

## Photoinduced Electron-Transfer Reactions of Platinum(II) Terpyridyl Acetylide Complexes: Reductive Quenching in a Hydrogen-Generating System

Rupesh Narayana-Prabhu and Russell H. Schmehl\*

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

Received November 28, 2005

The one-electron reduction of [(mpt)Pt(CCPHCl)]ClO<sub>4</sub> [mpt = 4'-(4-methylphenyl)-2,2',6',2''-terpyridyl; CCPHCl = chlorophenyl acetylide] by a series of amine donors was investigated in a CH<sub>3</sub>CN solution. The excited state has a lifetime of 550 ns in the absence of quencher in degassed CH<sub>3</sub>CN. Quenching rate constants were >10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup> even for trialkylamines. Transient absorption spectroscopy provided convincing evidence for the production of the one-electron-reduced Pt complex, even with quenchers that could potentially serve as H-atom donors. The transient spectrum obtained in the presence of triethylamine exhibits, in addition to bleaching of the Pt<sup>II</sup> complex absorption, a maximum at ~360 nm and broad absorption from 500 to 800 nm, indicating that the reduced complex has a complex electronic structure and is not easily assigned as a terpyridyl anion radical.

employed in true catalytic water cleavage systems, depending on the nature of the photoreaction and subsequent thermal reactions, leading to H<sub>2</sub> production. If the excited-state reaction involves H abstraction from the substrate (in this case, dihydropyridine), the Pt<sup>II</sup> complexes may be relatively limited in their utility because only H-atom donors could serve as quenchers. Alternatively, if the excited-state reaction is an electron transfer or proton-coupled electron transfer, these Pt<sup>II</sup> complex photocatalysts could then be used with donors that exhibit reversible one-electron transfer. In this work, we report an investigation of the mechanistic aspects of the photoreaction of a platinum(II) terpyridyl acetylide complex with a variety of reductive quenchers; the work clearly illustrates that one-electron reduction of the excited-state complexes occurs upon photolysis, even with donors that could also serve as H-atom donors.

In a fascinating publication in 2004, Tung and Wu described the use of platinum(II) terpyridyl acetylide complexes to photocatalytically produce H<sub>2</sub> in the presence of various dihydropyridine sacrificial donors.<sup>10</sup> The work was interesting because the Pt<sup>II</sup> complexes represented homogeneous monometallic photocatalysts for H<sub>2</sub> production under reducing conditions. Such systems could potentially be

The chromophore [(mpt)Pt<sup>II</sup>(CCPhCl)]ClO<sub>4</sub> [mpt = 4'-(4-methylphenyl)-2,2',6',2''-terpyridyl; CCPHCl = 2-(*p*-chlorophenyl)acetylide] was prepared according to literature methods.<sup>2,9</sup> The reductive quenchers diethyl-1,4-dihydro-2,6-dimethyl-3,5-pyridinecarboxylate (DHP), triphenylamine (TPA), and diphenylamine (DPA) were obtained from Aldrich and used as received. Triethylamine (TEA; Aldrich) and diisopropylamine (DiPA) were distilled from KOH prior to use. *N,N,N',N'*-Tetramethylphenylenediamine (TMPD; Aldrich) was purified by sublimation. *N*-Methylphenothiazine (MPTH; Aldrich) and *N,N,N',N'*-tetramethylbenzidine (TMB; Aldrich) were used as received.

The acetylide complex ([Pt<sup>II</sup>(CCPhCl)]ClO<sub>4</sub>) is weakly luminescent in a CH<sub>3</sub>CN solution at room temperature with a maximum of 625 nm, and the lifetime in N<sub>2</sub>-degassed CH<sub>3</sub>CN is 550 ns. The luminescence is quenched in the presence of all of the amines studied, and Stern–Volmer quenching rate constants measured by intensity quenching are given in Table 1. An estimate of the excited-state reduction potential was obtained using an approach analogous to that of Meyer and co-workers (with alkoxyaryl quenchers).<sup>1</sup> The [Pt]<sup>+\*/</sup>[Pt]<sup>0</sup> potential was found to be 1.4 ± 0.1 V vs saturated

