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Structure and Photochemistry of Nitrocobalt(III) Tetraphenylporphyrin with Axial Triphenylphosphine in Toluene Solutions

Haruna Adachi,[†,‡] Hiroyuki Suzuki,[†,‡] Yoshio Miyazaki,[§] Yasuhiro Iimura,[†] and Mikio Hoshino*[,†,‡]

The Institute of Physical and Chemical Research, Wako, Saitama 351-0198, Japan,
Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology,
Nagatsuda-machi, Midori-ku, Yokohama, Kanagawa 226-8502, Japan, and Department of
Chemistry, Faculty of Engineering, Toyo University, Kujirai, Kawagoe, Saitama 350-8585, Japan

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Thermal and photochemical reactions of nitroaquacobalt(III) tetraphenylporphyrin, $(NO_2)(H_2O)Co^{III}TPP$, have been investigated in toluene solutions containing triphenylphosphine, $P\phi_3$. It is found that $P\phi_3$ thermally abstracts an oxygen atom from the NO_2 moiety of $(NO_2)(H_2O)Co^{III}TPP$ with a rate constant 0.52 M^{-1} s^{-1}, resulting in the formation of nitrosylcobalt porphyrin, (NO)CoTPP. The 355-nm laser photolysis of $(NO_2)(H_2O)Co^{III}TPP$ at low concentrations of $P\phi_3$ ($<1.0 \times 10^{-4}$ M) gives $Co^{II}TPP$ and NO_2 as intermediates. The recombination reaction of $Co^{II}TPP$ and NO_2 initially forms the coordinately unsaturated nitritocobalt(III) tetraphenylporphyrin, $(ON–O)Co^{III}TPP$, which reacts with $P\phi_3$ to yield nitro(triphenylphosphine)cobalt(III) tetraphenylporphyrin, $(NO_2)(P\phi_3)Co^{III}TPP$. Subsequently, the substitution reaction of the axial $P\phi_3$ with H_2O leads to the regeneration of $(NO_2)(H_2O)Co^{III}TPP$. From the kinetic studies, the substitution reaction is concluded to occur via a coordinately unsaturated nitrocobalt(III) porphyrin, $(NO_2)Co^{III}TPP$. At higher concentrations of $P\phi_3$ ($>4 \times 10^{-3}$ M), $(NO_2)(H_2O)Co^{III}TPP$ reacts with $P\phi_3$ to form $(NO_2)(P\phi_3)Co^{III}TPP$: the equilibrium constant is obtained as $K = 4.3$. The X-ray structure analysis of $(NO_2)(P\phi_3)Co^{III}TPP$ reveals that the $P–Co–NO_2$ bond angle is 175.0(2)° and the bond length $Co–NO_2$ is 2.000(7) Å. In toluene solutions of $(NO_2)(H_2O)Co^{III}TPP$ containing $P\phi_3$ ($>4 \times 10^{-3}$ M), the major light-absorbing species is $(NO_2)(P\phi_3)Co^{III}TPP$, which yields (NO)CoTPP by continuous photolysis. The laser photolysis of $(NO_2)(P\phi_3)Co^{III}TPP$ gives $Co^{II}TPP$, NO_2, and $P\phi_3$ as initial products. The NO_2 molecule is suggested to be reduced by $P\phi_3$ to yield NO, and the reaction between NO and $Co^{II}TPP$ gives (NO)CoTPP. The quantum yield for the photodecomposition of $(NO_2)(P\phi_3)Co^{III}TPP$ is determined as 0.56.

Introduction

Cobalt(III) nitro complexes have been extensively studied as reagents for thermal dioxygen activation and oxygen atom transfer reactions.[1−7] For nitrocobalt(III) porphyrins, $(NO_2)Co^{III}P$, the nature of the sixth axial ligands has been known as one of the factors which regulate the reactivity of the nitro group toward oxidation of organic molecules.[8] Thus, the effects of the axial ligand of $(NO_2)Co^{III}P$ on oxygen atom transfer have been examined by the X-ray structure analysis, cyclic voltammetry, and the analysis of the oxidation products from alkenes.[8]

With regard to photochemistry, laser photolysis studies of nitroaquacobalt(III) tetraphenylporphyrin, $(NO_2)(H_2O)Co^{III}TPP$, have shown that the principal photoreaction is the dissociation of NO_2.[9] The products, NO_2 and $Co^{II}TPP$,

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* To whom correspondence should be addressed. Fax: 048-462-4668. Phone: 048-467-9426. E-mail: hoshino@postman.riken.go.jp.

