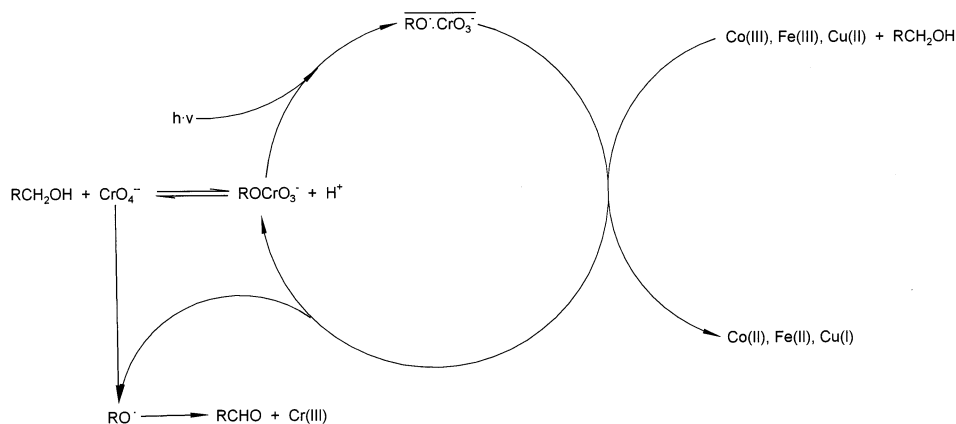


Fig. 13. Photoassisted reduction of selected transition metal complexes of Co(III), Fe(III), and Cu(II) in the presence of chromic acid esters.

proceeds via photochemical formation of short-lived and strongly reducing chromium(V) intermediates [109–116]. However, thermal side reactions between chromic acid esters and radicals formed in the course of the photoreaction lead to the termination of that photoassisted cycle.

Fig. 14 displays schematically a very efficient photoinduced chain oxidation of alcohols to the corresponding aldehydes and ketones [117]. Photochemically generated phenyl radicals behave as chain carriers which regenerate themselves thermally by an excess of diphenyliodonium ions. This light-induced chain reaction is due to second-sphere effects of ion pairs consisting of diphenyliodonium cations and cyanomolybdate(IV) anions that lead to ion pair charge-transfer (IPCT) as discussed in the following section.

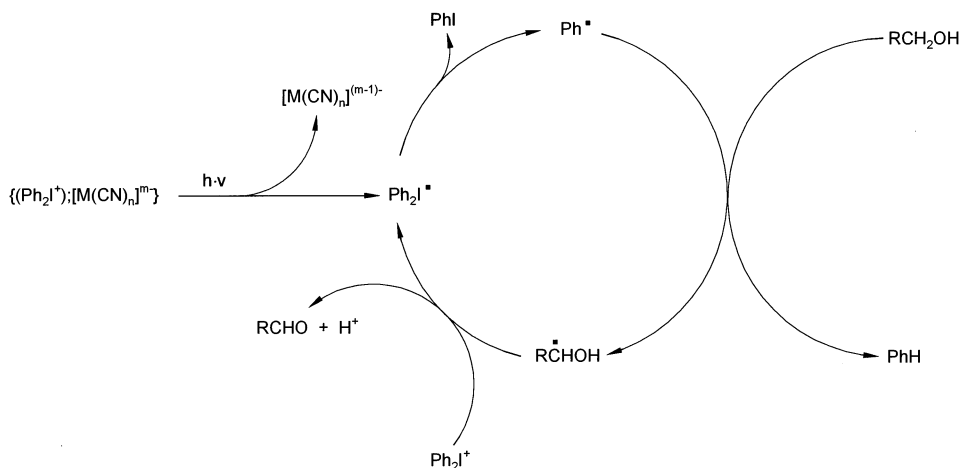


Fig. 14. Photoinduced chain oxidation of alcohols induced by ion pair charge transfer compounds of the kind $\{\text{Ph}_2\text{I}^+; [\text{Mo}(\text{CN})_8]^{4-}\}$ (Ph_2I^+ : diphenyliodonium cation).

