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Photochemistry and photocatalytic reactions of mixed-ligand azido transition metal complexes

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Dedicated to Professor Wolfgang Beck on the occasion of his 60th birthday

Abstract

Mechanistic details of the photolysis of mixed-ligand azido metal(II) complexes 1 (M = Pd(II), Pt(II), Ni(II); X-X = 2 PR_3, $R_2P(CH_2)_nPR_2$, R-N=CH-CH=N-R) are discussed with respect to formation of intermediate isomerization products, metal(I) complexes and azidyl radicals, respectively.

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(1)

Coordinatively unsaturated metal(0) complexes formed as the ultimate products in the course of photoreaction (1) exhibit catalytic activity. Thus, oxidative addition has been observed with photochemically generated platinum(0) and palladium(0) species whereas photoinduced cyclotrimerization of alkynes has been detected in the presence mixed-ligand azido nickel(II) complexes.

1. INTRODUCTION

Photolysis of mixed-ligand azido complexes [1-3] provides a route for generation of electron-rich metallo fragments which are known to be catalytically active species in homogeneous complex catalysis.

One of the possible reaction pathways to generate them photochemically is based on designing a coordination sphere around a transition metal ion consisting of reducing ligands such as azide, oxalate, dithiooxalate, malonate and others (here we will concentrate on N_3^- exclusively) and metal(0) and/or metal(I) stabilizing ligands such as π-acceptor ligands like α-diimine and phosphine ligands, see eqn (1).

Therefore, we have prepared [1,4,5] a number of mixed-ligand azido complexes of nickel(II), copper(II), platinum(II) and palladium(II) with both phosphine and diphosphine ligands and aliphatic and aromatic α-diimine ligands, respectively. All these mixed-ligand complexes are very light sensitive. Unlike most simple transition metal azides, these complexes are not explosive due to their mixed-ligand coordination spheres. Hence, they can be handled without particular precautions.

Here we will concentrate on some mechanistic details of the photochemistry of mixed-ligand azido complexes, particularly of palladium(II) and platinum(II), and we want to discuss some preliminary results of photochemical reactions of the corresponding nickel(II) complexes. Furtheron, some photocatalytic reactions induced by these complexes will also be considered. Preferably oligomerization reactions of acetylene and some of its derivatives are discussed. At the beginning, however, we will summarize some general aspects of photochemical reactions of mixed-ligand azido complexes as known from the literature.

2. GENERAL ASPECTS OF PHOTOCHEMICAL REACTIONS OF MIXED-LIGAND AZIDO METAL(II) COMPLEXES

It is rather surprising that the photodecomposition of mixed-ligand azido complexes of nickel(II), palladium(II) and platinum(II) has attracted only little attention in the recent years. Some of these results will be discussed briefly.

Reed [6] has demonstrated the formation of *singlet nitrene* upon UV irradiation of $[Ni(tet\text{-}a)(N_3)_2]$ (tet-a means a tetradentate N-macrocyclic ligand) which is in accordance with previously reported mechanistic studies carried out by Basolo and Reed [7].

Beck and Fehlhammer [8] reported qualitative results showing that $[Pd(N_3)_2(PPh_3)_2]$ gives the dimeric species $[Pd_2(N_3)_2(PPh_3)_2]$ upon irradiation due to *photodissociation* of the phosphine ligand.

Nelson [9] demonstrated the photochemically induced reversible *cis-trans isomerization* of palladium(II) mixed-ligand azido complexes with benzyl phosphines as additional ligands.

Again, Beck [10,11] has pointed out that platinum(II) azido complexes are photosensitive and undergo *photoredox processes* which, however, were not further charactereized.

Bartocci and Scandola [12] described for the first time the photochemical formation of platinum(I) complexes and *azidyl radicals* upon irradiation into the N_3-Pt charge transfer region of azido(diethylenetriamine)platinum(II) nitrate.

Detailed investigations carried out by Vogler [13-16] revealed the formation of platinum(0) species and azidyl radicals upon irradiation of various mixed-ligand azido platinum complexes.

Finally, it has recently be shown by Srivastava [17] that mixed-ligand palladium(II) and platinum(II) complexes with azide and α-diimines as ligands behave as very sefficient *photosensitizers* for the singlet oxygen generation.