- \* To whom correspondence should be addressed. E-mail: russ@tulane.edu.
- (1) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815.
  - (2) Buechner, R. F.; Haines, R. J.; Cunningham, C. T.; McMillin, D. R. *Inorg. Chem.* **1997**, *36*, 3952.
  - (3) Shimada, E.; Nagano, M.; Iwahashi, M.; Mori, Y.; Sakaguchi, Y.; Hayashi, H. *J. Phys. Chem. A* **2001**, *105*, 2997.
  - (4) Guo, F.; Sun, W.; Liu, Y.; Schanze, K. *Inorg. Chem.* **2005**, *44*, 4055.
  - (5) Jonsson, M.; Wayner, D. D. M.; Luszyk, J. *J. Phys. Chem.* **1996**, *100*, 17539.
  - (6) Cortes, M.; Oppenheimer, J. D.; Downey, K. E.; Cummings, S. D. *Inorg. Chim. Acta* **2002**, *333*, 148.
  - (7) Guo, Q. X.; Bo, L.; Yao, S. D.; Liu, Y. C. *J. Photochem. Photobiol., A: Chemistry* **1996**, *93*, 27.
  - (8) Sun, W. W.; Yang, Q. Z.; Wu, L. Z.; Tung, C.-H. *Appl. Phys. Lett.* **2003**, *82*, 850.
  - (9) Yang, Q.-Z.; Wu, L.-Z.; Wu, X.-X.; Zhang, L.-P.; Tung, C.-H. *Inorg. Chem.* **2003**, *41*, 5653.
  - (10) Zhang, D.; Wu, L.-Z.; Zhou, L.; Han, X.; Yang, Q.-Z.; Zhang, L.-P.; Tung, C.-H. *J. Am. Chem. Soc.* **2004**, *126*, 3440.

## COMMUNICATION

**Table 1.** Rate Constants for Quenching  $[(\text{mpt})\text{Pt}^{\text{II}}(\text{CCPhCl})]\text{ClO}_4$  Emission with Amine Donors in  $\text{CH}_3\text{CN}$  from Intensity Quenching

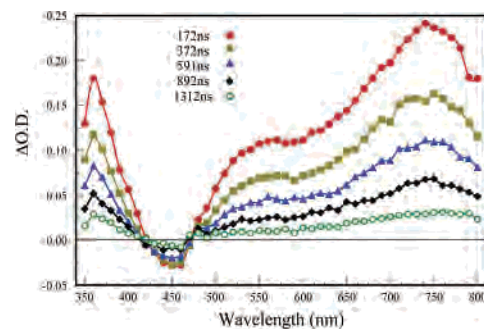
quencher	$E^\circ(\text{Q}^+/\text{Q})$ , V vs SCE <sup>5,6,8</sup>	$k_q$ , $\times 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$
TMB	0.43	20
TMPD	0.12	26
MPTH	0.79	30
TPA	1.06	16
DPA	1.24	19
TEA	1.15	7
DiPA		4
DHP		43

calomel electrode (SCE). Thus, the emissive excited state of this platinum(II) terpyridyl acetylide derivative is a strong oxidant.

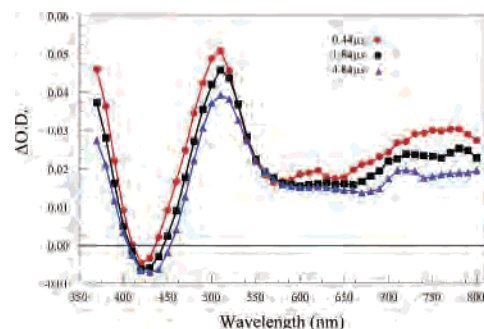
The photoproducts of the quenching reaction and back electron transfer were examined using nanosecond transient absorption spectroscopy. Figure 1 shows the transient absorption spectrum obtained following pulsed laser excitation into the metal-to-ligand charge-transfer absorption of  $[(\text{mpt})\text{Pt}^{\text{II}}(\text{CCPhCl})]\text{ClO}_4$  in  $\text{CH}_3\text{CN}$ . The spectrum exhibits bleaching at 450 nm and strong absorption in the blue ( $\lambda_{\text{max}} = 360 \text{ nm}$ ) and red ( $\lambda_{\text{max}} = 750 \text{ nm}$ ) and decays with a lifetime of 550 ns, matching that of the luminescence. The decays are monoexponential at all wavelengths examined. The spectrum is similar to that obtained by others for closely related complexes.<sup>4,8</sup>

