PHOTODISSOCIATION OF MONOPYRIDINATE OF CHLOROCHROMIUM(III) TETRAPHENYLPORPHYRIN IN ACETONE. STUDIES ON THE REACTIVE STATE AND LIGAND EXCHANGE REACTION BY LASER PHOTOLYSIS

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Received 18 September 1989

The title compound, ClCr(III)TPP–Py (Py=pyridine), in acetone photodissociates the axial pyridine, probably from the $^4S_1$ state, to give ClCr(III)TPP as an initial product with yield of ≈0.16 upon 532 and 355 nm excitation. The initial product, ClCr(III)TPP, reacts with both pyridine and acetone to yield ClCr(III)TPP–Py and ClCr(III)TPP–Ac (Ac=acetone). The monoacetonate complex, ClCr(III)TPP–Ac, further exchanges the axial acetone for pyridine to regenerate ClCr(III)TPP–Py.

1. Introduction

Axial ligation of synthetic metalloporphyrins has been a subject of extensive studies for understanding the biological role of axial ligands in naturally occurring hemoproteins [1–4]. For chromium porphyrins, studies on axial ligation by optical absorption and ESR spectroscopy have revealed that their physical and chemical properties are markedly affected by the nature of the axial ligand [5]. It, therefore, is expected that the axial ligand gives a significant effect on the electronic structure of the chromium porphyrins, not only in the ground state but also in excited states.

In 1975, Gouterman et al. [6] reported that chloromeso-tetraphenylporphinatochromium(III), ClCr(III)TPP, in a mixture of *n*-butanol and 3-methylpentane exhibits dual luminescence originating from the trip-quartet, $^4T_1$ and the trip-sextet $^6T_1$ states. Later Harriman also observed luminescence from ClCr(III)TPP in ethanol [7]. However, the excited-state nature of chlorochromium porphyrins having a sixth ligand has not yet been reported.

In the present work, we found that the monopyridinate of ClCr(III)TPP, ClCr(III)TPP–Py, releases the axial pyridine upon 355 and 532 nm excitation. The reactive state responsible for ligand ejection as well as the mechanism of the ligand exchange reaction is discussed on the basis of nanosecond laser photolysis studies.

2. Experimental

Chloro-meso-tetraphenylporphinatochromium(III), ClCr(III)TPP, was synthesized and purified as in the literature [5]. Reagent grade acetone and pyridine were used without further purification.

Absorption and luminescence spectra were recorded on a Hitachi 330 spectrophotometer and a Hitachi MPF 4 spectrofluorimeter, respectively. Laser photolysis studies were carried out by using an Nd–YAG laser (model HY 500 from JK Lasers Ltd.) equipped with second (532 nm), third (355 nm), and fourth (266 nm) harmonic generators. The detection system of transient spectra has been described elsewhere [8].

The concentrations of ClCr(III)TPP in acetone

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solutions ranged from 5.36×10^{-6} to 2.45×10^{-5} M throughout this study.

Sample solutions were prepared in the dark in order to minimize photodecomposition of ClCr(III)TPP. The solutions, if necessary, were deaerated by bubbling with pure argon gas.

3. Results

Earlier studies on ligand exchange reactions have demonstrated that ClCr(III)TPP reacts with an acetone molecule to give the monoacetonate complex, ClCr(III)TPP–Ac (Ac=acetone) [5]. The axial acetone in ClCr(III)TPP–Ac is known to be readily replaced by N-donor ligands [5].

Fig. 1 shows the absorption spectra in the Soret band region observed for ClCr(III)TPP in the acetone solutions containing $(0\text{–}6.2)\times10^{-2}$ M pyridine. The spectrum of ClCr(III)TPP–Ac in acetone has an absorption peak at 446 nm with the molar absorption coefficient of 3.0×10^{5} M^{-1} cm^{-1}. With increase in the pyridine concentration, the spectrum gradually changes to that of ClCr(III)TPP–Py with isosbestic points, indicating the presence of the following equilibrium:

$$\mathrm{ClCr(III)TPP\text{–}Ac + Py \rightleftharpoons ClCr(III)TPP\text{–}Py + Ac},$$

$$K=\frac{[\mathrm{ClCr(III)TPP\text{–}Py}][\mathrm{Ac}]}{[\mathrm{ClCr(III)TPP\text{–}Ac}][\mathrm{Py}]}.$$

According to the method reported by Miller and Dorough [9], the equilibrium constant K was determined as 4.9×10^{4}.