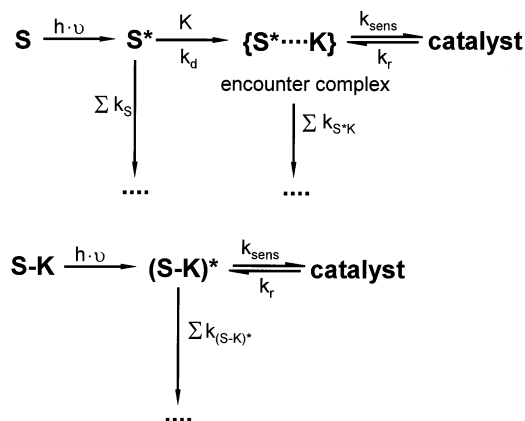


Fig. 15. Comparison of dynamic (upper scheme) and static spectral sensitization (**K**, transition metal complex; **S**, sensitizer; k_x , corresponding rate constants).

2.2. Spectral sensitization of photocatalytic systems

The spectra of coordination compounds are frequently characterized by weakly absorbing d–d transitions in the visible region and intense intraligand and charge-transfer transitions in the ultraviolet. These high-energy transitions are mostly responsible for the catalytically interesting photoinduced electron-transfer reactions. Therefore, the catalyst which will generate the photo reactions must be sensitized to make the photocatalytic processes utilizable [20,118,119].

As shown in Fig. 15, the dynamic sensitization of transition metal complexes [120] can be diminished significantly due to disadvantageous bimolecular processes. The concept of the static spectral sensitization is very useful to overcome this disadvantage (Fig. 15) [118,119].

Static spectral sensitization is based on the linking of a sensitizer (**S**) and a transition metal complex (**K**) in one closed unit (**S–K**) by ionic, covalent or coordinate bond interaction between both components. A further possibility consists in the utilization of low energy states originating from ion pair (IPCT), mixed-valence (IT) or ligand-to-ligand (LL') and metal to ligand (ML) charge-transfer.

In the following section, examples will be given to show how low energy spectroscopic transitions can be used to shift the photosensitivity of photoreactions of transition metal complexes into the visible region and how this kind of spectral sensitization can be applied to photocatalytic processes.

Although the first example of static sensitization with chromophoric ligands was reported by Adamson nearly 30 years ago [155], results are scarce for systems using both additional chromophoric ligands and low-energy CT states for spectral sensitization in the low-energy region. Mixed-ligand complexes containing both monodentate or polydentate chromophoric ligands (e.g. azo dyes and other dye chelate ligands) and photoredox-sensitive ligands (e.g. oxalate and other carboxylato ligands) have seldom been investigated.

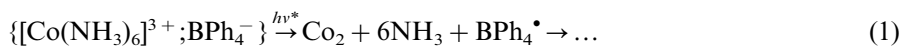
Alternatively, it is possible to shift the low-energy CT band of a given class of light-sensitive mixed-ligand complexes by coordination of ligands which are characterized by favorable positions of the LUMO and HOMO with respect to the appropriate central ion. Thus, the photosensitivity of the cobalt(III)/oxalate unit can be shifted into the visible region by coordination of diverse α -diimine ligands [70,72,76–78,156]. However, the excitation of such IL and low-energy CT states does not necessarily lead to an electronic perturbation of the complex molecule, which would produce photo redox reactions. Very fast deactivation of the excited states may occur as a competing pathway instead of the desired sensitized photoreactions.

Spectral sensitization due to ion pair formation may be achieved either by ion pairs consisting of metal complexes with ionic dyes [121] or by systems distinguished by low-energy ion pair charge-transfer (IPCT) states [54,122,123].

Ion pairs which are distinguished by electronic interactions as well as the normal electrostatic forces between counter ions are of particular value because electronic interactions often lead to changed spectroscopic and photochemical properties. Spectroscopic changes due to ion pairing are characterized by the appearance of novel transitions that are described as ion pair charge-transfer (IPCT) transitions [129–132]. The classical works of Linhard [124] and Adamson [125] with cobalt(III) hexammine iodide showed for the first time how second-sphere effects due to ion pairing change both the spectroscopic and photochemical properties of such compounds. The variation of the Co(III) coordination sphere in ion pairs with I^- strongly influences the spectroscopic behavior [126–128].

Octacyanomolybdate/tungstate(IV) and other easily oxidizable cyanometallates form ion pairs with diareneiodonium cations distinguished by strong IPCT bands in the visible region [103,117,127,128,133,134]. This kind of ion pairing leads to spectral sensitization of the photo oxidation of $[Mo(CN)_8]^{4-}$ and other cyanometallates down to 550 nm. Certainly, the photosensitivity of diareneiodonium cations is shifted in the same manner as shown in Fig. 16. Fig. 14 illustrates the above mentioned application of this sensitization effect in the initiation of photoinduced chain processes with visible light.