Summarizing the results published so far on the photochemistry of mixed-ligand azido complexes of nickel(II), palladium(II), and platinum(II) it may be concluded that apart from Vogler's work only few mechanistic investigations have been performed in order to elucidate systematically the highly interesting photochemistry of these complexes.

Thus, in dealing with the photochemistry of these mixed-ligand complexes the following reaction pathways have to be considered:

- *photosubstitution* as well as *photodissociation* processes,
- *photoredox reactions* leading to either intermediate *nitrene derivatives* or *azidyl radicals* together with the generation of reduced metal centers,
- photochemically induced *cis-trans isomerization*,
- *photosensitization reactions* generating singlet oxygen.

The following part will summarize some of our results concerning mechanistic details of photochemical reactions of the mixed-ligand complexes.

3. PHOTOCHEMICAL INVESTIGATIONS OF PALLADIUM(II), PLATINUM(II) AND NICKEL(II) MIXED-LIGAND AZIDO COMPLEXES [1,2]

Stationary photolysis of $[Pt(N_3)_2(PPh_3)_2]$ at 280 nm under an argon atmosphere was accompanied with the appearance of a shoulder at 430 nm in the UV/Vis spectrum (Figure 1) and the disappearance of the platinum(II) complex. The quantum yield was measured to be $\Phi = 0.8$ in $CHCl_3$. $[Pt_2(PPh_3)_4]$ and nitrogen were analyzed as the final products of the stationary photolysis under these experimental conditions. The quantum yield indicates the high efficiency of this photoredox reaction [1].

Irradiation under the same conditions but in the presence of oxygen leads to the very efficient formation of the bis(triphenyl phosphine)peroxoplatinum(II) complex (Figure 1) and concomitant generation of nitrogen.

By using $CHCl_3$ as a solvent no difference in the stationary photolysis of $[Pd(N_3)_2(PPh_3)_2]$ in both oxygen and argon atmosphere was found (Figure 2). In both cases a very efficient formation of (ϕ_{313} = 0.6) of $[PdCl_2(PPh_3)_2]$ was observed as the result of oxidative addition reactions of $CHCl_3$ to metal(0) species produced by charge-transfer excitation of the mixed-ligand complex. Using more concentrated solutions, the photochemical formation of $[Pd_2(N_3)_2(PPh_3)_2]$ has been confirmed as proposed by Beck and Fehlhammer[8].

Flash photolysis in the μs time-scale performed with the same mixed-ligand complexes of palladium(II) and platinum(II) under an argon atmosphere revealed the intermediate formation of a solvent-stabilized $[Pt(CH_3CN)(PPh_3)_2]$ fragment. Using an oxygen atmosphere it could be shown that a short-lived intermediate had already reacted within the time-scale of microseconds to give a peroxo complex as discussed above.

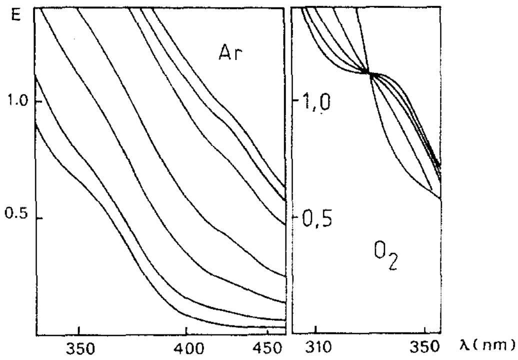


Figure 1. Stationary photolysis of $[Pt(N_3)_2(PPh_3)_2]$ in $CHCl_3$ (argon and oxygen atmosphere, respectively)

