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Facile Preparation of 3,4-Diarylpyrroles and Hydrogen by a Platinum(II) Terpyridyl Complex

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With visible-light irradiation of the platinum(II) terpyridyl complex **1** (λ > 450 nm), an effective photocatalytic conversion from readily available 3,4-diaryl-2,5-dihydropyrroles (**2a**−**2e**) to 3,4-diarylpyrroles (**3a**−**3e**) and hydrogen (H_2) is achieved with high efficiency and large catalytic turnover in a homogeneous solution.

Square-planar platinum(II) complexes are appealing from a photochemical perspective owing to their unique features, i.e., visible-light absorption, long lifetime, and binding of a hydrogen atom at the platinum(II) center.[1−6] The coordinatively unsaturated metal center is sensitive to environmental changes and is capable of associating with substrates that are recognized to be important in homogeneous catalysis and bond activation.[1] Excitation of these complexes with light can activate the metal site, producing a more reactive electrophilic species. In earlier reports, binuclear $Pt_2(\mu\text{-}P_2O_5H_2)_4{}^{4-}$ established the first photocatalytic system of platinum(II) complexes that converts isopropyl alcohol into acetone and hydrogen.[2] Mononuclear terpyridylplatinum(II) complexes were recently found to photocatalytically produce hydrogen in the presence of Hantzsch 1,4-dihydropyridines.[3] These studies demonstrate that platinum(II) complexes in the excited state are fascinating even though the use of this kind of complex in a photocatalytic system to offer attractive synthetic routes remains rare.

In this Communication, we report an effective photocatalytic C−H bond activation system to access 3,4-diarylpyrroles. Pyrroles represent an important class of heterocycles that are subunits of a tremendous range of natural products and the building blocks of porphyrins and conjugated polymers as well.[6−9] The broad utility has made pyrroles important synthetic targets. In particular, 3,4-disubstituted pyrroles have generated considerable interest.[6−8] Selective substitution at β positions of pyrroles is generally believed to be a challenge in many synthetic programs because most aromatic substitution reactions of the heterocyclic ring tend to occur predominantly at the more electronically favorable α position. While many elegant examples using thermal reactions have been documented,[8] a photocatalytic approach to synthesizing 3,4-disubstituted pyrroles has not been realized.

The present work is to provide a photocatalytic protocol for facile preparation of 3,4-functionalized pyrroles. Herein, platinum(II) terpyridyl complex **1** and 3,4-diaryl-2,5-dihydropyrroles (**2a**−**2e**) were used (Scheme 1). 3,4-Diaryl-2,5-dihydropyrroles (**2a**−**2e**) were selected as substrates because (i) they can be easily prepared from very cheap starting materials by the McMurry coupling of dicarbonyl compounds with $TiCl_4$/Zn and (ii) Chen and co-workers found in 2005 that irradiation of 3,4-diaryl-2,5-dihydropyrroles with UV light in a CH_2Cl_2 solution resulted in 3,4-diarylpyrrole formation except for undergoing the typical ring-closed

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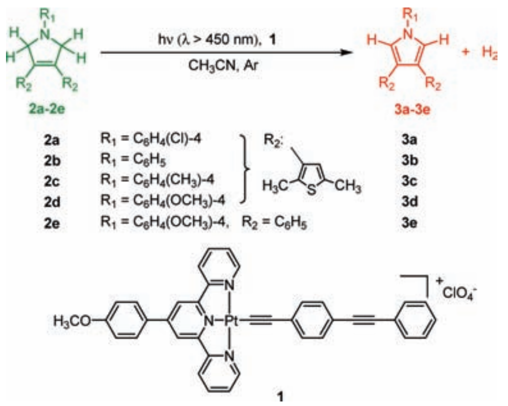
Scheme 1



photochromic reaction.[10] To develop a photocatalytic approach for the preparation of 3,4-functionalized pyrroles from a synthetic point of view, we expect that the platinum(II) complex may act as a catalyst to conduct such a photochemical transformation. As will be discussed later, this is indeed the case. Upon irradiation with visible light ($\lambda > 450$ nm), a catalytic amount of complex **1** is capable of activating the C(sp^3)−H bonds at the α position of 3,4-diaryl-2,5-dihydropyrroles (**2a**−**2e**) and producing 3,4-diarylpyrroles (**3a**−**3e**) with high efficiency and large catalytic turnover.