Upon addition of the reversible one-electron reductant MPTH at concentrations high enough to quench nearly all of the luminescence, a transient species is generated that has the spectrum shown in Figure 2. The spectrum has a maximum near 500 nm, close to that reported for the MPTH cation radical (520 nm).<sup>3,7</sup> The transient decays over a period of several hundred microseconds and can be fit assuming equal-concentration second-order kinetics; if it is assumed that the 500-nm absorbance results from the MPTH cation radical alone, the rate constant for back electron transfer is estimated to be  $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , close to the diffusion limit. The transient spectrum also exhibits absorption features in the blue (<400 nm) and throughout the red; these features may be attributed to the one-electron-reduced Pt complex (vide infra). It should also be noted that solutions of the Pt complex and MPTH exhibit no permanent change upon prolonged photolysis, suggesting the reduced Pt complex is stable for at least hundreds of microseconds. This is expected because reductive cyclic voltammograms of the Pt complex, obtained at sweep rates of 100 mV/s, are reversible.

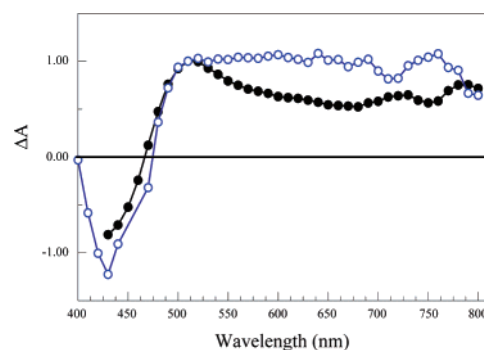
The transient spectrum of a solution of the Pt complex and TEA following pulsed laser excitation is shown in Figure 3B. TEA is an irreversible electron donor that undergoes deprotonation following one-electron oxidation to yield a strongly reducing radical.<sup>9</sup> As a result, electron transfer from TEA to the photoexcited Pt complex is expected to result in the formation of 2 mol of reduced complex. The ultimate decomposition product of the TEA is the *N,N*-diethylethyliminium ion, which does not absorb visible light. Thus, the transient spectrum obtained should represent the difference between the spectrum of the one-electron-reduced Pt complex and the starting Pt complex. The figure shows bleaching at wavelengths near the ground-state absorption



**Figure 1.** Transient absorption spectra of  $[(\text{mpt})\text{Pt}^{\text{II}}(\text{CCPhCl})]\text{ClO}_4$  in room-temperature  $\text{CH}_3\text{CN}$  obtained following 455-nm excitation.



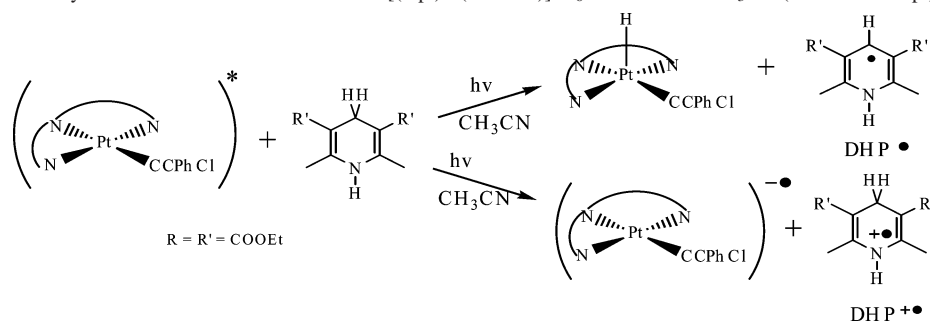
**Figure 2.** Transient absorption spectra of  $[(\text{mpt})\text{Pt}^{\text{II}}(\text{CCPhCl})]\text{ClO}_4$  in the presence of 7.7 mM MPTH in  $\text{CH}_3\text{CN}$ .  $\lambda_{\text{ex}} = 455 \text{ nm}$ .



**Figure 3.** Normalized transient absorption spectra of  $[(\text{mpt})\text{Pt}^{\text{II}}(\text{CCPhCl})]\text{ClO}_4$  in the presence of (A) 8.4 mM DHP (closed circles) and (B) 10 mM TEA (open circles) in  $\text{CH}_3\text{CN}$  following 455-nm excitation.

maximum and broad, featureless absorption throughout the remainder of the visible.