[†] The Institute of Physical and Chemical Research.

[‡] Tokyo Institute of Technology.

[§] Toyo University.

(1) Tovrog, B. S.; Diamond, S. E.; Mares, F. *J. Am. Chem. Soc.* **1979**, *101*, 270−272.
(2) Tovrog, B. S.; Mares, F.; Diamond, S. E. *J. Am. Chem. Soc.* **1980**, *102*, 6616−6618.
(3) Diamond, S. E.; Mares, F.; Szalkiewicz, A.; Muccigrosso, D. A.; Solar, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 4266−4268.
(4) Elcolani, C.; Paoletti, A. M.; Pennesi, G.; Rossi, G. *J. Chem. Soc., Dalton Trans.* **1991**, 1317−1321.
(5) Muccigrosso, D. A.; Mares, F. Diamond, S. E.; Solar, J. P. *Inorg. Chem.* **1983**, *22*, 960−965.
(6) Mares, F.; Diamond, S. E.; Regina, F. J.; Solar, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3545−3552.
(7) Andrews, M. A.; Chang, T. C.-T.; Cheng, C.-W. F. *Organometallics*, **1985**, *94*, 268−274.
(8) Goodwin, J.; Bailey, R.; Pennington, W.; Rasberry, R.; Green, T.; Shasho, S.; Yongsavanh, M.; Echevarria, V.; Tiedeken, J. Brown, C.; Fromm, G,; Lyerly, S.; Watson, N.; Long, A.; De Nitto, N. *Inorg. Chem.* **2001**, *40*, 4217−4225.

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Table 1. Crystallographic Data for $(NO_2)(P\phi_3)Co^{III}TPP\cdot CHCl_3$

formula $CoCl_3PO_2N_5C_{63}H_{44}$	$Z = 4$
cryst color, habit: dark violet, plate	fw = 1099.34
$a = 24.641(3)$ Å	$\lambda = 1.541\ 78$ Å
$b = 9.6405(5)$ Å	μ(Cu Kα) = 47.42 cm^{-1}
$c = 21.724(1)$ Å	$T = 24.5$ °C
cryst system:^{a} orthorhombic	$\rho_{calcd} = 1.415$ g cm^{-3}
space group $Pca2_1$ (No. 29)	$R^b = 0.050$
$V = 5160.6(7)$ Å^3	$R_w{}^c = 0.063$

^{a} $\alpha = \beta = \gamma = 90°$. ^{b} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.046$. ^{c} $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2\}^{1/2} = 0.056$.

recombine to give nitritocobalt(III) tetraphenylporphyrin, $(O{=}NO)Co^{III}TPP$, as an intermediate, which eventually returns to $(NO_2)(H_2O)Co^{III}TPP$.[9]

In this paper, we describe (1) thermal and photochemical reactions of $(NO_2)(H_2O)Co^{III}TPP$ in the presence of triphenylphosphine ($P\phi_3$), (2) the structure of nitro(triphenylphosphine)cobalt(III) tetraphenylporphyrin, $(NO_2)(P\phi_3)Co^{III}TPP$, studied by X-ray crystallography, and (3) photodissociation of NO_2 from $(NO_2)(P\phi_3)Co^{III}TPP$.

Experimental Section

Reagent grade chloroform, toluene, benzene, and triphenylphosphine were used without further purification. Nitric oxide gas (99.99%) was supplied from Takachiho Chem. Ind. Ltd.

Nitroaquacobalt(III) tetraphenylporphyrin, $(NO_2)(H_2O)Co^{III}TPP$, was synthesized and purified according to the method described previously.[9] Nitro(triphenylphosphine)cobalt(III) tetraphenylporphyrin, $(NO_2)(P\phi_3)Co^{III}TPP$, was synthesized by the reaction of 147 mg of $(NO_2)(H_2O)Co^{III}TPP$ and 320 mg of $P\phi_3$ in 100 mL of chloroform at room temperature. The reaction finished within a few minutes after mixing $(NO_2)(H_2O)Co^{III}TPP$ and $P\phi_3$. After removal of residual solids by filtration, *n*-hexane was added slowly on the surface of the chloroform solution. $(NO_2)(P\phi_3)Co^{III}TPP\cdot CHCl_3$ was obtained as dark violet crystals: the yield is ca. 50%. The crystals were used for the chemical analysis and the determination of the molecular structure by X-ray crystallography. Anal. Calcd for $(NO_2)(P\phi_3)Co^{III}TPP\cdot CHCl_3$: C, 68.83; H, 4.03; N, 6.37. Found: C, 68.32; H, 3.98; N, 6.25.