The photochemical reaction was carried out in a degassed CH_3CN solution at room temperature. Typically, 100 mL of a saturated solution of substrate **2** and photocatalyst **1**, i.e., 18.5 mg of **1** and 0.376 g of **2c**, in a Pyrex reactor was irradiated by a 500 W high-pressure Hanovia mercury lamp. A glass filter was used to cut off light below 450 nm, thus guaranteeing that only **1** was irradiated. After 3 h of irradiation, the concentrated reaction mixture was extracted with ethyl acetate to afford 3,4-diarylpyrrole **3**, i.e., 0.370 g of **3c**, in 97% yield and at the same time to precipitate complex **1** from the solution. The direct irradiation of **2** in CH_3CN at $\lambda = 254$ nm mainly afforded the ring-closed isomer with the formation of **3** in a yield of less than 20% (Figure S1 in the Supporting Information), but irradiation with visible light at $\lambda > 450$ nm led to no product formation, suggesting that a catalytic amount of **1** significantly accelerates the photochemical reaction.

The photocatalytic reaction process was evidenced by UV−vis spectra. Complex **1** exhibits broad absorption bands between 250 and 550 nm (Figure 1a). Thanks to the lower-energy band of the $d\pi(Pt) \rightarrow \pi^*(terpy)$ metal-to-ligand charge-transfer (MLCT) characteristic absorption of **1** ranging from 380 to 550 nm,[3] the reaction could be followed up to complete conversion of **2a** to **3a**. Irradiation of **1** and **2a** in a CH_3CN solution quickly decreased the absorbance at 260−330 nm for **2a**, accompanied by a growth with a maximum at 290 nm, a typical absorption of **3a** in the difference absorption spectra (Figure 1b). The well-defined isosbestic point at 264 nm suggests that **2a** and **3a** are present in the solution, and **1** is stable without any decomposition. This observation is also in line with ^1H NMR spectral changes before and after irradiation (Figure S2 in the Supporting Information). Similar behavior was observed for the other 3,4-diaryl-2,5-dihydropyrroles studied in this work under the same conditions (Figure S2 in the Supporting Information). In spite of the conversion changing with the irradiation time, no secondary byproduct was detected during the course of the reaction. The quantum yields (Φ) for **2a**−**2e** were determined with the initial concentration of 1×10^{-2} M (Table 1). On the basis of the molar ratio of the produced **3** to **1**, the turnover at the end of irradiation was over 1000.

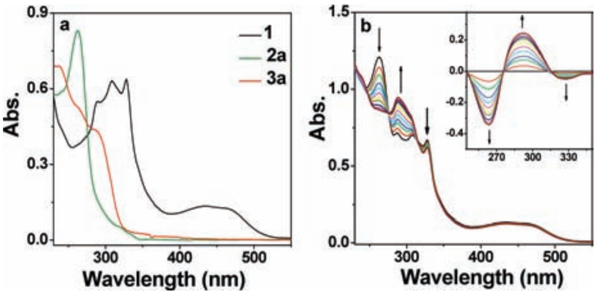


Figure 1. (a) UV−vis absorption spectra of **1** (9×10^{-6} M), **2a**, and **3a** in CH_3CN. (b) Absorption spectral changes of **2a** (1.7×10^{-5} M) and **1** (9×10^{-6} M) in CH_3CN with irradiation at $\lambda > 450$ nm. The inset shows the difference absorption spectra with irradiation time: 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 min.

