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Palladium versus Platinum: The Metal in the Catalytic Center of a Molecular Photocatalyst Determines the Mechanism of the Hydrogen Production with Visible Light**

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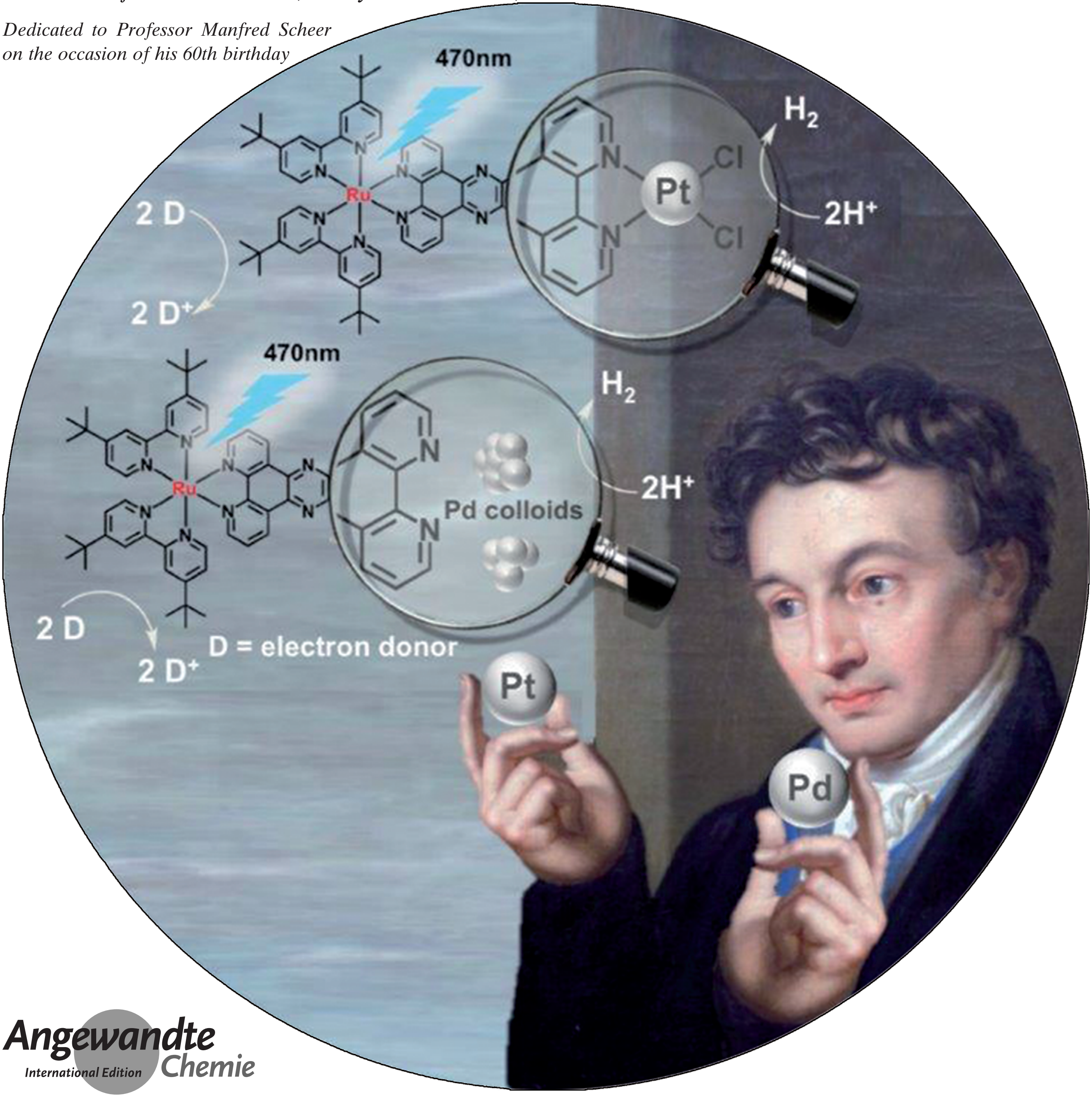
Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday