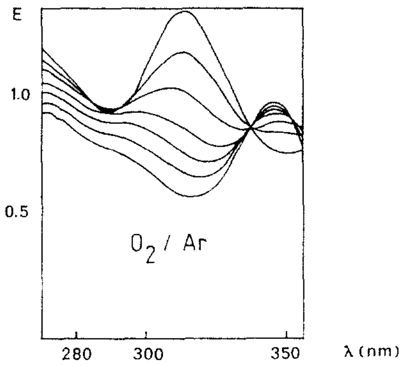
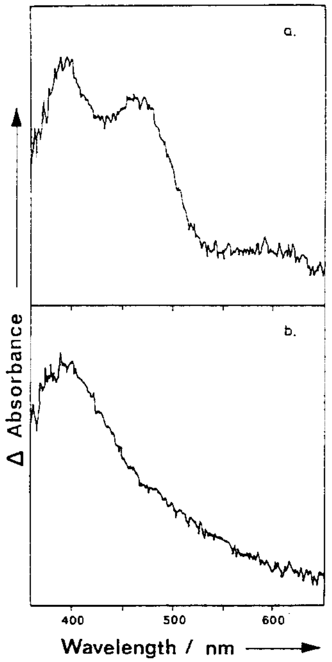


Figure 2. Stationary photolysis of $[Pd(N_3)_2(PPh_3)_2]$ in $CHCl_3$

Since flash photolysis in the microsecond time-scale has shown that primary reaction steps escape detection, ns-laser flash photolysis experiments have been performed in order to detect the corresponding short-lived intermediates. The difference spectra in Figure 3 exhibit two maxima at 380 - 390 nm and 460 nm, respectively.



20 ns after the Flash (308 nm, CH_2Cl_2)

1 ms after the Flash (308 nm, CH_2Cl_2)

Figure 3. Laser flash photolysis of $[Pt(N_3)_2(PPh_3)_2]$ at room temperature

The 460 nm band disappears within a lifetime of 35 to 210 us depending on the solvent used (CH_3CN < CH_2Cl_2 < 2-MeTHF) following a 1st order decay. The band at 460 nm belongs to a thermally unstable intermediate assigned to $[Pt(N_3)(PPh_3)_2]$. In attempt to stabilize this platinum(I) intermediate at low temperature, UV/Vis as well as IR spectroscopic investigations have been performed at 133 K and 183 K in solution and in a PVC matrix at 10 K. However, the mixed-ligand platinum(I) complex could not be stabilized under these conditions. Instead, the solvent-stabilized intermediate $[Pt(PPh_3)_2(2\text{-}MeTHF)_2]$ has been observed by low-temperature UV/Vis spectroscopy (Figure 4).

Both low-temperature and PVC matrix IR spectroscopy show a distinct change of the asymmetric stretching band of coordinated azide (Figure 5) which can be interpreted as a result of photochemical cis-trans isomerization as a minor side way of the general photoredox reaction.

Finally, metal(I) mixed-ligand complexes like $[Pd(N_3)(PPh_3)_2]$ and $[Pt(N_3)(PPh_3)_2]$ as well as azidyl radicals have been detected by EPR spin trapping [18].

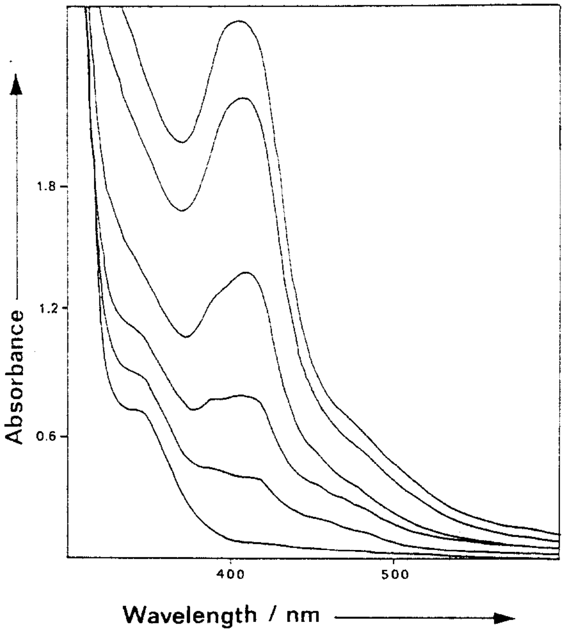


Figure 4. Stationary photolysis of $[Pt(N_3)_2(PPh_3)_2]$ at 133 K (λ_{irr}: 351, 364 nm; $5 \cdot 10^{-4}$ M in 2-MeTHF) shows the appearance of a new band at 424 nm.