Tetraphenylborate forms ion pairs with cobalt(III) ammine complexes distinguished by IPCT bands down to 550 nm [135,136,161]. Very efficient photo-induced electron-transfer reactions occur after the photochemical excitation of these IPCT states leading to Co(II) and short-lived tetraphenylboron radicals (Eq. (1)):



Both, Co(II) and phenyl radicals, the latter formed very rapidly from BPh_4^\bullet radicals, behave as very efficient catalysts applicable to photoimaging processes.

Ion pair compounds like $\{[Cu(diimine)_2]^{2+}; BPh_4^-\}$ [137], $\{bpyH_2^{2+}; [Co(CO)_4]^- \}$ [138], $\{[Cr(en)_3]^{3+}; [M(CN)_6]^{4-} \}$ [139] which undergo photoinduced electron-transfer reactions, when excited in the IPCT range, may serve as further examples of how photoreactions can be initiated by low-energy excitation.

In some aspects, mixed-valence compounds with intervalence transfer (IT) properties are comparable with ion pairs. Mixed-valence compounds with IT behavior

may be described by using the conceptual approach proposed by Robin and Day [140] and Hush [141–143]. Mixed-valence complexes distinguished by trapped valencies of both metal centres are especially important for spectral sensitization. The extremely small electron delocalization between the two centres leads to the appearance of IT bands observable from the ultraviolet to the near infrared. Intervallence transitions are due to electron-transfer from one metal centre to the other, either within a binuclear bridging complex compound (inner-sphere mechanism) or within an ion pair (outer-sphere mechanism). The energy of the IT band depends strongly on the redox asymmetry of both metal centres, the kind of bridging ligand and the dielectric properties of the solvent [143–145]. Therefore, it is feasible to design mixed-valence complexes characterized by spectroscopic transitions from the ultraviolet to the near infrared range, thus providing interesting pathways to static spectral sensitization.

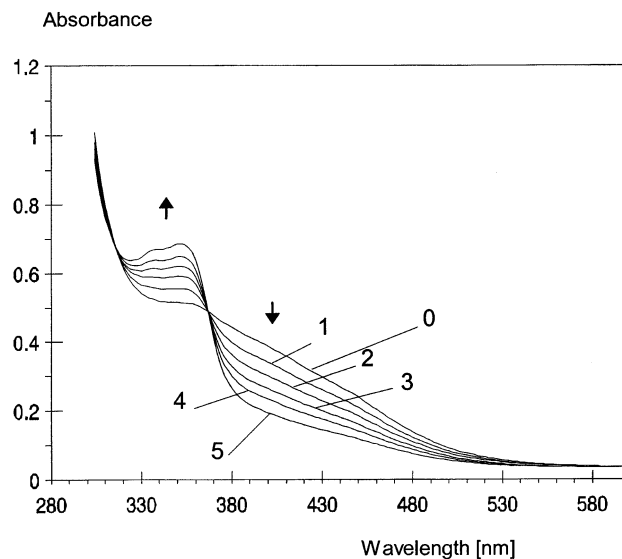


Fig. 16. Photolysis of $\{\text{Ph}_2\text{I}^+; [\text{W}(\text{CN})_8]^{4-}\}$ in ethanol in dependence on the irradiation time (0–5 min, $\lambda_{\text{irr}} = 436 \text{ nm}$).

Cyano-bridged dimeric transition metal complexes like the Vogler/Kunkely systems consisting of ruthenium(II) and cobalt(III), as well as iron(II) and cobalt(III) [146,147] belong to the first examples demonstrating photoinduced electron-transfer reactions due to IT excitation.

Mixed-valence compounds based on cyanometallates combined with a second metal centre offer a considerable potential for static sensitization processes [144,145,148–154]. Thus, octacyanomolybdate(IV) forms mixed-valence compounds with IT transitions ranging from the ultraviolet to the near infrared as shown in Fig. 17 [144].