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Abstract: *To develop highly efficient molecular photocatalysts for visible light-driven hydrogen production, a thorough understanding of the photophysical and chemical processes in the photocatalyst is of vital importance. In this context, in situ X-ray absorption spectroscopic (XAS) investigations show that the nature of the catalytically active metal center in a* $(N^{\wedge}N)MCl_2$ *(*$M = Pd$ *or Pt) coordination sphere has a significant impact on the mechanism of the hydrogen formation. Pd as the catalytic center showed a substantially altered chemical environment and a formation of metal colloids during catalysis, whereas no changes of the coordination sphere were observed for Pt as catalytic center. The high stability of the Pt center was confirmed by chloride addition and mercury poisoning experiments. Thus, for Pt a fundamentally different catalytic mechanism without the involvement of colloids is confirmed.*

Photocatalytic splitting of water has received tremendous attention owing to its potential in solving the looming energy crisis. However, until now, for the majority of such systems very little is known about the interplay between light absorption, electron transfer, and catalytic turnover. Especially intramolecular photocatalysts consisting of a photocenter, a bridging ligand, and a catalytic center offer the opportunity to investigate this interplay with a large variety of spectroscopic techniques. For instance, by resonance Raman, steady-state (UV/Vis), and time-resolved spectroscopy (TRS) a detailed insight into the primary light absorption and the intramolecular charge-transfer processes towards the catalytic center is facilitated.[1–4] Theoretical methods (DFT and TDDFT) give additional information on the initial electron-transfer processes and support the elucidation of subsequent reactions at the catalytic center.[1,5] However, although the above mentioned methods give a the large amount of information about the photochemical properties of the precatalyst, little information is obtained for the catalytically active state. For a better comprehension of such photocatalysts, the structure of the catalytic center in its active state is of crucial importance. In this context, X-ray absorption spectroscopy (XAS) can deliver valuable data, which significantly improve the correlation between the results obtained from the photophysical investigations and the catalytic reaction processes.[6,7] Recently, it was shown that the dinuclear Ru–Pd complex, $[(tbbpy)_2Ru(tpphz)Pd(Cl)_2]^{2+}$ (tbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridin, tpphz = tetrapyrido[3,2-*a*:2′3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine) (**RuPd**) is capable of forming hydrogen under irradiation with visible light in the presence of an electron donor. In addition, photocatalytic hydrogenation of an alkyne could also be observed with exclusive selectivity for the *cis* product. This result in conjunction with other techniques supported the view of a relatively stable molecular catalytic center.[1] Hammerström and co-workers could show for a different Ru–Pd complex that photocatalytic hydrogen generation is accompanied by the destruction of the complex and formation of colloidal particles which might be functioning as catalytic centers.[8] Sakai and co-workers have shown that related ruthenium–platinum complexes are active photocatalysts for hydrogen formation. They presented evidence that the platinum center in these complexes does not decompose leading to colloid formation.[9–11] As the stability of an intramolecular photocatalyst is of paramount importance for the overall catalytic activity and the validity of conclusions drawn from spectroscopic investigations we decided to investigate the $[(tbbpy)_2Ru(tpphz)Pt(Cl)_2]^{2+}$ (**RuPt**) complex (Figure 1) under catalytic conditions. We present herein preliminary structural characterizations based on NMR spectroscopy and mass spectrometry (MS) data together with photophysical investigations. In addition we performed in situ X-ray absorption (XAS) measurements and mercury-poisoning experiments designed to eliminate colloids from catalytic mixtures. Based on the comparison with **RuPd** it appears that **RuPt** is a stable catalyst and no colloids are formed. Furthermore, such systematic comparison of two photocata-

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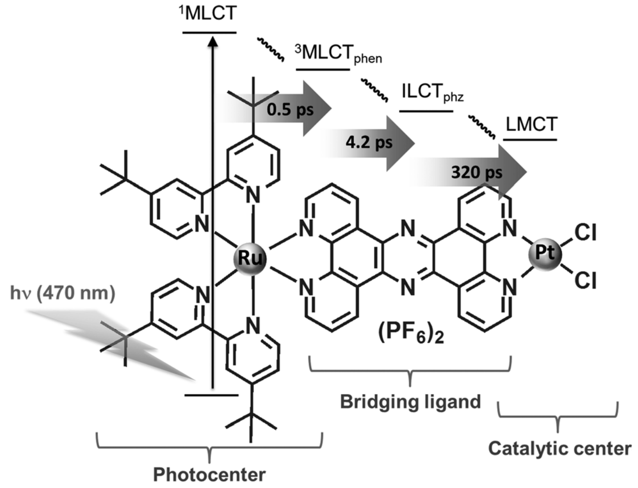

Figure 1. Structure and light-induced dynamics of **RuPt** based on the initial excitation of the Ru photocenter in acetonitrile (assignment of excited states is based on literature data:[3] MLCT = metal-to-ligand charge transfer, ILCT = intra-ligand charge transfer, LMCT = ligand-to-metal charge transfer).

lysts bearing identical ligand fragments and differing only in the nature of the catalytically active metal center allows the influence of the catalytically active metal on the nature of the catalytically active species to be studied without bias from different organic metal-binding motifs.