Summarizing these results of photochemical reactions of mixed-ligand azido complexes of palladium(II) and platinum(II) with phosphines as additional ligands it can be concluded:

Charge-transfer excitation of these complexes leads to a short-lived primary intermediate, which has been identified as $[M(N_3)(PPh_3)_2]$, together with the formation of azidyl radicals, eqns. (2) - (4).

$$[M(N_3)_2(PR_3)_2] \xrightarrow{h\nu} [M(N_3)_2(PR_3)_2]^* \qquad (2)$$

$$[M(N_3)_2(PR_3)_2]^* \longrightarrow [M(N_3)(PR_3)_2] + \cdot N_3 \qquad (3)$$

$$\cdot N_3 \longrightarrow 1.5\ N_2 \qquad (4)$$

The palladium(I) and platinum(I) complexes decay according to a first-order rate law to the desired coordinatively unsaturated electron-rich metallo fragments, eqn. (5), which are interesting species with respect to their catalytic activity.

$$[M(N_3)(PR_3)_2] \longrightarrow [M(PR_3)_2] \qquad (5)$$

The coordinatively unsaturated species are temporarily stabilized by solvent molecules (S), eqn. (6), but, finally, they dimerize in a dark reaction to the well known metal-metal bonded complexes, eqn. (7).

$$[M(PR_3)_2] + 2\ S \longrightarrow [M(PR_3)_2S_2] \qquad (6)$$

$$2\ [M(PR_3)_2S_2] \longrightarrow [M_2(PR_3)_4] + 4\ S \qquad (7)$$

However, photochemically induced cis-trans isomerization, eqn. (8), has to be considered as a minor side reaction leading to the corresponding *trans* mixed-ligand azido complex which photodecomposes to the same final products as outlined above.

$$cis\text{-}[M(N)_2(PR_3)_2] \longrightarrow trans\text{-}[M(N)_2(PR_3)_2] \longrightarrow \ldots \qquad (8)$$

Both synproportionation reactions of metal(II) species with metal(0) intermediates to metal(I) complexes and disproportionation of metal(I) species to metal(II) and metal(0) complexes could be ruled out by careful kinetic investigations.

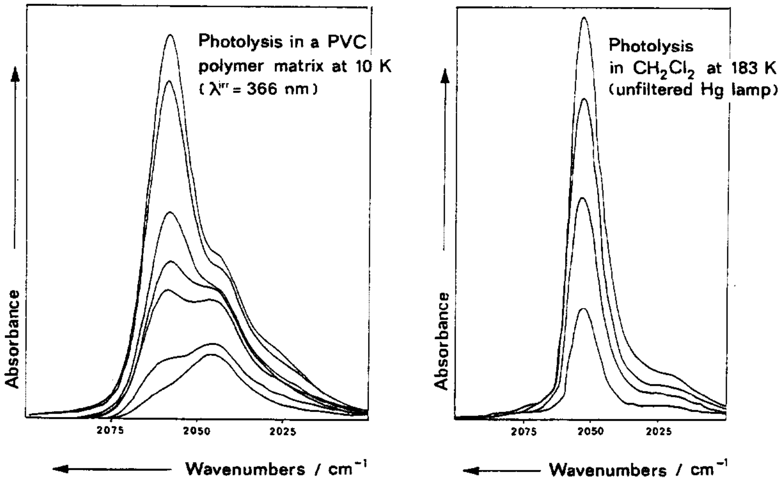


Figure 5. IR spectroscopic evidence for intermediate cis-trans isomerization of $[Pt(N_3)_2(PPh_3)_2]$ at low temperature.

Moreover, some unusual photoreactions have been observed in addition to photoredox decomposition and light-induced cis-trans isomerization [19]. Thus, photosubstitution of phosphine ligands has been observed upon irradiation of $[Pd(N_3)_2(PPh_3)_2]$ in the presence of p-nitrosodimethylaniline (p-NDMA) and other weak donor ligands, eqn. (9).

$$[Pd(N_3)_2(PPh_3)_2] \xrightarrow[\text{p-NDMA}]{h\nu} [Pd(N_3)_2(PPh_3)(\text{p-NDMA})] + PPh_3 \qquad (9)$$

No photoredox reactions have been observed under these conditions confirming earlier qualitative results published by Beck and Fehlhammer [8].