In an acetone solution, luminescence from ClCr(III)TPP–Ac is almost undetectable at room temperature. However, ClCr(III)TPP–Py gives luminescence, although still weak; the peak intensity of the luminescence spectrum is located around 835 nm. Taking account of the previous studies on luminescence of chromium porphyrins [6], we consider that the excited state responsible for luminescence of ClCr(III)TPP–Py is ascribed to the trip-quartet state, $^{4}T_{1}$, which is in thermal equilibrium with the trip-sextet state, $^{6}T_{1}$.

Fig. 2 shows the transient spectra observed for an aerated acetone solution of ClCr(III)TPP–Py containing 1.24×10^{-2} M pyridine after 355 nm laser pulsing. The transient spectrum taken at 50 ns after pulsing exhibits a negative peak around 455 and two positive ones around 470 and 395 nm. At 1 μs after pulsing, the first transient spectrum, which decays according to first-order kinetics with the rate constant of 8.5×10^{6} s^{-1}, completely disappears, leaving the second transient spectrum having a positive peak at 447 and a negative one at 458 nm. The second transient spectrum taken 1 μs after pulsing is transformed to the third one according to first-order ki-

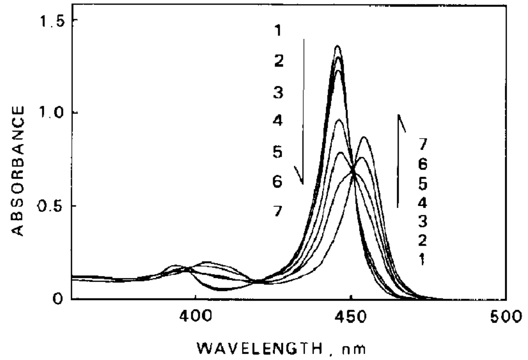

Fig. 1. Absorption spectra of ClCr(III)TPP (5.36×10^{-6} M) in aerated acetone solutions at room temperature containing [Py]: (1) 0 M; (2) 2.48×10^{-5} M; (3) 4.96×10^{-5} M; (4) 2.48×10^{-4} M; (5) 4.96×10^{-4} M; (6) 1.24×10^{-3} M; (7) 6.20×10^{-2} M.

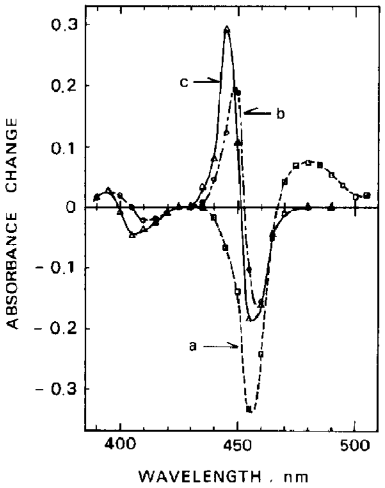

Fig. 2. Transient spectra observed for an aerated acetone solution of 5.36×10^{-6} M ClCr(III)TPP containing 1.24×10^{-2} M Py after a 355 nm laser pulse: (a) at 50 ns; (b) at 1 μs; (c) at 500 μs.

netics with a rate constant of 6.4×10^3 s^{-1}. The third transient spectrum with the positive and negative peaks at 445 and 455 nm, respectively, was found to decay uniformly in the whole wavelength region studied. The decay of the transient follows first-order kinetics with a rate constant of 6.6×10 s^{-1}.

As described above, laser photolysis of ClCr(III)TPP–Py gives three transient species. The transient spectrum of the first species with the decay rate constant of 8.5×10^6 s^{-1} can be obtained by subtracting the transient spectrum measured at 1 μs from that at 100 ns. The spectrum thus obtained is found to be similar to the triplet–triplet absorption spectrum of usual metal tetraphenylporphyrins originating from the porphyrin ligand [10]. As mentioned later, the transient species is ascribed to the $^6T_1$ state of ClCr(III)TPP–Py.

The second transient spectrum with the decay rate constant of 6.4×10^3 s^{-1} closely resembles the difference spectrum (ClCr(III)TPP – ClCr(III)TPP–Py) obtained by subtracting the spectrum of ClCr(III)TPP–Py in acetone from that of ClCr(III)TPP in the non-coordinating solvent CH_2Cl_2. This result indicates that the second transient is attributed to ClCr(III)TPP free from the sixth ligand. The second transient is found to be the precursor of the third transient species.

