Photochemical properties of a Ru/Pd based photocatalyst for the solar driven generation of hydrogen with HPLC

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Abstract

These studies do show the formation of photoinduced intermediates as evidenced by species with absorption maxima at up to 600 nm, involving reduced bridging ligands such as shown in the following structure. No information concerning the photostability of the photocatalyst is available. In this studies we wish to carry out HPLC studies to investigate the issue of the photostability of the photocatalyst. The photochemical properties of this complex together with a number of analogues compounds **1-2**, $[(tbbpy)_2Ru(tpphz)](PF_6)_2$ - $[(tbbpy)_2Ru(tpphz)PdCl_2](PF_6)_2$ will be investigated initially in acetonitrile, subsequently their stability under photocatalytic conditions, in the presence of TEA and an under argon atmosphere.

Keywords: Photochemical, Ruthenium, Palladium, Soler driven, Hydrogen, HPLC.

1. Introduction

In the light of the rapidly increasing need for sustainable energy interest in the conversion of solar energy is growing. Solar energy is utilized as a source for thermal or electrical energy (photovoltaic cells) [1], however, its application in light driven catalytic systems may open a route towards highly energy efficient chemical reactions. One of the approaches used is the use of catalytic systems that include light harvesting transition-metal complexes for the photolysis to convert the light energy into chemical energy [2,3]. Transition-metal complexes have a distinct advantage over semiconductors as their photophysical properties can be tuned through ligand modification. Aided by this versatility, researchers have devised a variety of catalytic systems capable of performing the reduction half-reaction of water cleavage, in which the excited state of the transition-metal complex is quenched by charge transfer to an electron relay [4]. Early works report the successful use of $[Ru(bpy)_3]^{2+}$ (bpy=2,2'-bipyridine) as a photo

sensitizer, in combination with an electron relay species, and typically employ a platinum catalyst [5,6]. In this report Ru-complexes were used to study if they are appropriate to cleave water and so produce hydrogen.

The central processes in natural photosynthesis are light driven electron transfer from the special-pair to the primary acceptor, and the subsequent charge separation to enable the reduction of substrates. The transfer of these design principles to artificial systems has led to the development of catalytic multi-component systems for the photo catalytic production of hydrogen [7]. In these systems, photoredox-active metal complexes and separate redox catalysts are used to facilitate directed photo induced electron transfer. For example, Grätzel et al. showed that heterogeneous photo catalyst systems can be used for the generation of hydrogen [8], Currao et al. reported the photochemical [9]. However, in these heterogeneous systems, the electron-transfer processes depend on many interfacial parameters that are difficult to influence. Homogeneous systems, consisting of a photoactive Ru complex and an electron relay of Pd/Pt complexes, which generate H_2 in intermolecular reactions, have also been described. Their effectiveness is limited by the instability of the reduced photo catalysts [4].

In an intramolecular photocatalyst it should be easier to control photoinduced electron transfer by precise tuning of the physical properties and orientation of the molecular components. If it were also possible to slow down charge recombination processes, efficient photocatalytic systems may become feasible. Rau and coworkers recently reported a dinuclear compounds (See Figure.1) which produces hydrogen upon irradiation with a turn-over-number of (TON) of 56 [10], recently values of up to 250 have been obtained in the presence of water [11]. Other such catalysts have also been reported [4,12].
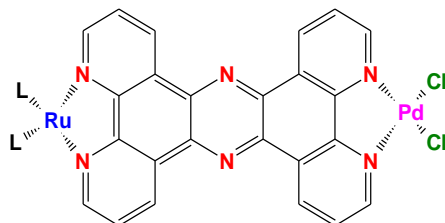

Figure 1. *Structure of [(tbbpy)$_2$Ru(tpphz)PdCl$_2$]$^{2+}$ where L = 4,4'-di-tert-butyl-2,2'-bipyridine and tpphz = tetrapyrido[3,2-a:2',3'c:3'',2'',- h:2''',3'''-j]phenazine.*