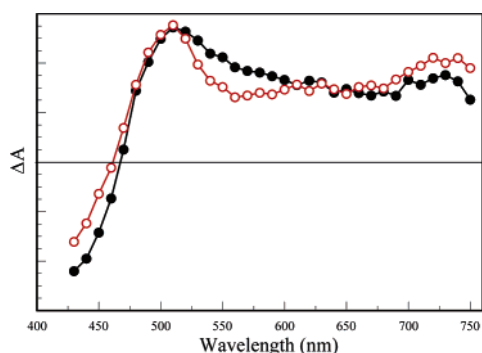
When DHP is used as a quencher, electron-transfer and H-atom-transfer pathways are possible. H-atom transfer from the DHP to the Pt complex would result in a five-coordinate Pt species that could be characterized as a platinum(III) hydride (Scheme 1). Both electron-transfer and atom-transfer DHP products would react to ultimately form the pyridine product (via disproportionation or deprotonation followed by one-electron oxidation). The intermediate Pt species formed by electron transfer and by H-atom abstraction are likely to have absorption spectra that differ significantly because electron density distributions in the two species certainly differ. As a result, a comparison of the transient spectra obtained using DHP with those of quenchers that are clearly one-electron donors should provide evidence relating to the mechanism of the quenching reaction involving DHP. Figure 3A shows transient spectra obtained with DHP and TEA as quenchers of the Pt complex excited state.

**Scheme 1.** Possible Pathways for the Reaction of Photoexcited [(mpt)Pt(CCPHCl)]PF<sub>6</sub> with DHP in CH<sub>3</sub>CN (N $\wedge$ N $\wedge$ N = mpt)

Because DHP absorbs strongly below 400 nm, transient spectral data could only be obtained at wavelengths longer than 420 nm.

The figure illustrates strong similarities between the two spectra, but the DHP-quenched sample does exhibit a maximum at 500 nm that is clearly present when TEA is used as a quencher. The spectrum obtained using DHP as a quencher did *not* evolve with time after the first few hundred nanoseconds, suggesting that the initially formed DHP<sup>•</sup> or DHP<sup>•+</sup> does not absorb significantly in the visible (or has already reacted to form the pyridine product).

A definitive spectrum of the one-electron-reduced Pt complex could also be obtained by other means. One approach is to employ spectral subtraction, using the transient spectrum obtained from quenching of the Pt complex with MPTH and the spectrum of MPTH<sup>•+</sup>, a stable cation radical.



**Figure 4.** Normalized spectra obtained for [(mpt)Pt<sup>II</sup>(CCPhCl)]ClO<sub>4</sub> in the presence of (A) 8.4 mM DHP (closed circles) and (B) 7.7 mM MPTH (open circles) in CH<sub>3</sub>CN after subtraction of the MPTH<sup>•+</sup> spectrum.

Figure 4 shows the spectrum obtained via this subtraction procedure and the spectrum from quenching directly with DHP. The similarity of the two spectra is clearly evident and serves to further suggest that the species obtained upon quenching with DHP is the one-electron-reduction product.

In summary, this work has expanded upon the observation of Tung and Wu that dihydropyridines quench the luminescence of platinum(II) terpyridyl acetylides in nonaqueous solutions by providing evidence to indicate that the primary photoreaction involves one-electron reduction of the photoexcited Pt complex. The implication of this is that subsequent protonation of the reduced complex is required for the formation of hydridoplatinum(III) species that can ultimately lead to the evolution of H. Of greater significance is the implication that reversible one-electron donors can be used as quenchers of the Pt<sup>II</sup> complex excited state and that water or other simple molecules may serve as proton donors. However, preliminary results of photolysis of the Pt<sup>II</sup> complex quenched by TEA in wet acetonitrile indicate that H is *not* produced. We are presently working to more fully elucidate the mechanism of H production in these systems.

**Acknowledgment.** The authors thank the U.S. Department of Energy, Office of Chemical Sciences (Grant DE-FG02-96ER14617), for support of this work.

**Supporting Information Available:** Cyclic voltammetry and flash photolysis studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC052045C