The Photochemical excitation of low-energy IT states may initiate a catalyst generating electron-transfer reaction. Scavengers can be used to avoid fast back

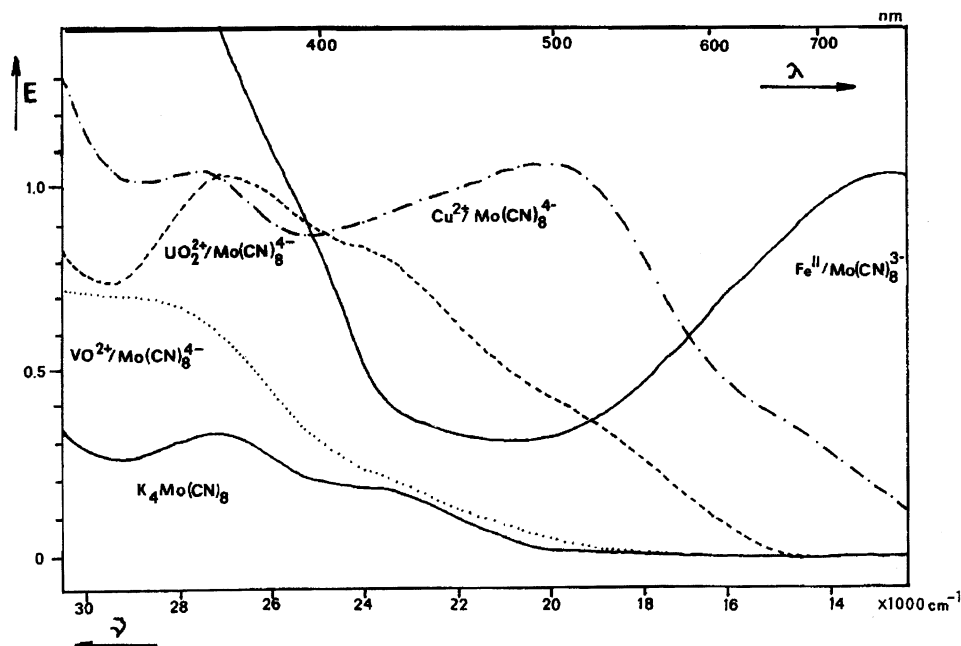


Fig. 17. UV-Vis spectra of mixed-valence compounds with $[\text{Mo}(\text{CN})_8]^{4-}$ in aqueous solution compared with $\text{K}_4[\text{Mo}(\text{CN})_8]$.

electron-transfer which diminishes the efficiency of the spectrally sensitized formation of catalysts especially shown for $\{\text{Cu}^{2+}; [\text{Mo}(\text{CN})_8]^{4-}\}$ mixed-valence compounds [145,149,152]. As the use of chemical scavengers proved unsuccessful for various reasons, photons as physical scavengers for short-lived but photosensitive

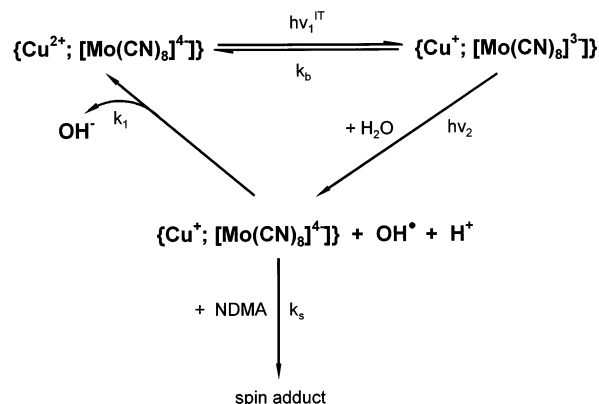


Fig. 18. Scheme of two-photon processes observed with $\{\text{Cu}^{2+}; [\text{Mo}(\text{CN})_8]^{4-}\}$ mixed-valence compounds ($h\nu_1^{\text{IT}}$, IT excitation; $h\nu_2$, Mo(V) excitation; NDMA, *p*-nitrosodimethylaniline as OH scavenger; $k_{x\gamma}$, corresponding rate constants).