Table 1. Quantum Yield and Free-Energy Change Δ*G* of the Photocatalytic Conversion

	substrate				
	2a	**2b**	**2c**	**2d**	**2e**
Φ	0.09	0.10	0.12	0.15	0.16
$\Delta E_{ox}/V^a$	1.24	1.15	1.06	0.91	0.92
$\Delta G/V^a$	−0.29	−0.38	−0.47	−0.62	−0.61

[a] Δ*G* was calculated by the equation $\Delta G = \Delta E_{ox} - \Delta E_{red} - E_{0,0} - e^2/\varepsilon a$, where ΔE_{ox} and ΔE_{red} vs NHE are the oxidative and reductive potentials of **2** and **1**, respectively, which were measured by cyclic voltammetry in a degassed CH_3CN solution with 0.1 M n-Bu_4NPF_6 as the supporting electrolyte. E_{red} is −0.53 V for **1**, and $e^2/\varepsilon a$ is 0.05 V in CH_3CN. $E_{0,0}$ refers to the lowest excited energy of **1** in CH_3CN (2.11 V).

To understand the effective photocatalytic conversion, luminescence quenching measurements were performed. Complex **1** is emissive at $\lambda_{max} = 628$ nm in CH_3CN at room temperature.[3] As **2** was introduced into the solution, the luminescence of **1** was quenched dramatically (Figure S3 in the Supporting Information). Analysis of the time-resolved decays evidences that the luminescence decay is monoexponential with quenching constants on the order of 10^9 $M^{-1} \cdot s^{-1}$, following Stern−Volmer kinetics (Table S1 in the Supporting Information). Because the energy of the singlet excited state of **1** is much lower than that of **2a**−**2e**, singlet energy transfer from excited **1** to **2a**−**2e** is thermodynamically impossible. Instead, the shorter lifetime and luminescence quenching of **1** may be attributed to photoinduced electron transfer (PET) from **2a**−**2e** to excited **1**. Calculation of the free-energy change (Δ*G*) by the Rehm−Weller equation reveals that the electron-transfer process from **2a**−**2e** to the triplet **1** is exergonic (Table 1). Because only complex **1** is excited, it is therefore reasonable to think that in this case PET from **2** to excited **1** is responsible for the luminescence quenching.

PET is further evidenced by a flash-photolysis investigation at room temperature. Figure 2 displays the time-resolved absorption difference spectra for **1** and for **1** with **2c**, respectively, in a degassed CH_3CN solution. Upon laser

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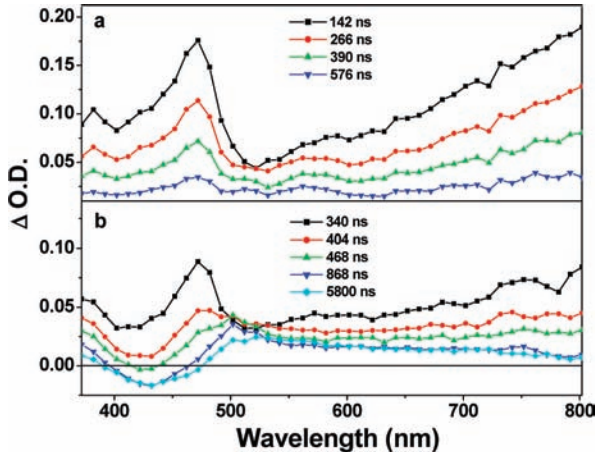

Figure 2. (a) Transient absorption spectra of **1** in CH_3CN at room temperature. (b) Transient absorption spectra of **1** with **2c** (7.7×10^{-4} M). [**1**] = 6.0×10^{-5} M; λ_{ex} = 355 nm.

