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Tsubasa Nishimura, Yoshihiro Miyake,\* and Hiroshi Shinokubo

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## Synthesis, Properties, and Reactivities of Ruthenium(II) Carbonyl 5,15-Diazaporphyrins

Tsubasa Nishimura, Yoshihiro Miyake,\* and Hiroshi Shinokubo

Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603

E-mail: miyake@chembio.nagoya-u.ac.jp

We have succeeded in the synthesis of ruthenium(II) carbonyl 5,15-diazaporphyrin complexes **2** having pyridines as axial ligands. The structures, properties, and reactivities under photoirradiation of **2** are compared with those of the corresponding ruthenium porphyrins.

Metalloporphyrins based on a variety of transition metals such as iron, manganese, ruthenium, and so on have attracted considerable attention as catalysts for selective oxidation of saturated C-H bonds<sup>1,2</sup> since the discovery of the enzymes cytochrome P450. In particular, ruthenium porphyrin complexes are extensively studied as effective catalysts for epoxidation of alkenes, oxidation of alcohols, oxidation of sulfides, hydroxylation of alkanes.<sup>3-7</sup> Electron deficient ruthenium porphyrins, where electron withdrawing groups are introduced to the porphyrin ligands, exhibit high catalytic activity for the oxidation of organic compounds. For example, Groves and co-workers have reported that carbonylruthenium(II) 5,10,15,20tetrakis(pentafluorophenyl)porphyrin **3a** works as an efficient catalyst for the oxidation of alkenes (Chart 1).<sup>7-8</sup>

5,15-Diazaporphyrins **1M** are  $18\pi$  porphyrinoids, which exhibit electron deficient nature owing to imine-type sp<sup>2</sup>hybridized nitrogen atoms at *meso*-positions (Chart 1).<sup>10-12</sup> We have explored unique reactivities and properties of 5,15diazaporphyrins.<sup>11a-11d</sup> As an extension of our study, we have developed the synthesis of carbonylruthenium(II) 5,15diazaporphyrins **2**, which are expected to work as an oxidation catalyst because of their electron deficient nature. Here we disclose the structures, properties, and reactivities of **2**.



**Chart 1**. Carbonylruthenium(II) porphyrins and 5,15diazaporphyrins.

Treatment of free-base diazaporphyrin  $1H_2$  (Mes = 2,4,6-trimethylphenyl) with  $Ru_3(CO)_{12}$  (1.0 equiv) in *o*-dichlorobenzene at 160 °C for 5 h afforded carbonylruthenium 5,15-diazaporphyrin 2a in 29% yield

(Scheme 1). Further treatment of 2a with pyridine (1.1 equiv) and N,N-dimethyl-4-aminopyridine (DMAP) (1.1 equiv) in THF at room temperature for 1 h smoothly furnished the corresponding ruthenium complexes 2b and 2c having pyridine and DMAP as axial ligands in 43% and 70% yields, respectively. Formation of these ruthenium complexes 2a-2c was confirmed by their <sup>1</sup>H and <sup>13</sup>C NMR and high-resolution electro-spray ionization time-of-flight (HR-ESI-TOF) mass spectra. <sup>1</sup>H NMR spectra of **2** displayed three methyl protons on the mesityl group, suggesting the presence of axial ligands such as CO, pyridine, and DMAP. The complex 2a is insoluble in toluene,  $CH_2Cl_2$ , and  $CHCl_3$ , but soluble in THF. The coordination of THF to the ruthenium center as an axial ligand may prevent the aggregation of 2a. In fact, the complexes 2b and 2c having pyridine and DMAP as axial ligands are soluble in toluene, CH<sub>2</sub>Cl<sub>2</sub>, and CHCl<sub>3</sub>.



**Scheme 1**. Synthesis of carbonylruthenium(II) 5,15diazaporphyrins **2**.

Recrystallization of ruthenium diazaporphyrins **2b** and **2c** from CHCl<sub>3</sub>/hexane and CH<sub>2</sub>Cl<sub>2</sub>/methanol afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structures of **2b** and **2c** (Figures 1a and 1b).<sup>13,14</sup> The structure of diazaporphyrin core in **2b** was quite similar to that in **2c**. The mean plane deviations in **2b** and **2c** are 0.08108 and 0.08468 Å, suggesting their planar structures. The bond lengths of C–O bond in **2b** (1.139(4) Å) and **2c** (1.148(3) Å) are shorter than those in ruthenium porphyrin **4b** (1.165(11) and 1.153(10) Å) (Figure S2).<sup>14</sup> This fact clearly shows that the electron deficient nature of diazaporphyrins affects the  $\pi$ -back donating ability of the ruthenium center.