The third transient spectrum with the decay rate constant of 6.6×10 s^{-1} is identical with the difference spectrum (ClCr(III)TPP–Ac – ClCr(III)TPP–Py) in acetone, leading to the conclusion that the third transient is ascribed to ClCr(III)TPP–Ac.

We have also carried out laser photolysis studies of ClCr(III)TPP–Py in oxygen saturated and deaerated acetone solutions containing 1.24×10^{-2} M pyridine. The results are summarized as follows: (1) The decay rate constant of the $^6T_1$ state in degassed solution is determined as 6.9×10^6 s^{-1} which is slightly smaller than that (8.5×10^6 s^{-1}) in aerated solutions. (2) In the oxygen saturated solution, the decay rate constant of the $^6T_1$ state is obtained as 1.5×10^7 s^{-1} which is 2.2 times larger than that in the deaerated solution, probably owing to the effective quenching of the $^6T_1$ state by oxygen. (3) The yields of the $^6T_1$ state, ClCr(III)TPP, and ClCr(III)TPP–Ac were independent of the concentration of oxygen. (4) The rate constants for the decay of ClCr(III)TPP and ClCr(III)TPP–Ac are not affected by oxygen.

Because of the fact that, in oxygen saturated solutions, the $^6T_1$ state is quenched while the yield of ClCr(III)TPP is not diminished, we conclude that the $^6T_1$ state is not the precursor of ClCr(III)TPP.

The effects of pyridine on the photochemistry of ClCr(III)TPP–Py were examined. We observed that (1) the yield and the decay of the $^6T_1$ state of ClCr(III)TPP–Py are not affected by the pyridine concentration, (2) both the rate constant, k_{obsd}, and the yield, Φ, for the formation of ClCr(III)TPP–Ac from ClCr(III)TPP are markedly dependent on the pyridine concentration: the rate constant increases with an increase in the pyridine concentration while the yield decreases, and (3) the rate constant, k_{AP}, for the decay of ClCr(III)TPP–Ac increases with increase in the pyridine concentration and levels off at concentrations higher than 0.1 M pyridine.

On the basis of these observations, the photoreaction of ClCr(III)TPP–Py in acetone is expressed as

$$\mathrm{ClCr(III)TPP{-}Py} \xrightarrow{h\nu} {}^6\mathrm{T}_1\,,$$

$$\mathrm{ClCr(III)TPP{-}Py} \xrightarrow{h\nu} \mathrm{ClCr(III)TPP+Py}\,,$$

$$\mathrm{ClCr(III)TPP+Ac} \xrightarrow{k_{Ac}} \mathrm{ClCr(III)TPP{-}Ac}\,,$$

$$\mathrm{ClCr(III)TPP+Py} \xrightarrow{k_{Py}} \mathrm{ClCr(III)TPP{-}Py}\,,$$

$$\mathrm{ClCr(III)TPP{-}Ac+Py} \xrightarrow{k_{AP}} \mathrm{ClCr(III)TPP{-}Py+Ac}\,.$$

Upon laser excitation, ClCr(III)TPP–Py gives rise to the formation of the $^6T_1$ state and ClCr(III)TPP. The latter reacts with both acetone and pyridine to yield ClCr(III)TPP–Ac and ClCr(III)TPP–Py with rate constants, k_{Ac} and k_{Py}, respectively. The monoacetonate complex, ClCr(III)TPP–Ac, exchanges the axial ligand Ac for pyridine with the rate constant, k_{AP}, to regenerate ClCr(III)TPP–Py. It is found that k_{AP} is two orders of magnitude smaller than the rate for the decay of ClCr(III)TPP, $k_{Ac}[Ac]+k_{Py}[Py]$, in the whole pyridine concentration range studied.