Diffraction data for a single crystal of $(NO_2)(P\phi_3)Co^{III}TPP\cdot CHCl_3$ were collected at 297 K on an Enraf-Nonius CAD4 diffractometer, equipped with graphite-monochromated Cu Kα radiation. In Table 1 are listed the crystallographic data. The structure was solved by direct methods and refined by full-matrix least-squares techniques. $(NO_2)(P\phi_3)Co^{III}TPP\cdot CHCl_3$ is crystallized in the acentric space group $Pca2_1$ and is polar in the *c*-axis direction. A typical example of the external shape of the crystal is shown in Figure 1S of the Supporting Information. The absolute structure was determined by two methods, an *R*-factor ratio test[10] and a comparison between $F_{o\ diff}$ $(=|F_o(+)| - |F_o(-)|)$ and $F_{c\ calc}$ $(=|F_c(+)| - |F_c(-)|)$. The ratios between $R_w = 0.062$ and $R_{w-inv} = 0.109$ for inverted absolute structure indicate the correct absolute structure at more than 99.9% significance level. Further, as shown in Table 1S of the Supporting Information, the signs of $F_{c\ calc}$ values were consistent with those of $F_{o\ diff}$ when the significant difference $(=|F_{c\ calc}|/\{\sigma[F_o(+)]^2 + \sigma[Fo(-)]^2\}^{1/2})$ is larger than 1.61 Bijvoit mates. Thus, the atomic parameters in Table 1S of the Supporting Information give the correct absolute structure, which corresponds to the external shape of the crystal shown in Figure 1S of the Supporting Information. The experimental details have been listed in the CIF file of the Supporting Information.

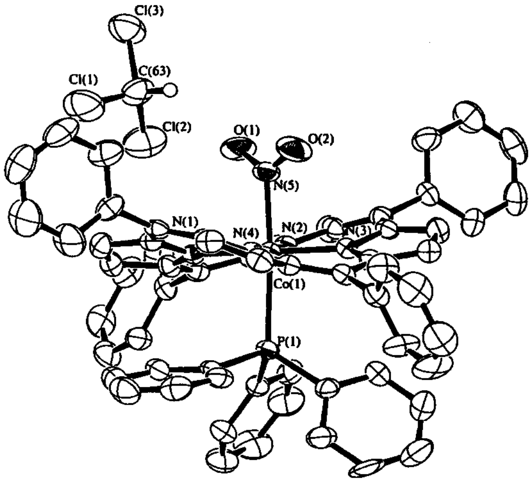

Figure 1. Molecular structure of $(NO_2)(P\phi_3)Co^{III}TPP\cdot CHCl_3$. Hydrogen atoms and a solvent molecule, $CHCl_3$, are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg)

atoms	dist	atoms	angle
Co−N1	1.949(6)	N1−Co−P1	87.0(2)
Co−N2	1.968(6)	N2−Co−P1	95.7(2)
Co−N3	1.936(6)	N3−Co−P1	93.4(2)
Co−N4	1.918(6)	N4−Co−P1	88.3(2)
Co−N5	2.000(7)	N5−Co−P1	175.0(2)
Co−P1	2.424(2)	Co−N5−O1	118.9(5)
N5−O1	1.212(8)	Co−N5−O2	117.2(6)
N5−O2	1.210(9)	N1−Co−N5	89.5(3)
C5−C21	1.51(1)	N2−Co−N5	87.8(3)
C10−C27	1.498(10)	N3−Co−N5	90.1(3)
C15−C33	1.48(1)	N4−Co−N5	88.2(3)
C20−C39	1.48(1)	O1−N5−O2	124.0(7)

Absorption spectra were recorded on a Hitachi 330 spectrophotometer. Water contents in toluene were measured with a Karl Fischer titrator (AQ-7, Hiranuma Ind. Co.). Continuous photolysis was made by a 250 W mercury lamp (Ushio 250 D) with a cutoff filter ($\lambda > 350$ nm). Laser photolysis studies were carried out with the use of a Nd:YAG laser, model HY 500 from JK Laser Ltd., equipped with second (532 nm), third (355 nm), and fourth (266 nm) harmonic generators. The detection systems of the transient spectra were described elsewhere.[11]

Results

Molecular Structure of $(NO_2)(P\phi_3)Co^{III}TPP\cdot CHCl_3$. Figure 1 shows the molecular structure of $(NO_2)(P\phi_3)Co^{III}TPP\cdot CHCl_3$ determined by X-ray crystallography. The atomic coordinates, anisotropic displacement parameters, bond lengths, and bond angles are listed in the CIF file of the Supporting Information.

