Photocatalytic Reduction of Acetylpyridine to Pinacol Using [*fac*-Re(bpy)(CO)$_3${4-(MeCO)py}]$^+$ (bpy = 2,2'-bipyridine, py = pyridine)

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[*fac*-Re(bpy)(CO)$_3${4-(MeCO)py}]$^+$ can act as an efficient photocatalyst for the reduction of 4-acetylpyridine to a pinacol (py-CMeOHCMeOH-py) in the presence of triethanolamine. The reaction proceeds via formation of a pinacol complex [*fac*-Re(bpy)(CO)$_3$(py-CMeOHCMeOH-py)]$^+$.

Rhenium bipyridine complexes [*fac*-Re(bpy)(CO)$_3$X]$^{n+}$ (n = 0 or 1; bpy = 2,2'-bipyridine; X = neutral or anionic monodentate ligand) have received a great deal of attention with regard to their photochemical properties.[1] Irradiation of these complexes with an amine causes an electron transfer from the amine to the excited rhenium complexes to produce the one-electron reduced complexes [*fac*-Re(bpy$^{\bullet -}$)(CO)$_3$X]$^{(n-1)+}$.[2] The reduced complexes bring about interesting photochemical reactions such as CO_2 reduction,[3] ligand substitution,[4] ethylation of the bpy ligand,[5] and rearrangement of the ligand from CN-pyridine to CN$^-$.[6]

We report here that [*fac*-Re(bpy)(CO)$_3${4-(MeCO)py}]$^+$ (**1**) acts as an efficient photocatalyst for the reduction of 4-acetylpyridine [4-(MeCO)py] to a pinacol type compound 2,3-di(4-pyridyl)-2,3-butanediol (py-CMeOHCMeOH-py) (**2**) in the presence of triethanolamine (TEOA).[7] This photocatalytic reaction does not proceed via simple photosensitization of **1** for the electron transfer, but proceeds via the reaction on the ligand of the Re-complex.

Irradiation of a TEOA / DMF (1/5, v/v, 4 cm^3) solution of **1** (2.60 mmoldm^{-3}) and excess 4-(MeCO)py (56.8 mmol dm^{-3}) at 405 nm caused white precipitate in the reaction cell. The ^{1}H- and ^{13}C-NMR spectral measurements indicated that the product is **2**, by comparing with those of the commercial species.[8] Figure 1 shows the formation of **2** with 405 nm irradiation.[9] The pinacol **2** increased linearly until 4 h, and the quantum yield for the formation of **2** was 0.25.[10] The amount of **2** was almost constant by prolonged irradiation, e.g., 51% yield (2 × [**2**] / [4-MeCOpy] used) at 20 h irradiation with a turnover number of 5.5. The 4-(MeCO)py has very weak absorption at 405 nm. Actually, the yield of **2** for 4 h irradiation in the absence of **1** was 0.4%, which is much less than that in the presence of **1** by a factor of 128. This finding indicates that the formation of **2** is photocatalyzed by **1**.

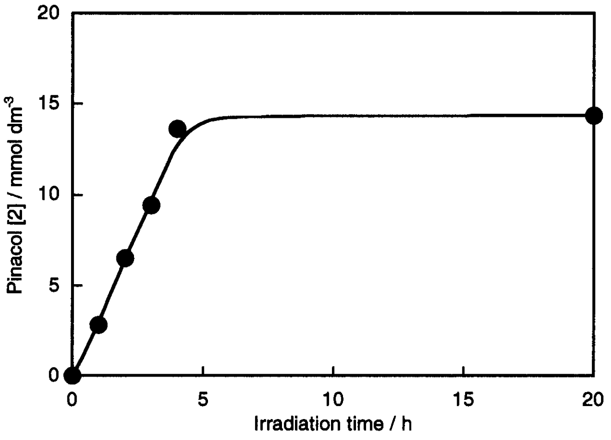

Figure 1. Irradiation-time dependence of the formation of **2.**

To elucidate the changes of the structure of the complex by irradiation, electrospray (ES) mass spectra of the reaction solutions were measured.[11] Before irradiation, the spectrum consisted of a large peak of **1** (*m/z* = 548). After irradiation started, the peak of **1** became small and an outstanding peak appeared at *m/z* of 671, corresponding to a complex with **2** as a ligand, i.e., the pinacol complex [*fac*-Re(bpy)(CO)$_3$(py-CMeOHCMeOH-py)]$^+$ (**3**) (Figure 2). The peak of **3** was detected until the formation of **2** stopped. This observation indicates that **3** acts as an important intermediate in the photocatalytic formation of **2**.

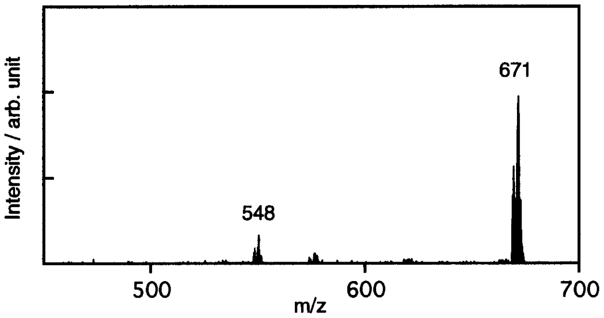

Figure 2. ES-mass spectrum of a TEOA / DMF solution of **1** and excess 4-(MeCO)py after 2 h irradiation at 405 nm.