From the scheme described above and $k_{AP} \ll k_{Ac}[Ac]+k_{Py}[Py]$, the absorbance change,

ΔD, of the second transient spectrum is formulated as

$$\Delta D = \Delta D_{\infty} + (\Delta\epsilon_{AC} - \Delta\epsilon_{BC} k_{Ac}[Ac]/k_{obsd}) \exp(-k_{obsd} t) . \quad (1)$$

Here

$$\Delta D_{\infty} = \Delta\epsilon_{BC}[Cr^{III}(0)] \times k_{Ac}[Ac]/(k_{Ac}[Ac] + k_{Py}[Py]) , \quad (2)$$

$$k_{obsd} = k_{Ac}[Ac] + k_{Py}[Py] , \quad (3)$$

$$\Delta\epsilon_{AC} = \epsilon_A - \epsilon_C , \quad (4)$$

$$\Delta\epsilon_{BC} = \epsilon_B - \epsilon_C , \quad (5)$$

where ΔD_{∞} is the absorbance change at an infinite time, $[Cr^{III}(0)]$ is the initial concentration of ClCr(III)TPP produced upon laser excitation, and ϵ_A, ϵ_B, and ϵ_C are the molar absorption coefficients of ClCr(III)TPP, ClCr(III)TPP–Ac, and ClCr(III)TPP–Py, respectively. For derivation of eq. (1) we ignored the backward reactions

$$\text{ClCr(III)TPP–Ac} \xrightarrow{k_1} \text{ClCr(III)TPP} + \text{Ac} ,$$

$$\text{ClCr(III)TPP–Py} \xrightarrow{k_2} \text{ClCr(III)TPP} + \text{Py} .$$

When k_1 or k_2 is not negligible in comparison with k_{Ac} or k_{Py}, ΔD cannot be simply expressed as a single exponential function of time. We found that ΔD measured experimentally follows eq. (1) in the whole pyridine concentration range studied. This finding implies $k_{Ac} \gg k_1$ and $k_{Py} \gg k_2$ that are almost equivalent to neglect of these backward reactions. Eq. (3) predicts that the plot of k_{obsd} versus pyridine concentration, [Py], gives a straight line. Fig. 3 shows the plot of k_{obsd} obtained from the absorbance change, ΔD, of the second transient spectrum, represented as a function of [Py]. From the slope and intercept of the line, the rate constants are determined as $k_{Ac}[Ac] = 5.7 \times 10^3\ s^{-1}$ and $k_{Py} = 5.9 \times 10^4\ M^{-1}\ s^{-1}$.

The absorbance change, ΔD_{∞}, at an infinite time can be measured from the decay or the rise curve of ΔD because of $k_{AP} \ll k_{Ac}[Ac] + k_{Py}[Py]$. According to eq. (2) we plotted $1/\Delta D_{\infty}$ against [Py]. From the slope and intercept of the line, the ratio of the rate constants, $k_{Py}/k_{Ac}[Ac]$, is obtained as $10.0\ M^{-1}$. This value is in good agreement with that calculated from the rate constants $k_{Ac}[Ac]$ and k_{Py} obtained above.

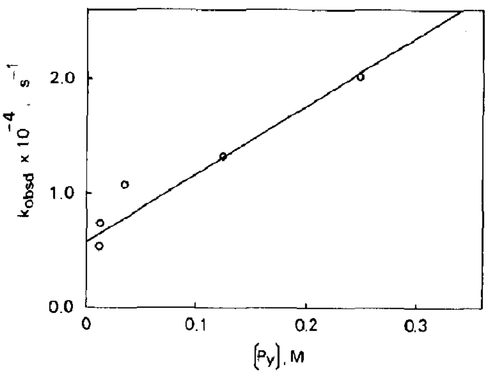

Fig. 3. Plot of k_{obsd} versus [Py] (see text).

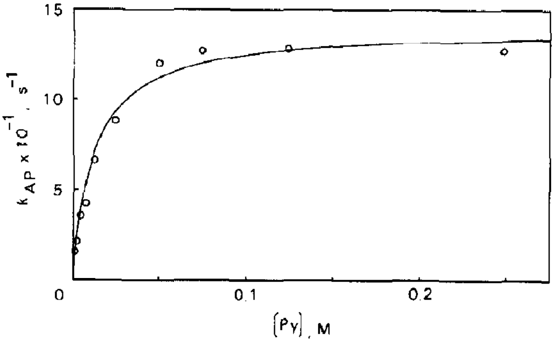

Fig. 4. Plot of k_{AP} versus [Py]. The solid curve is the rate constant calculated according to the reaction scheme (see text).

Fig. 4 shows the plot of the decay rate constant, k_{AP}, of the third transient spectrum (ClCr(III)TPP–Py), represented as a function of [Py]. The rate constant increases with increase in [Py] and exhibits leveling off at [Py] > 0.1 M. This result, in connection with the mechanism of the substitution reaction of the axial acetone by pyridine, is discussed later.