The hetero-dinuclear Ru–Pd complex used as photocatalyst consists of the following three components: A photoactive ruthenium (II) fragment acting as a light absorber. [13]. A PdCl$_2$ unit which, when coordinated at the other end of the assembly, acts as a   catalytic centre. A bridging unit connecting the two metal centres through conjugated reducible π-electron system. In the presence of the sacrificial agent triethylamine (TEA) efficient hydrogen formation is observed [10]. The photoinduced electron-transfer processes taking place to allow for the intramolecular hydrogen evolution. By comparing the photophysics of the [(tbbpy)$_2$Ru(tpphz)]$^{2+}$ precursor with that of the supramolecular catalyst RuPd [14] a reaction scheme was proposed as shown in (Figure 2 and Scheme 1).
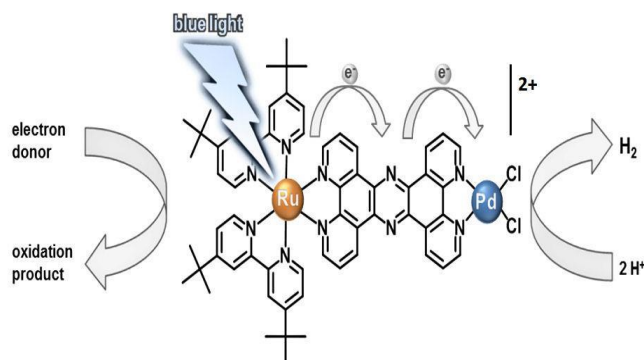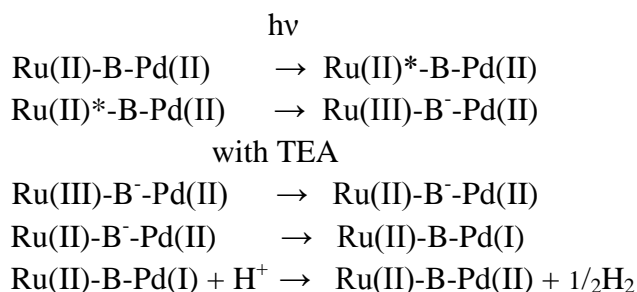
Figure 2. *Schematic presentation of the photoinduced hydrogen generation process [10].*

The individual processes are outlined below in Scheme 1.;

$$h\nu$$
$$Ru(II)\text{-}B\text{-}Pd(II) \quad \rightarrow \quad Ru(II)^*\text{-}B\text{-}Pd(II)$$
$$Ru(II)^*\text{-}B\text{-}Pd(II) \quad \rightarrow \quad Ru(III)\text{-}B^-\text{-}Pd(II)$$
$$\text{with TEA}$$
$$Ru(III)\text{-}B^-\text{-}Pd(II) \quad \rightarrow \quad Ru(II)\text{-}B^-\text{-}Pd(II)$$
$$Ru(II)\text{-}B^-\text{-}Pd(II) \quad \rightarrow \quad Ru(II)\text{-}B\text{-}Pd(I)$$
$$Ru(II)\text{-}B\text{-}Pd(I) + H^+ \rightarrow \quad Ru(II)\text{-}B\text{-}Pd(II) + 1/_2 H_2$$

Scheme 1*. Proposed reaction pathway based on Figure .2. where B =bridging ligand [10].*

Although as outlined above photophysical studies on this Ru/Pd photocatalytic system have been carried out. Nothing is known about the photochemical stability of the photocatalyst. UV/Vis studies have been carried out during the photocatalytic reactions as shown in Figure 3.
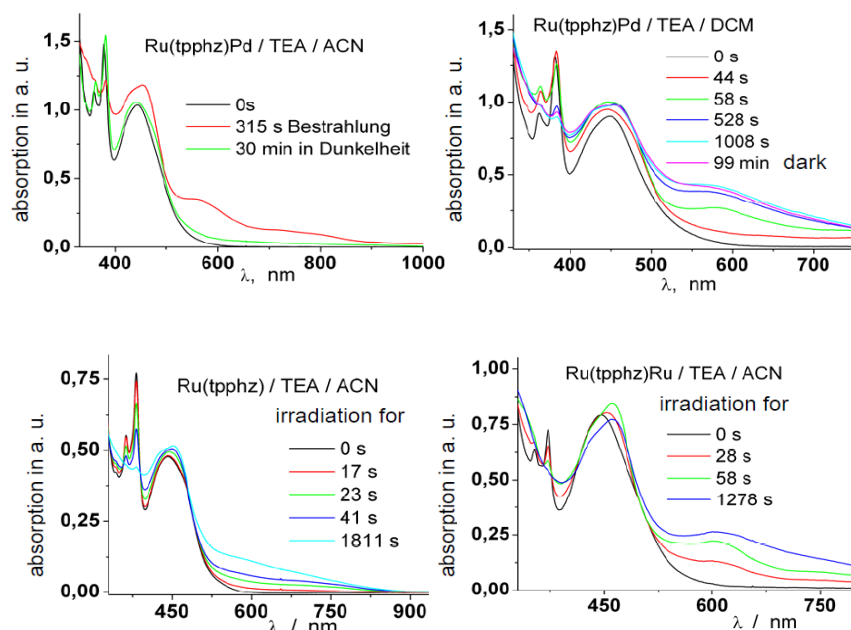

Figure 3. *UV/vis spectra of Ru(tpphz) compound 1, and Ru(tpphz)Pd, compound 2, with visible light (470nm) [11].*

These studies do show the formation of photoinduced intermediates as evidenced by species with absorption maxima at up to 600 nm, involving reduced bridging ligands such as shown in the following structure.
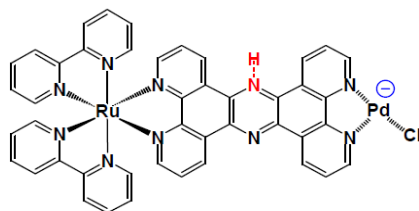

Figure 4. Structure of potential intermediate shows a reduced bridging ligand and a loss of chloride.