RuPt can be synthesized from the mononuclear ruthenium precursor and [Pt(DMSO)$_2$Cl$_2$]. The structural characterization by NMR spectroscopy and MS suggest that the platinum center is coordinated in a square-planar fashion with two chloro ligands in analogy to the previously characterized **RuPd**.[12]

The UV/Vis spectroscopic properties of both systems are very similar (Figure 2). The absorption spectrum of **RuPt** reveals the characteristic broad Ru^{2+}-centered metal-to-ligand charge-transfer (MLCT) absorption in the visible part of the spectrum ($\lambda_{max} = 448$ nm). Theoretical calculations show that this band is obtained from a superposition of six MLCT states having identical orbital characters in both **RuPd** and **RuPt** (**RuPt**: S$_2$, S$_9$, S$_{11}$, S$_{12}$, S$_{15}$, S$_{16}$, see Figure S6 and S7, table S5 and S6 in the Supporting Information).[12] Therefore, similar initial photoexcitation is expected in both compounds. The range between 350 and 400 nm is different for **RuPd** where a structure of the n–π* and π–π* transitions between 350 and 400 nm is present. This structure is absent for **RuPt**. The calculations reveal that the main band of **RuPd** in this region is an n–π* excitation (state S$_{28}$), which has a greatly decreased intensity and is bathochromically shifted to 407 nm.[12]

To decipher the photoinduced charge-transfer dynamics in **RuPt**, ultrafast time-resolved transient absorption experiments were carried out (Figure S1).[12] The results indicate that absorption of light within the MLCT band of **RuPt** is followed by a multi-step excited-state relaxation, which—in analogy to work on **RuPd**[3,13] and **RuOs**[14]—is assigned to a step-wise electron- or energy-transfer from the Ru center to the secondary metal center: When dissolved in acetonitrile to mimic the rather polar environment used in the catalysis experiments, formation of the ³MLCT-state centered on the phenanthroline (phen) part of the tpphz ligand in less than one ps is followed by intra-ligand charge-transfer (4.2 ps) from the phenanthroline part of the tpphz to its phenazine (phz) moiety. Finally, a slower process is observed (320 ps), which is assigned to the depopulation of the phenazine-centered Ru-based MLCT state and a transfer onto the (bipyridine)dichloroplatinum sphere takes place (Figure 1). These photoinduced dynamics of **RuPt** follow closely the ones observed for **RuPd**[12] and show that changing the second metal center has no significant influence on the intramolecular photophysical processes in the subnanosecond region.

To investigate the effect of the change of the catalytically active metal center on the catalytic activity of the photocatalyst, a solution of **RuPt** containing acetonitrile, water, and triethylamine was irradiated with visible light (470 nm) under conditions identical to those used for **RuPd**.[1] This resulted in the generation of molecular hydrogen over the course of 10 h (see Figure 3). The constant turnover frequencies (TOF; TOF = TON/t) of 0.7 reached a total turnover number (TON; $n(H_2)/n$(catalyst)) of 7. This value is significantly lower than

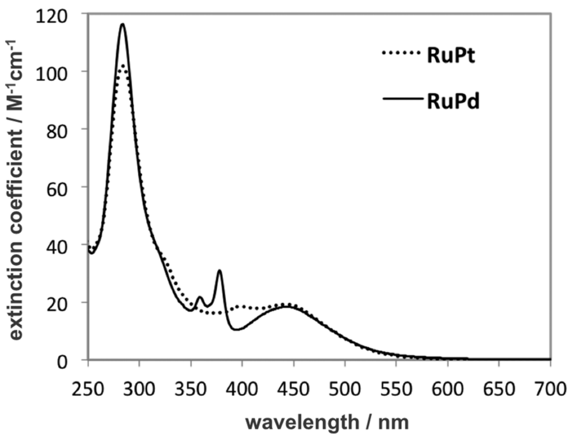

Figure 2. Steady-state absorption spectra of **RuPd** (black line) and **RuPt** (dotted line) dissolved in acetonitrile.