Some of our preliminary results suggest that the photochemical behavior of mixed-ligand azido complexes of nickel(II) is quite different and appears to be much more complicated as compared to the platinum and palladium analogues.

Irradiation of solutions of $[Ni(N_3)_2(PR_3)_2]$ in hexane under an argon atmosphere leads to photodissociation of the phosphine ligand (Φ_{366} = 0.1) whereas in halocarbon solvents the formation of $[NiCl_2(PR_3)_2]$ was observed. Prolonged irradiation in CCl_4 gives the corresponding nickel(III) complex [19]. Figure 6 shows the UV/Vis spectra of the staionary photolysis of nickel(II) mixed-ligand azido complexes performed under reaction conditions described above.

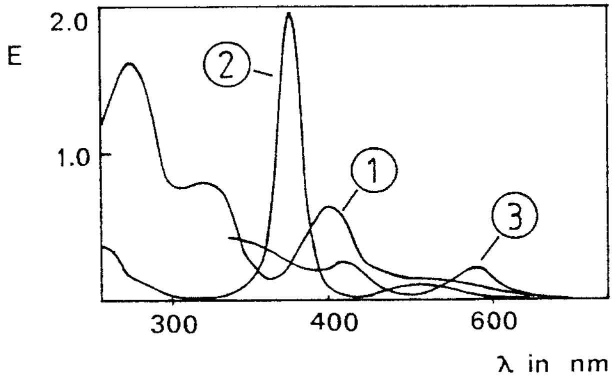
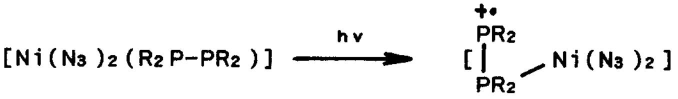


Figure 6. UV/Vis spectra of the final products of the photolysis of $[Ni(N_3)_2(P^nBu_3)_2]$. (1: formation of $Ni(N_3)_2$ in n-hexane; 2: production of $[NiCl_2(P^nBu_3)_2]$ in CCl_4 under Ar; 3: prolonged irradiation in CCl_4, formation of $[NiCl_3(P^nBu_3)_2]$).

No azidyl radicals have been detected upon irradiation by EPR spin trapping technique. A light-induced decrease of the asymmetric stretching band of azide ligands with concomitant appearance of a new band around 2050 cm^{-1} which belongs to a labile intermediate (Figure 7) has been detected IR spectroscopically [20].

The EPR detection of a C-centered radical using nitrosodurene as a spin trap (a_N = 1.416±0.010 mT; a_H (or a_P) = 0.833±0.010 mT) suggests a light-induced electron transfer between the metal center and the phospine ligand, eqn. (10) [21]. However, no EPR evidence for lower-valent nickel complexes have been found so far.



$$[Ni(N_3)_2(R_2P\text{-}PR_2)] \xrightarrow{h\nu} [\overset{+\bullet}{PR_2}\text{|}PR_2 \diagup Ni(N_3)_2] \qquad (10)$$

Further mechanistic studies to elucidate the rather complicated mechanistic details are in progress.

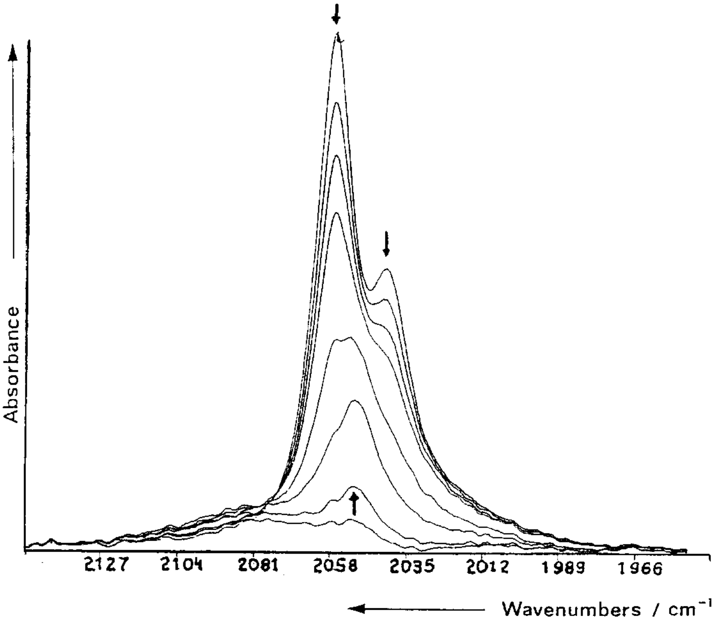


Figure 7. IR spectroscopic evidence for the formation of an intermediate during the stationary photolysis of $[Ni(N_3)_2(DPPE)]$ in CH_2Cl_2 at room temperature.