No information concerning the photostability of the photocatalyst is available. In this chapter we wish to carry out HPLC studies to investigate the issue of the photostability of the photocatalyst. The photochemical properties of this complex together with a number of analogues compounds **1-2**, (See Figure.5 below) will be investigated initially in acetonitrile, subsequently their stability under photocatalytic conditions, in the presence of TEA and an under argon atmosphere.
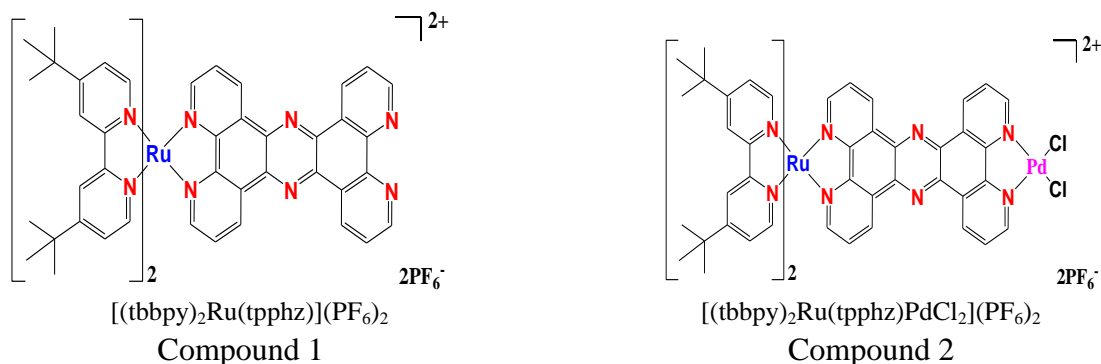

[(tbbpy)$_2$Ru(tpphz)](PF$_6$)$_2$
Compound 1

[(tbbpy)$_2$Ru(tpphz)PdCl$_2$](PF$_6$)$_2$
Compound 2

Figure 5. Chemical structures of the systems investigated in this study: The mononuclear building block compound 1, compound 2.

2. Experimental Section

2.1 Material and Methods

All complexes investigated were synthesized by and received from the group of Prof Sven Rau, Erlangen, Germany. All samples were used as received, with no further purification. All solvents employed were of HPLC grade or better and used as received unless otherwise stated.

2.2 Chromatographic Analysis

For the investigation the following chromatographic conditions were used.

High performance liquid chromatography (HPLC) was carried out on using a Varian Pro Star. All Samples were dissolved in the eluent in CH_3CN and filtered through a 0.45 micron filter prior to injection. The samples- $[(tbbpy)_2Ru(tpphz)](PF_6)_2$ (1) , $[(tbbpy)_2Ru(tpphz) PdCl_2](PF_6)_2$ (2), in CH_3CN , without TEA/ or with TEA, were analysed using a mobile phase of CH_3CN/H_2O 70/30 containing 0.02 M KNO_3 and detection wavelengths of 280 - 430 nm and a flow rate 2.0 cm^3 min^{-1}. The temperature control was set at 24° C.

2.3 Preparation of Samples for Photo-Catalysis.

Preparation of sample solutions was carried out in the absence of ambient light, and solutions were wrapped in aluminium foil and carefully sealed to avoid exposure to light, and evaporation. Samples were always prepared fresh, immediately prior to the measurements. Photolysis experiments carried out in acetonitrile only were carried out in aerated solutions. Samples investigated under photocatalytic conditions containing triethylamine (TEA) were deoxygenated using argon for 30 minutes to copy the conditions used. A ~ $1x10^{-4}$ M solution of the complexes in acetonitrile was used for irradiations both without TEA and with TEA. For the experiments carried out under photocatalytic conditions a TEA concentration of $1x 10^{-4}$ M was used.

2.4 Photochemical Studies

The photochemical experiments were carried out at room temperature in air-equilibrated solution in a 1 cm quartz, Light sources For illumination, we used LED light emitting diodes $\lambda = 470$ nm LAMP type L-7113PBC-BLUE. (sacrificial agent) and took 5 ml sample of above concentration solution for irradiation at 470nm (blue light) (irradiation time).

Figure 6. shows the reactor where the catalytic solutions were irradiated by blue LEDs (470 nm wavelength).