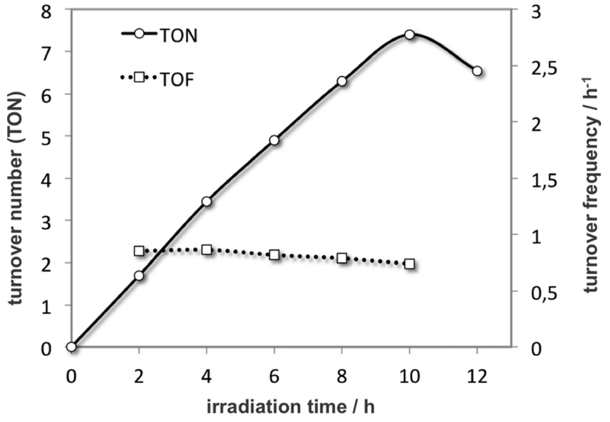

Figure 3. Catalytic activity of **RuPt** ($c = 70$ μM) in a mixture of acetonitrile, water, and triethylamine under irradiation with visible light (470 nm).

the activity observed for the palladium complex[15] (TON = 238) but compares well with other intramolecular Ru–Pt photocatalysts.[11] Most importantly, the lack of an induction phase and the constant TOF suggests a different mechanism for **RuPt** than for **RuPd**, which shows an induction period of 2 h and a TOF that fluctuates significantly (2.4 h^{-1} to 15 h^{-1}).

As we recently reported, for **RuPd** the dissociation of a chloride ligand at the Pd center is assumed, owing to the electron transfer from the Ru photocenter to the catalytic center.[1] Accordingly, the addition of TBACl ($N(C_4H_9)_4Cl$) in 2000-fold excess led to a complete deactivation of the photocatalyst. In contrast, **RuPt** shows no significant change of the catalytic activity on addition of TBACl under identical conditions (Table S2),[12] indicating a stable Pt−Cl bond during catalysis.

To obtain insight into the reactions occurring at the catalytic centers upon illumination of the pre-catalyst within the MLCT band (470 nm), simultaneous X-ray absorption near-edge structure (XANES) measurements for the samples were performed under photocatalytic conditions. Figure 4A shows the Pd K-edge XANES spectra of **RuPd** in a standard catalytic mixture[1,12] after different irradiation times in comparison with Pd metal and [(bpy)$PdCl_2$] as references. Before irradiation the spectrum of **RuPd** is similar to that of [(bpy)$PdCl_2$] with only some increase of the first peak intensity indicating their structural similarity. After 5 min of irradiation (470 nm) no significant changes are observed, however, after 35 min the spectrum of the catalyst is similar to that of Pd metal which indicates the formation of Pd centers in a metal-like environment under catalytic conditions. The percentage of atoms with a metal-type environment increases as a function of time (see Table S1), indicating a continuous increase in the number of palladium centers in metal-like state upon prolonged irradiation. This observation may be an explanation for the highly variable TOF for **RuPd** during the first few hours of catalysis.[1,8]

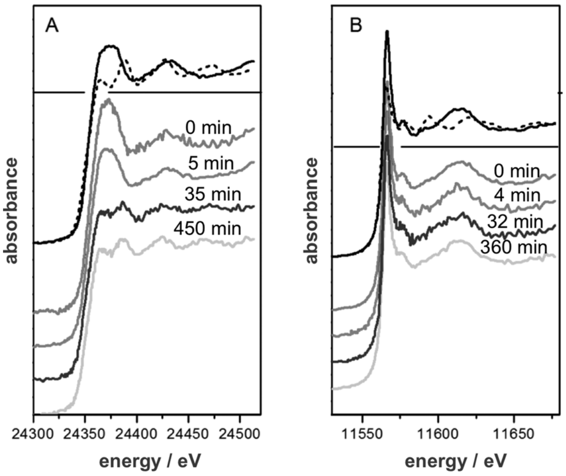

Figure 4. XAS spectra of A) **RuPd** and B) **RuPt** as a function of the irradiation time under catalytic conditions (below the vertical lines).The spectra of reference compounds are shown above the vertical lines. A) spectra of the reference compound [(bpy)$PdCl_2$] (solid line) and a Pd metal foil (dashed line). The spectra of **RuPd** under catalytic conditions are shown after 0 min, 5 min, 35 min, and 450 min irradiation. B) the X-ray absorption spectra of [(bpy)$PtCl_2$] (solid line) and a Pt metal foil (dashed line) are shown together with spectra of **RuPt** under catalytic conditions after 0 min, 4 min, 32 min, and 360 min irradiation.