In IR spectra, ruthenium diazaporphyrins **2** exhibited strong CO stretching absorption, of which positions are influenced by the nature of the second ligands (Table 1).<sup>15</sup> The  $v_{co}$  frequencies of diazaporphyrin complexes **2a** and **2b** 

are higher than those of **4a** and **4b**, while the spectra of **2a** and **2b** show lower absorption bands than those of **3a** and **3b**. These results suggest that the order in the electron deficient nature as a ligand is  $3\mathbf{b} > 2\mathbf{b} > 4\mathbf{b}$ .



**Figure 1**. Crystal structures of (a) **2b**, (b) **2c**, and (c) **2d**. Hydrogen atoms and mesityl groups are omitted for clarity. The thermal ellipsoids are scaled at 50% probability level.

**Table 1.**  $v_{co}$  Frequencies of diazaporphyrin complexes<sup>4</sup>

compounds	$v_{\rm CO}  ({\rm cm}^{-1})$
2a	1952
2b	1954
<b>3</b> a	1975
<b>3</b> b	1963
<b>4a</b>	1944
4b	1948

<sup>*a*</sup> All spectra were measured using FT-IR spectrometer equipped with an ATR apparatus.

Electronic absorption spectra of **2b** and **4b** were measured in CH<sub>2</sub>Cl<sub>2</sub> (Figure 2). As compared to **4b**, the Qband of **2b** ( $\lambda_{max} = 556$  nm) was slightly bathochromic shifted and the molar extinction coefficient ( $\varepsilon$ ) was similar, while the Soret band ( $\lambda_{max} = 400$  nm) was blue-shifted and was weakened.

Photosubstitution reactions of the CO ligand in carbonylruthenium porphyrins have been extensively studied because the dissociation of CO ligand is an important step for their catalysis.<sup>16,17</sup> We conducted the photosubstitution reaction of **2b** and **4b**. Dissociation of CO from **2b** and **4b** upon visible-light (>380 nm) excitation in the presence of an excess amount of pyridine effectively provided the corresponding bis-pyridine complexes **2d** and **4d** (Scheme 2). The molecular structure of **2d** was confirmed by X-ray diffraction analysis (Figure 1c).<sup>18</sup> UV-Vis spectra changes during photoirradiation are shown in Figure 3. As the

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photoreaction of **2b** proceeded, new absorption bands appeared around 390 and 550 nm (Figure 3a). The observation of isobestic points clearly supports the direct transformation of **2b** into **2d**. A similar spectral change of **4b** also suggests that the photosubstitution reaction occurs (Figure 3b). From the absorption changes of the Q-band, we conducted the kinetic analysis (Figure S1): the rate constants of the photosubstitution reaction of **2b** and **4b** are determined to be  $6.8 \times 10^{-4}$  and  $1.1 \times 10^{-3}$  s<sup>-1</sup>, respectively.



Figure 2. Absorption spectra of 2b and 4b (CH<sub>2</sub>Cl<sub>2</sub>).







Figure 3. Absorption spectral changes of (a) 2b and (b) 4b during the photoirradiation.

We then investigated the catalytic activity of 2 and 4 in oxidation of alkenes (Scheme 3). Treatment of *p*-chlorostyrene with 1.2 equiv of 2,6-dichloropyridine *N*-oxide in the presence of 0.5 mol% of 4a in toluene at room temperature for 19 h afforded the corresponding epoxide in 77% yield. On the other hand, the use of the complex 2a

afforded none of the epoxide probably because of the low solubility of 2a in toluene. Furthermore, pyridine complexes 2b and 4b showed no catalytic activity. Increase of catalyst loading of 2b (2.5 mol%) did not affect the yield of epoxide. Unfortunately, the photoirradiation was not effective for this catalytic system. At present, we have not clarified the reason, but an axial ligand like pyridine may prevent the formation step of the reactive intermediate including the oxidation of 2b.



Scheme 3. Epoxidation of *p*-chlorostyrene.

In summary, we have succeeded in the synthesis of carbonylruthenium(II) 5,15-diazaporphyrins **2** having axial ligands. From X-ray analysis and IR spectra, we have found that 5,15-diazaporphyrin works as an electron deficient ligand to the ruthenium center. The photosubstitution reaction of the CO ligand in **2** proceeds smoothly. We believe these findings suggest the possibility of 5,15-diazaporphyrin as a useful ligand for unique molecular transformation. Further work is currently in progress in our group to develop 5,15-diazaporphyrin transition metal complexes as the oxidation catalyst of alkenes and alkanes.

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Supporting Information is available on http://dx.doi.org/10.1246/cl.\*\*\*\*\*.

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- 14 Crystallographic data for **2c**:  $C_{44}H_{40}N_8ORu$ ,  $M_w = 797.91$ , monoclinic,  $P_{2_1/c}$ , a = 14.9323(7), b = 18.2032(9), c = 13.8978(7)Å,  $\beta = 96.4600(10)$ , V = 3753.7(3) Å<sup>3</sup>, Z = 4, R = 0.0230 ( $I > 2.0 \sigma(I)$ ),  $wR_2 = 0.0607$  (all data), GOF = 1.046. Crystallographic data for **2c** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1542191.
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