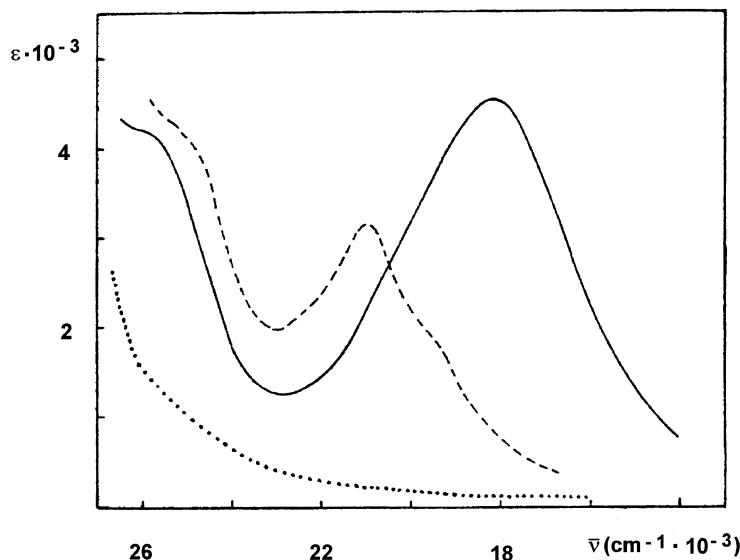


Fig. 19. UV-Vis spectra of $(\text{Et}_4\text{N})_2[\text{Ni}(\text{mnt})_2]$ (---), $[\text{Ni}(\text{dda})_2](\text{ClO}_4)_2$ (···), and $[\text{Ni}(\text{mnt})\text{dda}]$ (—) in acetone at room temperature (dda, diacetyldianile).

intermediates were used as displayed in Fig. 18. These results present a new type of sequential two-photon processes, based on mixed-valence compounds with IT behavior [151].

Low-energy ligand-to-ligand charge-transfer states (LL'CT) offer a further possibility for statically sensitized photoreactions including photocatalytic processes [157–160]. Thus, nickel(II) mixed-ligand complexes with dithiolate and α -diimine ligands are characterized by an unusual interligand charge transfer (LL'CT) band of medium intensity in the visible region (Fig. 19). Both, spectroscopic and quantum chemical investigations showed that the absorption maximum of the LL'CT band can be tuned by variation of the acceptor and donor ligand. For $[\text{Ni}(\text{mnt})(\alpha\text{-diimine})]$ complexes (mnt = maleonitriledithiolate) a maximum spectral shift of ≈ 200 nm is observed (α -diimine = diacetyldihydrazone: $\lambda^{\text{max}} = 470$ nm to α -diimine = phenanthrenequinone diimine: $\lambda^{\text{max}} = 678$ nm) [157–159]. The solvent polarity of these interligand bands correlates strongly with Reichardt's ET parameters. Further investigation is needed however, to make this interesting pathway of intramolecular sensitization applicable to photocatalytic systems.

3. Conclusions

The activation of transition metal complexes by visible and ultraviolet light provides definite advantages when compared with the usual thermal activation. The very convenient photochemical generation of catalytically active species should be

stressed in particular. Compared with thermal reaction pathways, catalysts form photochemically within one reaction step. The catalysts are usually generated with high selectivity and their constitution may frequently be identified very easily. The strategic synthetic design of transition metal complexes or organometallic compounds as well as the choice of the wavelength of irradiation (ligand field, charge-transfer, and intraligand excitation, respectively) allows for modeling of photoinduced catalytic or photoassisted reactions.

Photocatalytic reactions can be carried out at ambient temperature and normal pressure. This circumstance is of particular advantage when substrates or products are concerned that are heat sensitive or explosive. Photocatalysis accomplished at low temperatures often allows the isolation and identification of reactive intermediates, thus providing further insight into the mechanisms of various reaction pathways particularly in homogeneous complex catalysis.

However, photochemical side reactions, fast back electron-transfer processes and recombination reactions, may considerably limit the efficiency of photocatalytic reactions and the photochemical decomposition of the catalyst may further lead to the fast termination of photocatalytic cycles.

These disadvantages should also be taken into consideration when dealing with photocatalysis.

Finally, spectral sensitization is essential for the utilization of a broad range of photonic energy (e.g. solar energy) and should be considered when practical aspects are concerned.

Comparing the advantages and disadvantages of photocatalysis it is rather surprising that photocatalytic reactions have found only little industrial application so far. However, perspectively it can be assumed that attempts to apply photocatalysis in information recording, solar energy conversion, environmental decontamination and/or protection and synthesis of high-price organic compounds will improve considerably. Photons are among the most interesting energy sources of the future and will surely be used on a larger scale in the chemical industry.

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