In Table 2 are listed the selected interatomic distances. The Co−P distance is determined as 2.424(2) Å. The $P{-}Co{-}N_{NO_2}$ bond angle is 175.0(2)°, indicating that the $P{-}Co{-}N_{NO_2}$ bond is almost linear. The O−N−O angle of the NO_2 moiety in $(NO_2)(P\phi_3)Co^{III}TPP$ is 124.0(7)°, in moderate agreement with that (115.4°) in (NO_2)(Lut)-

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(9) Seki, H.; Okada, K.; Iimura, Y.; Hoshino, M. *J. Phys. Chem. A* **1997**, *101*, 8174−8178.

(10) Hamilton, W. C. *Statistics in Physical Science*; Ronald Press: New York, 1964; pp 157−161.

(11) Adachi, H.; Sonoki, H.; Hoshino, M.; Wakasa, M.; Hayashi, H.; Miyazaki, Y. *J. Phys. Chem. A* **2000**, *105*, 392−398.

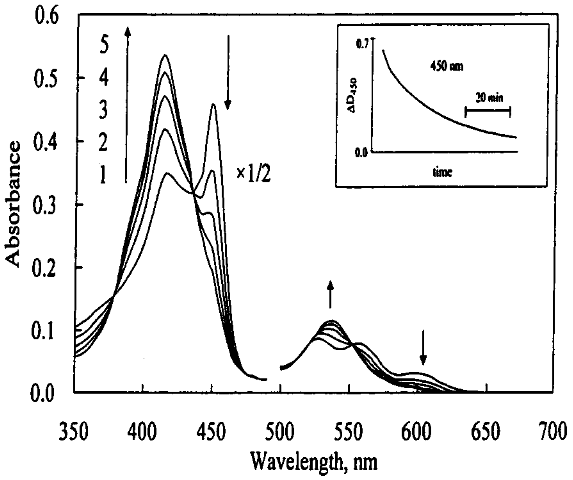

Figure 2. Time-dependent absorption spectral changes observed for the toluene solution of 1.01×10^{-5} M $(NO_2)(H_2O)Co^{III}TPP$ and 2.1×10^{-3} M $P\phi_3$: (1) 0 min; (2) 8 min; (3) 16 min; (4) 24 min; (5) 32 min. The inset shows the time profile of the absorbance change, ΔD_{450}, monitored at 450 nm.

$Co^{III}TPP$ (Lut = lutidine).[12] We have measured the O−N−O angles of $(NO_2)(H_2O)Co^{III}TPP$ and $(NO_2)(DMAPy)Co^{III}TPP$ (DMAPy = 4-(dimethylamino)pyridine): the former gives 122.8(3)°, and the latter 120.8°.[13] These values are in good accord with that obtained from $(NO_2)(P\phi_3)Co^{III}TPP$.

Thermal Reaction of $(NO_2)(H_2O)Co^{III}TPP$ with Triphenylphosphine. The absorption peaks of $(NO_2)(H_2O)Co^{III}TPP$ in toluene are located at 417, 525, and 555 nm. With an increase in $[P\phi_3]$, the absorption peaks of $(NO_2)(H_2O)Co^{III}TPP$ decrease in intensity and new peaks appear at 450, 560, and 598 nm owing to the formation of $(NO_2)(P\phi_3)Co^{III}TPP$. The absorption spectral changes observed for toluene solutions of $(NO_2)(H_2O)Co^{III}TPP$ at various concentrations of $P\phi_3$ are shown in Figure 2S of the Supporting Information. Since the spectral changes exhibit isosbestic points, the equilibrium reaction is expressed as

$$(NO_2)(H_2O)Co^{III}TPP + P\phi_3 \overset{K}{\rightleftharpoons} (NO_2)(P\phi_3)Co^{III}TPP + H_2O \tag{1}$$

Here K is the equilibrium constant. From eq 1, the absorbance, D_λ, at a wavelength λ is expressed as a function of $[P\phi_3]$

$$Y = (D_\lambda^0 - D_\lambda)/(D_\lambda \_ D_\lambda^\infty) = K[P\phi_3]/[H_2O] \tag{2}$$

where D_λ^0 and D_λ^∞ are the absorbances at $[P\phi_3] = 0$ and at an "infinite" concentration of $P\phi_3$, respectively. The plot of Y vs $[P\phi_3]$ gives a straight line with an intercept at the origin. The slope of the line affords $K/[H_2O] = 980$ M^{-1}. The concentration of water in toluene, 4.4×10^{-3} M, leads to $K = 4.3$. During the course of this study, we found that $(NO_2)(H_2O)Co^{III}TPP$ thermally reacts with $P\phi_3$ and eventually produces nitrosylcobalt tetraphenylporphyrin, $(NO)Co^{II}TPP$.