In summary, the results of photochemical reactions induced by charge-transfer excitation of palladium(II) and platinum(II) mixed-ligand azido complexes show that electron-rich metallo fragments of the corresponding metal(0) species can be obtained very conveniently from thermally stable precursors.

Irradiation of mixed-ligand nickel(II) complexes also leads to the generation of catalytically active intermediates, although their exact constitution is not yet known.

All these reactive and coordinatively unsaturated species have been investigated with respect to their catalytic behavior.

4. CATALYTIC REACTIONS INDUCED BY PHOTOCHEMICALLY GENERATED ELECTRON-RICH METALLO FRAGMENTS AND OTHER REACTIVE SPECIES

Recently Trogler [23] has summarized his results on the photogeneration of electron-rich metallo fragments from light-sensitive mixed-ligand oxalato complexes of platinum(II) also stabilized by additional phosphine ligands. He was able to show that photogenerated platinum(0) complex fragments are catalytically active with respect to various oxidative addition reactions of olefins, e.g. hydrosilation and deuterium exchange reactions.

Starting with mixed-ligand azido complexes of nickel(II), palladium(II), and platinum(II), we have been able to demonstrate the efficiency of photogenerated electron-rich metallo fragments for various kinds of oxidative addition reactions. Thus, hydrosilation and hydrogenation reactions of olefins as well as oxidative addition of various halocarbons have been observed. In the latter case mixed-ligand metal(II) halo complexes were formed together with the corresponding halocarbon radicals as detected by EPR spin trapping [23,24].

However, oligomerization reactions of acetylene and alkyne derivatives in the presence of photochemically generated electron-rich metallo fragments seem to be of much more interest, particularly with respect to cyclotrimerization reactions leading to benzene and benzene derivatives. In analogy, pyridine derivatives can be obtained from organic nitriles. It is expected that organic cyanates lead to pyrid-2-one derivatives.

Cyclooligomerization reactions of acetylene and alkyne derivatives are of considerable interest, although the required increased temperature and high pressure are strict limitation of the thermal homogeneous catalysis because of the explosivity of acetylene [25].

Photocatalysis should be of advantage to overcome these restrictions since generation of the catalyst is possible at ambient temperature and normal pressure, thus avoiding the danger of explosion of acetylene.

These advantages of photocatalyis have already been used in cyclization reactions of acetylene derivatives in the presence of light-sensitive $[Co(pyr)_6](BPh_4)_2$ as published by Biagini and Juris very recently [26].

Cyclotrimerization reactions of acetylene in the presence of organic nitriles, which should lead to 2-substituted pyridine derivatives, are also of particular interest. As it has been demonstrated very recently by Schulz [28] pyridine derivatives may be obtained photocatalytically using cyclopentadienyl bis(alkene)cobalt(I) complexes as precursors.

Nickel(II) mixed-ligand azido complexes have also been proven to be useful precursor compounds for the photocatalytic trimerization of acetylene to benzene using DMSO as a solvent and slightly increased temperature (50° C). Photocatalytic turnovers > 100 have been observed under these mild conditions.

Changing the solvent by weaker coordinating donors such as THF and 2-MeTHF also leads to an increased catalytic activity at ambient temperature of these complexes. Thus, we have been able to demonstrate [29] the photocatalytic trimerization of acetylene to benzene at 20° C at normal pressure in the presence of mixed-ligand azido complexes of palladium(II) and platinum(II) which are catalytically inactive even at elevated temperatures.