3. Results and Discussion

The same behaviour is observed for both fractions in compounds **1** and **2**. The reason for this temperature dependence was not further investigated but is most likely related to the presence of the

bridging ligand. As a result of this observation all further experiments were carried out at 24°C using a column heater. Due to the large variations in temperature that may occur in the laboratory, temperature effect could not always be avoided completely. A typical set of chromatograms for compounds **1-2** is shown in Figure 7.
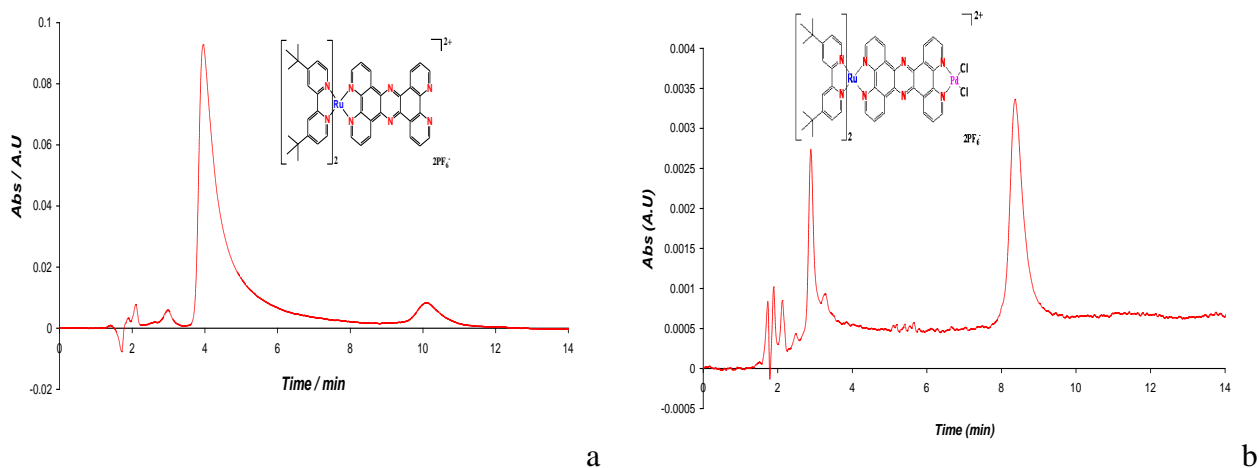

a   b

Figure 7. *HPLC traces of compounds 1(a) - 2(b) in CH₃CN 1*10⁻⁴ M Mobile phase CH₃CN/H₂O 70/30 containing 0.02 M KNO₃ at 430 nm and 24° C flow rate 2.0 cm³ min⁻¹.*

The retention times obtained for these compounds, together with these obtained in the presence of TEA are shown in Table .1. The table shows that the retention times, especially for compound 2 vary in the presence of TEA.

Table .1. *Retention times of compounds **1-2** in acetonitrile and in acetonitrile containing triethylamine.*

Compounds	Retention Time (min)	
	with TEA	without TEA
1	2.68	3.95
2	2.64	2.83

As a result the retention times observed are rather short, especially when compared with these observed for the dinuclear compounds in Chapters 3 and 4. The small variation of retention times, especially in the 1-3 minutes range leads to a considerably amount of overlap and this complicates the identification of the compounds formed as photoproducts. Note that the strong peak observed for compound **1** at about 8 min is assigned as compound 2. The peak for compound **2** is observed at about 3 minutes.

The chromatograms obtained for compounds **1** and **2** show a considerable amount of tailing. For compound 1 this is not unexpected since the free nitrogen atoms are most likely interacting with the stationary phase. Tailing for compound **2** is less and maybe this is related to the loss of chloride at the palladium centre.. A complication for the identification of the species observed in the chromatograms

for compounds **1-2** containing the tpphz ligand, is that these have the same optical absorption properties in the visible part of the spectrum. The formation of photoproducts can therefore be observed by HPLC but their identification by their spectral features is not possible in cases where the tpphz ligands is still bound. The one exception is that for compound 3 the intensity ratio of some of the peaks is slightly different. Part of the spectrum associated with the MLCT band, the broad feature, is more intense that the doublet of sharper peaks at higher energy. For the other tpphz containing compounds this is the other way around.

The chromatographic features observed for the compounds when TEA was added to the irradiated solutions to allow the study of the photochemical behaviour under "catalytic conditions" are shown in Figure 8.
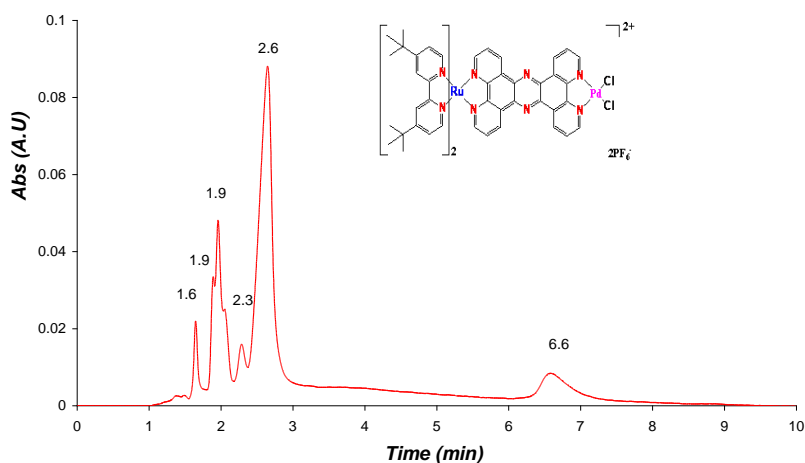

Figure 8. *Chromatograms obtained for compound 2 in CH$_3$CN 1*10^{-4} M Mobile phase CH$_3$CN/H$_2$O 70/30 containing 0.02 M KNO$_3$ at 280 nm and 24° C flow rate 2.0 cm^3 min^{-1}.*

By comparing Figures .8 and.9 and the data presented in Table 6.1 it is clear that the retention times of compounds **1-2** are changed upon the addition of TEA. For compound 4 no major changes are observed in it chromatographic behaviour in the presence of TEA.