Quantum yields for photodissociation of the axial pyridine in ClCr(III)TPP–Py were measured by the laser photolysis technique in order to elucidate the primary processes of the photochemistry of the chromium porphyrins. The yields Φ are expressed as

$$\Phi = [Cr^{III}(0)]/I_{abs} , \quad (6)$$

where $[Cr^{III}(0)]$ is the initial concentration of ClCr(III)TPP observed after laser pulsing and I_{abs} is the number of photons absorbed by ClCr(III)TPP–Py. Eqs. (2) and (6) give

$$\Phi = \Delta D_\infty \Gamma / \Delta\epsilon_{BC} I_{abs} \,. \tag{7}$$

Here

$$\Gamma = (k_{Ac}[Ac] + k_{Py}[Py]) / k_{Ac}[Ac] = 1 + 10.0[Py] \,. \tag{8}$$

The values of ΔD_∞ and $\Delta\epsilon_{BC}$ were measured at 445 nm: $\Delta\epsilon_{BC} = 1.8 \times 10^5$ M^{-1} s^{-1}. The value of Γ is calculated from [Py] of the solution.

For determination of I_{abs}, we prepared a benzene solution of zinc(II) tetraphenylporphyrin, ZnTPP, that has an absorbance identical with that of the acetone solution of ClCr(III)TPP–Py at a laser excitation wavelength. When the benzene solution was subjected to laser photolysis, the initial absorbance, ΔD_T, of the triplet ZnTPP monitored at 470 nm is expressed as $\Delta D_T = \Phi_{ST} \epsilon_{470} I_{abs}$. We can, therefore, readily determine I_{abs} with the use of ΔD_T, the molar absorption coefficient, ϵ_{470}, of the triplet ZnTPP ($\epsilon_{470} = 7.3 \times 10^4$ M^{-1} cm^{-1}), and the triplet yield, Φ_{ST} ($\Phi_{ST} = 0.83$) [10].

The quantum yields for photoejection of the axial pyridine obtained with the procedure mentioned above are 0.17±0.03 and 0.15±0.03 upon 532 and 355 nm laser excitation, respectively.

4. Discussion

The laser photolysis studies of ClCr(III)TPP–Py in deaerated acetone revealed that the transient having the decay rate constant of 6.9×10^6 s^{-1} is quenched by oxygen, indicating that the transient is ascribed to an excited state. It has been proposed [6] that chromium porphyrins have the trip-quartet state, $^4T_1$, which lies closely higher in energy than the lowest trip-sextet state, $^6T_1$. Then, the transient can be ascribed to the $^4T_1$ or the $^6T_1$ state.

On the basis of detailed studies on luminescence from ClCr(III)TPP at various temperatures, the difference in energy between the $^4T_1$ and the $^6T_1$ state has been estimated as 520 cm^{-1} [6]. According to the Boltzmann distribution, the ratio of the population of the $^4T_1$ state, N_{TQ}, to that of the $^6T_1$ state, N_{TS}, is

$$N_{TQ}/N_{TS} = \tfrac{2}{3} \exp(-\Delta E_{QS}/RT) \,, \tag{9}$$

where $\Delta E_{QS} = 520$ cm^{-1} [6]. Eq. (9) gives $N_{TQ}/N_{TS} = 0.05$ for ClCr(III)TPP at 300 K. This value implies that the major species is the $^6T_1$ state at room temperature. On the assumption that the energy difference, ΔE_{QS}, of ClCr(III)TPP–Py is approximately identical with that of ClCr(III)TPP, the excited state detected by laser photolysis of ClCr(III)TPP–Py is attributed to the $^6T_1$ state.

The rate constant for the decay of the $^6T_1$ state increases from 6.9×10^6 to 1.5×10^7 s^{-1} on going from the deaerated to the oxygen-saturated acetone solution owing to the quenching of the $^6T_1$ state by oxygen. However, the yield for the photodissociation of the axial pyridine in ClCr(III)TPP–Py is identical, irrespective of the presence or absence of oxygen. This result indicates that neither the $^6T_1$ nor the $^4T_1$ state is responsible for the photodissociation reaction. Further, the yield for the photodissociation of pyridine is scarcely dependent on the excitation wavelengths: $\Phi = 0.17 \pm 0.03$ at 532 nm and $\Phi = 0.15 \pm 0.03$ at 355 nm. These results suggest that the photodissociation of the axial pyridine occurs from the $^4S_1$ state of ClCr(III)TPP–Py.