Depending on the donor strength of the solvent, an alteration of the photocatalytic activity has been observed (DMSO < DMF < THF < 2-MeTHF). Thus, at ambient temperature and using DMSO as a solvent the production of traces of benzene has been observed photocatalytically only in the presence of $[Ni(N_3)_2(DPPP)]$ (DPPP = diphenyl phosphinopropane) whereas all other mixed-ligand complexes appeared to be inactive under these conditions. However, when 2-MeTHF and THF, respectively, were used as solvent, catalytic turnovers of about 100 have been observed for nickel(II), palladium(II), and platinum(II) mixed-ligand azido complexes.

However, detailed GC/MS analysis revealed that side reactions occur when low temperature and THF or 2-MeTHF were used. Thus, in addition the formation of benzene as the major product, iso- and cycloalkanes of chain length between 8 and 12 are produced. These results can be explained by assuming that THF and 2-MeTHF, respectively provide the source of hydrogen in photocatalytic reactions as it has also been pointed by Kisch [30]. However, the exact mechanism of the photocatalytic cyclotrimerization of acetylene and alkyne derivatives as well as the dependence of the formation of by-products on the solvent has still to be elucidated.

Finally, preliminary results seem to confirm the possibility of photocatalytic synthesis of benzene derivatives by using appropriate alkyne derivatives. This reaction also provides a route to 2-substituted pyridine derivatives starting from a mixture of organic nitriles and acetylene [19]. Therefore, photocatalytic generation of pyrid-2-one derivatives from cyanates and alkynes in the presence of mixed-ligand azido complexes appears to be also promising.

5. CONCLUDING REMARKS

The photogeneration of electron-rich metallo fragments from thermally stable nickel(II), palladium(II), and platinum(II) mixed-ligand azido (but also oxalato, dithiooxalato, and malonato) complexes with additional π-acceptor ligand was studied within the general framework of our investigations of photocatalysis induced by both light-sensitive Werner-type transition metal complexes and organometallic compounds [3,32-34].

Despite some critical remarks concerning the definition of photocatalytic reaction pathways [35], it seems to be of advantage to distinguish between photo-induced catalytic and photoassisted reactions as shown in Figure 8. Thus, depending on the purpose of application it is possible to design photocatalytic systems based on photochemically generated short-lived intermediates (*photoassisted reactions*) which may be used for example for the storage and conversion of solar energy, in modeling light-sensitive metallo enzymes as well as in organic synthesis. Photocatalytic systems based on long-lived photochemically generated catalysts (*photoinduced catalysis*) may be applied to unconventional photographic processes, photolithography and also to organic synthesis, particularly when photoinduced chain reactions are involved.

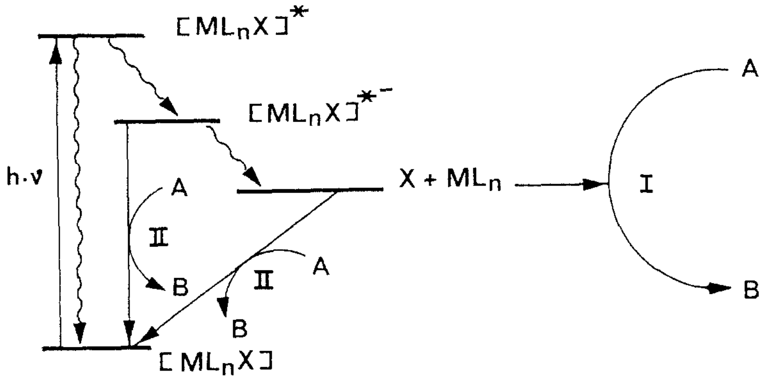


Figure 8. Simplified Jablonski diagram of photoinduced catalytic (I) and photoassisted (II) reactions. (I: photogeneration of a long-lived catalyst; II: photogeneration of a short-lived catalyst).

This paper is dealing with photocatalytic reactions in organic synthesis, and it was the intention to show some of the advantages (low temperature, normal pressure) when using photogenerated electron-rich metallo fragments in the cyclotrimerization of alkynes. Under similar aspects we have been able to prove the advantages of photocatalysis in oxygenation reactions of olefins in the presence of various metallo porphyrins [3,36-38] and metal acetylacetonates [39], respectively. A more comprehensive review on homogeneous photocatalysis in organic synthesis is going to be published elsewhere [40].

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