3.1 Photolysis of Compounds 1-2 in Acetonitrile.

As outlined in the last section in order to limit the effect of temperature of the chromatography all experiments were carried out at 24°C. The purpose of this chapter is to investigate the stability of compound **2** with respect to light. Since this compound is under investigation as a photocatalyst for the generation of hydrogen its photochemical behaviour needs to be determined. Compounds **1, 2** were investigated as well as model compounds. The first step in this study was the investigation of the photochemical stability of the compounds upon irradiation in acetonitrile. It has been shown before that this solvent can lead to light induced ligand exchange processes [15[a,b]]. The samples were irradiated for up to 2 hours and it was found that both are largely photostable under these conditions. Typical HPLC examples of this are shown in Figures .9 and 6.10 for compounds **1** and **2**. Similar results are obtained for the other two compounds.

These results clearly show that under the conditions used in these experiments the compounds are photostable for up to 2 hours. The photocatalytic experiments used to achieve hydrogen generation with compound **2** include the presence of a high concentration of TEA as a sacrificial agent in this work.
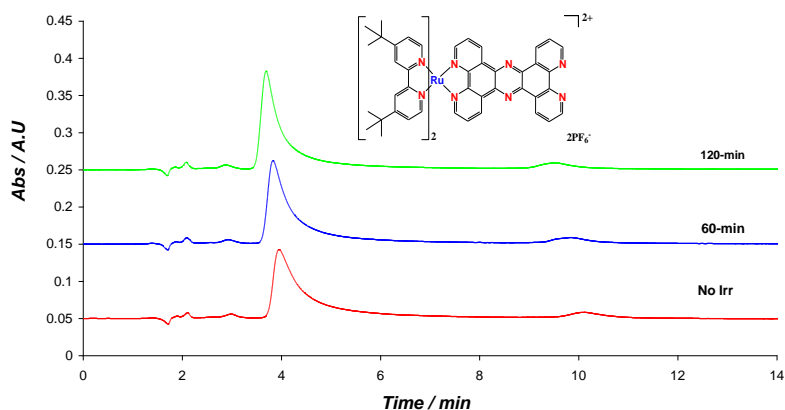

Figure 9. *Irradiation of compound **1**- [(tbbpy)$_2$ Ru (tpphz)](PF$_6$)$_2$ (1x10^{-4} M) in ACN at 24° C Detection wavelength 430 nm, Mobile Phase CH$_3$CN: H$_2$O 70:30 0.02 M KNO$_3$. Flow rate 2.0 cm^3/min.*

3.2 Photolysis of Compounds 1-2 in the Presence of TEA.

In the last section has been shown that in acetonitrile all the compounds are photostable for up to 2 hours under irradiation with visible light. In this section the stability of the compounds towards irradiation under catalytic conditions will be investigated. The major difference between the two irradiation conditions is the presence of triethylamine (TEA) which acts as a sacrificial agent in the photocatalytic process as outlined in the introduction. In addition the samples were also deaerated with argon before irradiation to mirror the conditions used for the photocatalytic process.

A very weak signal at 2.8 min is indicative of the formation of [(tbbpy)$_2$ Ru (tpphz)]$^{2+}$ (compound 1), while the nature of the species formed at 3.3 min could not be identified from its absorption spectrum.

As the next section shows compounds **1** and **2** behave very differently. The HPLC traces observed for compound **1** under the same conditions are shown in Figure 10.
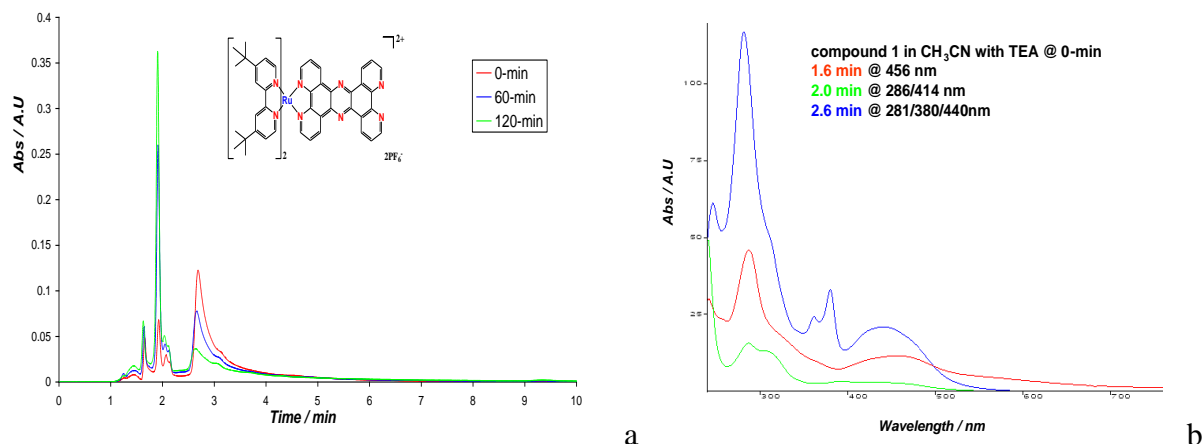
Figure 10. *HPLC traces obtained upon photolysis of compound 1and Absorption features of peaks identified, Temperature 24⁰ C. Irradiated in ACN in presence of TEA (2 M) using 470 nm LED irradiation from (0-120min) degassing with Ar before irradiation detection wavelength; 280 nm, Mobile Phase CH₃CN: H₂O 70:30 containing 0.02 M KNO₃ Flow rate 2.0 cm³ min.*