The different behavior of **RuPt** under catalytic conditions is also apparent in the X-ray absorption spectra (Figure 4B). The Pt L_3 XANES spectra of **RuPt** show no changes during catalysis. Even after 6 h of irradiation under catalytic conditions the structure of the XANES spectrum is identical to the structure of the [(bpy)$PtCl_2$] reference compound. In contrast, the XANES data show the **RuPd** catalyst undergoes a transformation within the first 35 min giving rise to metal-like palladium centers, whereas **RuPt** demonstrates a high stability during catalysis, while maintaining the N-N-Cl-Cl binding motif.

To elucidate the role of metal-like palladium centers played during catalysis, the mercury-drop method was applied.[16,17] To first verify the applicability of the mercury test, both photocatalysts were dissolved in acetonitrile and stirred for 9 h in the presence of elemental mercury and under the exclusion of light. The comparison of the ^{1}H NMR spectra of **RuPd** before and after the treatment with mercury reveals an extraction of the $PdCl_2$ catalytic center and the formation of the mononuclear Ru complex (Figure S4).[12,18,19] A similar effect was recently observed for a structurally related Ru–Pd complex.[20] Under identical conditions **RuPt** showed no reaction with mercury in acetonitrile. Subsequently, the activity of the photocatalysts in the light-driven hydrogen production under addition of elemental mercury was investigated. Therefore, the catalytic solution was mixed with a 100-fold molar excess of mercury and irradiated for 9 h. Addition of elemental mercury to a catalytic mixture of **RuPd** leads to a complete loss of catalytic activity.[12] However, owing to the direct reaction of mercury with **RuPd**, the contribution of colloidal Pd to the hydrogen formation cannot be evaluated. In contrast to **RuPd**, the catalytic activity of **RuPt** was maintained even in the presence of elemental mercury (Figure S3).[12] Hence a decomposition of **RuPt** and formation of colloidal platinum within the catalytic mechanism can be excluded. This result also ties in very well with the results of the XANES measurements and the TBACl addition experiments, where no change in the ligand environment of the platinum center under catalytic conditions was observed. The combination of the results obtained from three independent methods, supports the concept of a stable **RuPt** photocatalyst.

The results presented show that the exchange of the catalytically active metal center in these photocatalysts leads to drastically different catalytic reactions, but the photophysical processes of the compounds in pure solvents remain largely unaltered. Ultrafast spectroscopic investigations show that the light-induced electron-transfer processes in this new photocatalyst are comparable with those of the established **RuPd**. Based on the identification of metallic palladium species in the XANES experiments it appears that colloids are formed from **RuPd** under catalytic conditions. Considering the reported kinetics of the hydrogen production with **RuPd** (induction period, unstable and fluctuating TOF),[1] an involvement of colloidal Pd in the catalytic mechanism has to be assumed. Future investigations (cryo-TEM, dynamic light scattering (DLS), or emission quenching) on pre-synthesized Pd colloids in the presence of Ru chromophores are planned to gain more information about the actual role of the Pd colloids formed. Analogous hydrogen-production experiments with **RuPt** show an instant hydrogen formation and a constant TOF over several hours of catalysis. Moreover, XANES measurements and the addition of TBACl and elemental mercury confirm a high stability of **RuPt** under catalytic conditions. The significantly reduced activity of **RuPt**, relative to **RuPd**, is due to the different catalytic mechanisms, which in contrast to that of **RuPd** clearly is not based on ligand dissociation and concomitant metal reduction. For the platinum-containing catalysts a significant improvement of the catalytic activity through an optimized ligand structure around the catalytic center is needed. Based on the fact that the coordination environment of the platinum center in **RuPt** remains unchanged during catalysis as indicated by the XAS measurements, catalytic activity may be tuned by exchanging the chloride ligands with other ligands without interfering with the photochemical steps involved.

Keywords: hydrogen production · palladium · photocatalysis · platinum · X-ray adsorption spectroscopy

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