pulsing by 355 nm light, a strong transient absorption of the ^{3}MLCT state for **1** emerges immediately, the decay of which throughout the absorption region and the recovery of the bleach occurs on the same time scale, and can be well described by a monoexponential function. The lifetime (τ^0) of 270 ns obtained from the decays of the absorption transients as well as from the bleach recoveries is in quantitative agreement with that of the luminescence. While **2c** was introduced into **1** ([**1**] = 6.0×10^{-5} M and [**2c**] = 7.7×10^{-4} M), the ^{3}MLCT absorption of **1** was progressively replaced by a series of new absorptions. The generated transient species displays a new absorption throughout the near-UV and visible region with a maximum at 510 nm. The bleaching in the region of 400−500 nm may be attributed to the ground-state absorption of **1**. In the case of the ratio of **1** to **2c** being 1:12, the transient decay of **1** at 510 nm could be well described by a biexponential function. The shorter lifetime in comparison with that of **1** was found to be 80 ns (τ) with the addition of **2c**, consistent with the luminescence quenching experiment. Because in this case only **1** was excited, PET from **2c** to excited **1** indeed takes place. According to the lifetimes of **1** with a concentration of [**2c**] = 7.7×10^{-4} M and of **1** itself in CH_3CN, respectively, the rate constant for the PET process can be consequently obtained as k_{ET} = 11.0×10^9 $M^{-1} \cdot s^{-1}$, close to the diffusion limit. With reference to the detailed spectroscopic work by Schmehl on platinum(II) complexes,[5] on the other hand, the longer lifetime of 6.2 μs possibly results from the intermediate species formed by electron transfer. Moreover, the observed intense peak at 510 nm is quite similar to that reported for the pyrrole cation radical.[11] If we assume that the 510 nm absorbance originates from the pyrrole cation radical alone, the rate (k_{CR}) for the back electron transfer is determined to be 2.1×10^8 $M^{-1} \cdot s^{-1}$. Contrary to what is generally observed for pyrrole cation radicals in organic solvents,[11] the intermediate does not dimerize by a fast "cation radical−cation radical" coupling. Prolonged irradiation of **1** and **2** in CH_3CN led to no permanent change, indicating that the reduced platinum species is stable.

Although determination of the isotopic effect failed because of the complicated exchange of the deuterium substitution of **2**, the potential importance of single-hydrogen transfer in the photocatalytic process stimulated us to reexamine this reaction for hydrogen (H_2) production. Irradiation of the solution of **1** and **2** in acetonitrile resulted in hydrogen production, which was analyzed by gas chromatography on a 5 Å molecular sieve column with a thermal conductivity detector and a N_2 carrier gas. The molar ratio of **3** to H_2 is 1:1, and the material balance is greater than 99%. On the basis of the above results, we may deduce that when **2** is used as a quencher, electron transfer followed by the addition of proton leads to a five-coordinated platinum(III) species. In fact, the formation of **3** and H_2 by **1** supports an effective intramolecular hydrogen abstraction. The consecutive deprotonations of the pyrrole cation radical appear to be much faster because slow deprotonation reactions would result in bimolecular reactions between the two cation radicals and the neutral radicals arising from deprotonation of the cation radical, to produce oligopyrroles.[11]

On the basis of the above results, we propose that the photocatalytic reaction is initiated by PET followed by a proton-coupling process. The larger quantum yield for the electron-rich substrates than that for the electron-poor ones [substituent R_1 on the *N*-phenyl ring: OCH_3 (**2d**) > CH_3 (**2c**) > H (**2b**) > Cl (**2a**)] also supports that the PET process is responsible for the unique photochemical transformation (Table 1). Under irradiation conditions, **2** not only serves as the electron donor to the excited complex **1** but also acts as a proton donor to the photoreduced platinum center of **1**. The generated hydridoplatinum(III) species would consecutively react with the pyrrole radical to form **3** and **1**(IV)·H_2. Eventually, elimination of H_2 from the respective intermediates of **1**(IV)·H_2 regenerates complex **1** and completes the photocatalytic cycle.

To summarize, an effective photocatalytic approach to access 3,4-diarylpyrroles, important synthetic targets, is described in this work. With visible-light irradiation, the one-pot reaction proceeds in a homogeneous solution with a large catalytic turnover number. Moreover, complex **1** can be easily separated from the reaction mixture and reused five reaction cycles without losing catalytic activity. A spectroscopic study and product analysis demonstrate that the reaction is initiated by PET followed by a proton-coupling process, as a result, leading to 3,4-diarylpyrroles and H_2 formation.

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Supporting Information Available: Experimental details, procedures for the preparation of **1**−**3**, and luminescence quenching experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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