These spectra indicate the presence of $[Ru(tbbpy)_3]^{2+}$ at 1.6 min and at 2.6 minutes the presence of compound **1**. The composite peak at about 2.0 min indicates the presence of both free ligand and the $[(tbbpy)_2 Ru(CH_3CN)_2]^{2+}$ complex. The presence of the latter two species suggests that some light induced ligand exchange may have taken place already during the sample preparation. The HPLC traces in the figure above show a continuing decrease of the peak at 2.6 minutes, compound **1**, and an increase of the composite peak at about 2.0 minutes, which can, on the basis of the absorption spectra obtained, be assigned to a combination of the bridging ligand tpphz and the bis(CH₃CN) complex. The absorption spectra obtained from the hlpc experiments indicate that a species is formed with a retention time of about 2 minutes that has an absorption maximum at 280 nm. This indicates the formation of an organic species and this is therefore expected to be a ligand. Based on the spectral data observed it is not possible to determine whether this ligand is tpphz or tbbpy.

it is most likely that the tpphz ligand is lost. This photoinduced ligand exchange is clearly more efficient that observed for compounds 3 and 4 and can, on the basis of the absorption spectra obtained for the various species formed, be explained by the following reaction;

$$[(tbbpy)_2 Ru (tpphz)]^{2+} \quad \xrightarrow{h\nu} \quad [(tbbpy)_2 Ru(CH_3CN)_2]^{2+} + tpphz$$

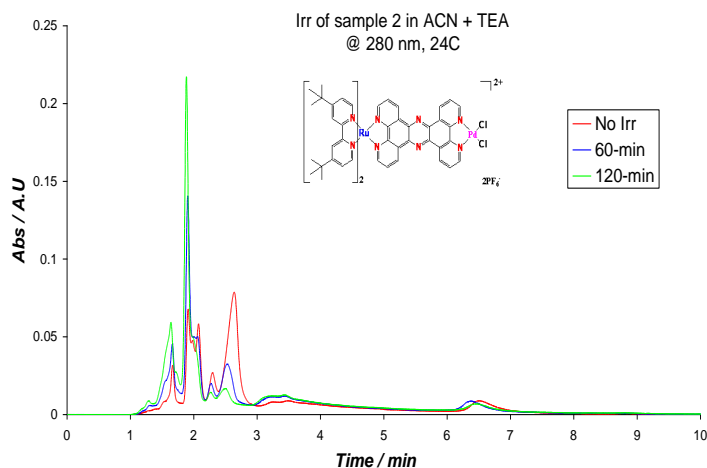The HPLC results obtained during the photolysis of compound 2 are shown in Figure 11 below:

Figure 11. *HPLC traces obtained upon photolysis of compound 2. Temperature 24° C. Irradiated in ACN in presence of TEA (2 M) using 470 nm LED irradiation from (0-120min) degassing with Ar before irradiation detection wavelength at 280 nm, Mobile Phase CH_3CN: H_2O 70:30 containing 0.02 M KNO_3 Flow rate 2.0 cm³ min.*