To clarify the role of 4-(MeCO)py, **1** was irradiated in TEOA / DMF without addition of free 4-(MeCO)py. Despite the absence of free 4-(MeCO)py in the initial solution, free 4-(MeCO)py was detected after the short period of irradiation (Figure 3). The yield of 4-(MeCO)py reached a maximum around 5 min irradiation (9%, based on [**1**] used) and then decreased. The appearance of free 4-(MeCO)py can be explained by the formation of one-electron reduced species **1**$^{\bullet -}$, which should be produced by photochemical electron transfer from TEOA [equation (1)] and subsequent ligand substitution with solvent molecules (S : TEOA or DMF) [equation (2)].[4,7]

$$\mathbf{1} + \mathrm{TEOA} \xrightarrow{h\nu} \mathbf{1}^{\bullet -} + \mathrm{TEOA}^{\bullet +} \qquad (1)$$

$$\mathbf{1}^{\bullet -} + \mathrm{S} \rightarrow [\textit{fac}\text{-}\mathrm{Re(bpy^{\bullet -})(CO)_3S}] + \text{4-(MeCO)py} \qquad (2)$$

It is noteworthy that the formation of **2** has induction period and appears after the decrease of free 4-(MeCO)py.

The ES-mass spectrum of the irradiated solution in the absence of free 4-(MeCO)py showed the formation of pinacol complex **3** and the solvent complexes, i.e., [*fac*-Re(bpy)-$(CO)_3$DMF]$^+$ (*m/z* = 500) and [*fac*-Re(bpy)$(CO)_3$TEOA]$^+$ (*m/z* = 576). When the formation of **2** was increased (10 to 20 min in Figure 3), the peak height of **3** in the ES-mass spectra decreased while those of the solvent complexes increased, indicating that **3** releases **2** to form solvent complexes.

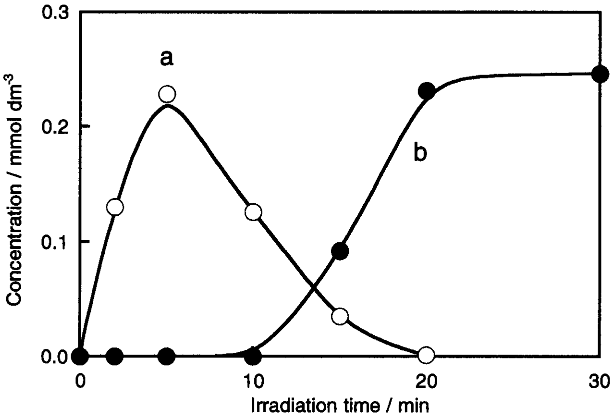

Figure 3. Changes in concentrations of (a) free 4-(MeCO)py and (b) **2** in TEOA / DMF solutions of **1** (2.60 mmol dm^{-3}) due to 405 nm irradiation.

Although the formation of **3** from **1** is still unclear, two mechanisms would be possible. One is the direct reaction of the one-electron reduced species $\mathbf{1}^{\bullet -}$ and/or its protonated form **1**-H• with free 4-(MeCO)py to produce $\mathbf{3}^{\bullet +}$, followed by the one-electron injection, and another is the coupling reaction of **1**-H• to form [Re(bpy)$(CO)_3$(py-CMeOHCMeOHpy)-$(CO)_3$(bpy)Re]$^{2+}$, followed by its cleavage to **3** and [Re(bpy)$(CO)_3$]$^+$. It should be noted that, in both cases, **2** is produced via the reaction on the ligand of the Re-complex and these mechanisms are different from the reported photosensitized pinacol formation explained by simple photoelectron transfer processes.[12]

Further application of this method to other pyridyl ketones and details of the reaction mechanisms are being investigated in our laboratory.

References and Notes

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7 The complex [**1**][SbF_6] was prepared according to a literature method, see H. Hori, J. Ishihara, K. Koike, K. Takeuchi, T. Ibusuki, and O. Ishitani, *J. Photochem. Photobiol. A: Chem.*, **120**, 119 (1999).

8 The decomposition temperature of **2** (215 – 217 °C) was also in good agreement with the reported value (219 - 220 °C) [M. J. Allen and H. Cohen, *J. Electrochem. Soc.*, **106**, 451 (1959)].

9 The amount of **2** was measured by a HPLC system. Column: Develosil-ODS-UG-5 (Nomura Chemical), mobile phase: a mixture (30 : 70, v/v) MeOH / KH_2PO_4-NaOH buffer (0.05 mol dm^{-3}, pH 5.9), detection wavelength: 270 nm. When the sample included solid, all the content in the reaction cell was diluted by EtOH to make a homogeneous solution, then subjected to the measurements. Other alcohol species such as 4-(MeCHOH)py were not observed.

10 The quantum yield was calculated by the equation (formation rate of **2**) / (light intensity). The light intensity was 1.49×10^{-8} einstein s^{-1} (1 einstein = 6.022×10^{23} photons).

11 The irradiated sample solution was introduced to the electrospray probe without any pretreatment. Details of the system, see H. Hori, J. Ishihara, K. Koike, K. Takeuchi, T. Ibusuki, and O. Ishitani, *Anal. Sci.*, **14**, 287 (1998).

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