Absorption spectroscopic studies confirmed that ClCr(III)TPP–Ac is in equilibrium with ClCr(III)TPP–Py in acetone solutions containing pyridine. Previous studies [11] suggest that the ligand exchange reaction is represented as

$$\text{ClCr(III)TPP–Ac} \underset{k_{Ac}}{\overset{k_1}{\rightleftharpoons}} [\text{ClCr(III)TPP}] + \text{Ac} \,,$$

$$[\text{ClCr(III)TPP}] + \text{Py} \underset{k_2}{\overset{k_{Py}}{\rightleftharpoons}} \text{ClCr(III)TPP–Py} \,,$$

where [ClCr(III)TPP] is the chromium(III) porphyrin free from the axial ligand yielded as an intermediate in the ligand exchange reaction. With the use of the steady-state approximation, d[ClCr(III)TPP]/dt=0, the reaction scheme described above leads to

$$k_{AP} = k_1 - \frac{k_{Ac}[Ac](k_1 - k_2)}{k_{Ac}[Ac] + k_2 + k_{Py}[Py]} \,, \tag{10}$$

where k_{Ac} is the rate constant for the decay of

Table 1
Kinetic parameters for ligand exchange reactions

	ClCr(III)TPP [a]	ClCr(III)TPP-Ac [b]
k_{Py} ($M^{-1}s^{-1}$)	5.9×10^4	7.3×10^4
k_{Ac} ($M^{-1}s^{-1}$)	4.2×10^2	7.8×10
k_1 (s^{-1})	–	1.4×10^2
k_2 (s^{-1})	–	2.7

[a] Rate constants determined from the decay of ClCr(III)TPP directly produced from ClCr(III)TPP–Py upon laser excitation.

[b] Rate constants determined from the decay of ClCr(III)TPP–Ac.

ClCr(III)TPP–Ac. The observed values of k_{AP} shown in fig. 4 are well interpreted in terms of eq. (10): k_{AP} increases with an increase in [Py] and levels off at large [Py] to give $k_{AP}(\infty)=k_1$ at an infinite concentration of pyridine. Eq. (10) is readily transformed to

$$\Sigma=(k_1-k_{AP})^{-1} = \frac{k_{Ac}[Ac]+k_2}{k_{Ac}[Ac](k_1-k_2)} + \frac{k_{Py}[Py]}{k_{Ac}[Ac](k_1-k_2)}, \qquad (11)$$

where $k_1=k_{AP}(\infty)=1.4\times10^2\ s^{-1}$. The plot of Σ versus [Py] gives a straight line. From the slope and intercept of the line and the equilibrium constant $K=k_1k_{Py}/k_{Ac}k_2=4.9\times10^4$, the rate constants are, respectively, determined as $k_{Ac}=78\ M^{-1}\ s^{-1}$, $k_{Py}=7.3\times10^4\ M^{-1}\ s^{-1}$, and $k_2=2.7\ s^{-1}$. The solid curve in fig. 4 is the calculated values of k_{AP} according to eq. (10) with the use of the rate constants, k_1, k_{Ac}, k_{Py}, and k_2 obtained above. The calculated values of k_{AP} are in good agreement with those obtained experimentally, suggesting that the ligand exchange reaction between ClCr(III)TPP–Ac and ClCr(III)TPP–Py takes place via [ClCr(III)TPP].

In table 1 are listed the rate constants, k_{Py}, k_{Ac}, k_1, and k_2, determined from the decay of ClCr(III)TPP and ClCr(III)TPP–Ac produced by laser photolysis of ClCr(III)TPP–Py in acetone solutions containing pyridine. The rate constants k_{Py} are in good accord. However, k_{Ac} obtained from the decay of ClCr(III)TPP–Ac is significantly smaller than that from the decay of ClCr(III)TPP yielded by photolysis of ClCr(III)TPP–Py. Since the difference in k_{Ac} far exceeds the experimental errors, [ClCr(III)TPP], which is a key intermediate in the ligand exchange reaction between ClCr(III)TPP–Ac and ClCr(III)-TPP–Py, is considered to have lower reactivity toward acetone than that directly produced from ClCr(III)TPP–Py upon laser excitation.

Further studies are in progress.

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