The HPLC results obtain for compound **2** look considerable more complicated than those obtained for the other three compounds. They do resemble those of compound **1** the most. The chromatogram obtained before any irradiation has taken place together with the absorption spectra obtained for the main species is shown below in Figure 12. A strong signal and 1.9min has been observed in all chromatograms and is organic in nature. What is most obvious is that the absorption spectra associated with tpphz complexes can be found over a wide range, the double absorptions at around 370 nm are found from 1.9 to 3.5 minutes. Apart from that one feature the traces obtained for compound **2** look similar to those shown for compound **1** earlier. It is clear that there is a strong overlap between different species. For example it proved not to be possible to improve the chromatographic conditions so that the retention time of compounds **1** and **2** would be different. This is not totally unexpected since the size and the charge of both compounds are the same. This will make the possible formation of compound **1** upon irradiation of **2** difficult to detect.
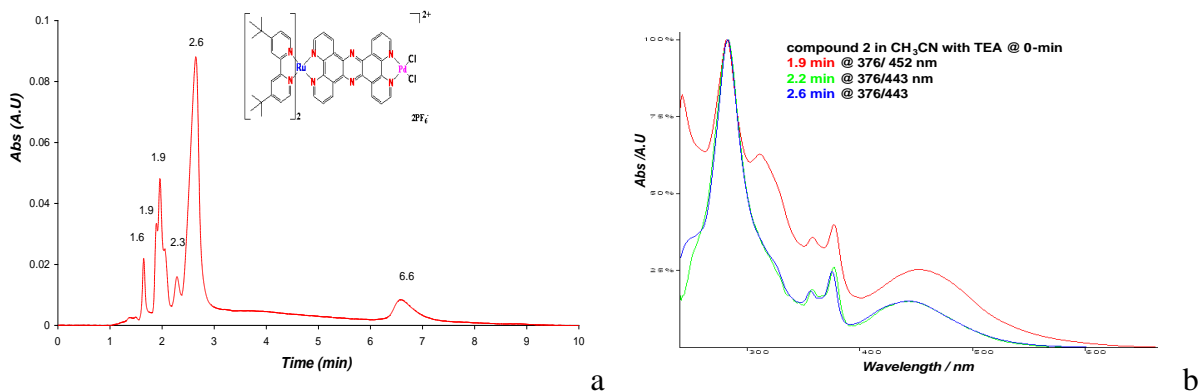
Figure 12. *Chromatogram (a) and absorption spectra (b) of most important peaks of compound **2** before photolysis.*

Both compound **1** and **2** show quite a bit of tailing and this may suggest that their chromatographic behaviour might be the presence of a free binding site on compound **1** and the possible liability of the chlorides of the palladium centre   Another important point is that since the compound contains a $PdCl_2$ group, chloride ions are available in earlier studies have shown that these will speed up photochemically induced ligand exchange processes [16[a,b]17]. A set of absorption spectra and the appropriate chromatogram obtained after photolysis for 120 min is shown below in Figure 13.
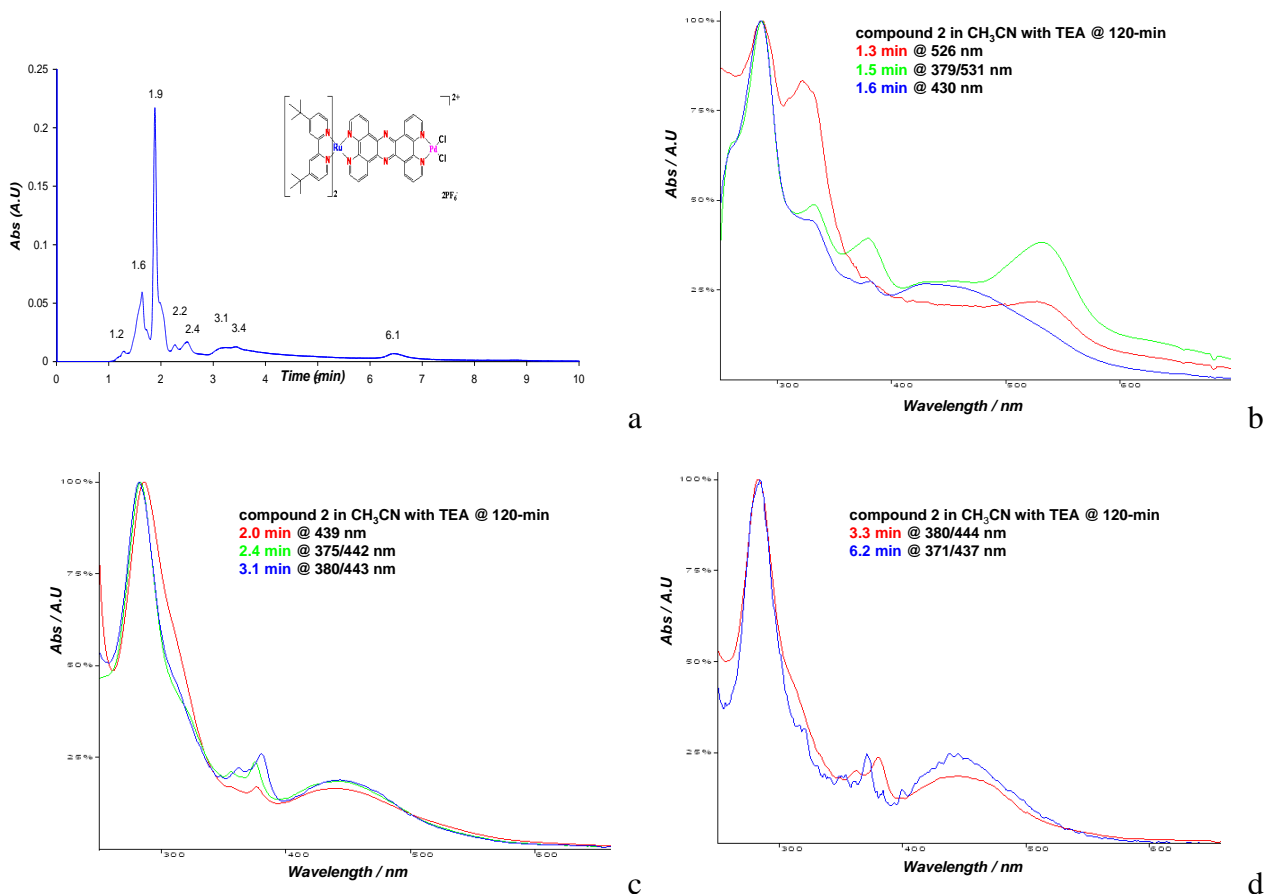

a

b

c

d

Figure 13. *Chromatogram (a) and absorption spectra (b,c,d) obtained for compound **2** after 120 min of irradiation.*

The chromatogram shows that after 2 hours of irradiation very little of compound 2 can be found in the reaction mixture. The main peaks observed are at 1.8 min, the so called organic peak, at 1.6 min, this is compound 4 present as an impurity from the synthetic process an unchanged peak at 6.4 min and a very broad signal covering the retention time range from 1.9 to 5 min. The absorption spectra obtained for peaks below 2 min retention time indicate a strong overlap between the different species and are therefore not that informative. The presence of absorption peaks at about 520 nm (retention time 1.3 min) indicates the presence of $[Ru(tbbpy)_2Cl_2]$ as outlined before.

Other species cannot be determined with certainly, but the presence of free tpphz bridging ligand and $[Ru(tbbpy)_2(CH_3CN)_2]^{2+}$ (retention times of 1.8 and 2.2 respectively) are likely to be present. The next section of the chromatogram, from 2 min to 6 min shows a number of species that all show the typical tpphz spectra features. A feature of these spectra is that they are not sensitive to the coordination pattern of the molecule. They can therefore not be used to identify the species present. As pointed out above also for compound **1** tailing of the peak is observed, but the signals at 3 min are not observed for any of the other compounds. In addition the peaks between 2 and 2.5 min also show tpphz features any may be related to the formation of compound **1**.

From the strong tailing of the peaks in the 2-5 min region it is difficult to determine the amount of material present and the absorption data present do not allow for a detailed analysis of the species formed. It is important however that in the photocatalytic process concerned with the generation of hydrogen, no hydrogen is formed in the first hour or so and that hydrogen formation continues for up to 24 hours. The chromatographic data suggest that up on photolysis a new species is formed and that therefore the original compound **2** is unlikely to be the photocatalyst, but may be acting as a precatalyst. It has been suggested [10,17] that compound **2** needs to lose a chloride ligand before it can act as a catalyst for hydrogen reduction. This lability of the chloride, already confirmed by the formation of $[Ru(tbbpy)_2Cl_2]$,   as   outlined   above   would   lead   to   the   formation   of   species   like $[(tbbpy)_2Ru(tpphz)PdClS]^{3+}$ and $[(tbbpy)_2Ru(tpphz)PdS_2]^{4+}$, where S is a solvent that could be water or acetonitrile. Quite a number of compounds could therefore be formed upon release of the chloride ions [18]. All would have a higher charge and would therefore be retained on the column for longer times as observed. The important observations of these studies is therefore that the data suggest that compound 2 is a pre catalyst and that during the photocatalytic process new, so far not identified tpph species are formed which could carry out the photocatalytic process [19].

4. Conclusion

In this work the photostability of the photocatalyst compound 1 and the model compounds 2 have been investigated both in acetonitrile and in acetonitrile containing triethylamine.   In acetonitrile all compounds are photostable for upto 2 hours. However, upon irradiation under "catalytic conditions", that is in the presence of TEA, both compounds **1** and **2** show photo induced rearrangements. The photolysis of the photocatalyst, compound **2**, shows that after the two hour irradiation the compound is transformed in a range of compounds. The nature of these cannot be established, apart from the fact that like for compound **1** the bis(acetonitrile) compound is observed as a product.

The most interesting observation is however that other tpphz complexes are formed. These cannot include compound **1** since this compounds decomposes to the acetonitrile complex and free bridging

ligand. The identification of the new products, which have retention times of between 2-5 minutes can at this stage, not be established mainly because of the fact that all tpphz complexes show absorption spectra which are indistinguishable. The fact that the photo produced species are observed at longer retention times suggests that they have a more positive charge. It is therefore postulated that the species which is assumed to be the active catalyst is formed. DFT calculations indicate that chloride loss from the Pd centre has to occur before hydrogen generation can take place. In addition the hydrogen formation has incubation time of about 2 hours. This would therefore agree quite well with the results obtained in this study. Nevertheless is seems likely from the HPLC experiments that such species are formed further research needs however to be carried out to establish this more fully.

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