Figure 2 shows the time-dependent absorption spectral changes observed for a toluene solution of $(NO_2)(H_2O)Co^{III}TPP$ and 2.1×10^{-3} M $P\phi_3$. The absorption spectrum measured at $t = 0$ indicates that the solution is a mixture of $(NO_2)(H_2O)Co^{III}TPP$ and $(NO_2)(P\phi_3)Co^{III}TPP$. The absorption bands of $(NO_2)(H_2O)Co^{III}TPP$ and $(NO_2)(P\phi_3)Co^{III}TPP$ decrease in intensity with time and ultimately change to those with the peaks located at 413 and 535 nm. The molar absorption coefficients (ϵ) of this product were calculated from the absorbances of the product and the initial concentration of $(NO_2)(H_2O)Co^{III}TPP$: $\epsilon = 1.15 \times 10^5$ M^{-1} cm^{-1} at 413 and $\epsilon = 1.34 \times 10^4$ M^{-1} cm^{-1} at 535 nm. This product is identified as (NO)CoTPP from the following facts.

Authentic (NO)CoTPP was made by nitrosylation of $Co^{II}TPP$ in toluene. The absorption spectrum and the molar absorption coefficients of (NO)CoTPP ($\epsilon = 1.08 \times 10^5$ M^{-1} cm^{-1} at 415 nm and $\epsilon = 1.31 \times 10^4$ M^{-1} cm^{-1} at 535 nm) are almost identical with those of the product mentioned above.

The addition of 10^{-2} M $P\phi_3$ to the toluene solution of (NO)CoTPP exhibits no change in the absorption peaks and molar absorption coefficients, indicating that $P\phi_3$ is not coordinated to the axial position of (NO)CoTPP. The laser photolysis of the product from $(NO_2)(H_2O)Co^{III}TPP$ and $P\phi_3$ confirms that the transient observed immediately after the pulse is $Co^{II}TPP$, which decays according to second-order kinetics: the bimolecular rate constant is obtained as 2.3×10^9 M^{-1} s^{-1}. This value is strictly in good accord with that (2.2×10^9 M^{-1} s^{-1}) obtained from the laser photolysis of authentic (NO)CoTPP. It has been well established that the photolysis of (NO)CoTPP gives NO and $Co^{II}TPP$, which return to (NO)CoTPP by the recombination reaction.[14] From these results, we conclude that (NO)CoTPP is the product obtained from the thermal reaction between $(NO_2)(H_2O)Co^{III}TPP$ and $P\phi_3$.

As shown in Figure 2, the spectral change of the thermal reaction of $(NO_2)(H_2O)Co^{III}TPP$ in the presence of $P\phi_3$ exhibits the isosbestic point until the end of the reaction. This implies that the rate for achievement of equilibrium (1) is much faster than the rate for the formation of (NO)CoTPP. The decay of $(NO_2)(P\phi_3)Co^{III}TPP$ was monitored at 450 nm. The absorbance, D_{450}, at 450 nm was found to decay according to first-order kinetics with a rate constant k_{obsd}. With the use of the absorbances $D_{450}(0)$ at $t = 0$ and $D_{450}(\infty)$ at $t = \infty$, we obtain

$$\Delta D_{450} = \Delta D^0_{450} \exp(-k_{obsd}t) \tag{3}$$

where $\Delta D_{450} = D_{450} - D_{450}(\infty)$ and $\Delta D^0_{450} = D_{450}(0) - D_{450}(\infty)$.

Figure 3 shows the plot of the rate constant, k_{obsd}, represented as a function of $[P\phi_3]$. The k_{obsd} value initially increases with an increase in $[P\phi_3]$ and levels off at $[P\phi_3] > 8.0 \times 10^{-3}$ M. As mentioned above, the species in the solution are $(NO_2)(H_2O)Co^{III}TPP$ and $(NO_2)(P\phi_3)Co^{III}TPP$. Thus, the possible reaction pathway for the formation of (NO)CoTPP is the oxo-transfer reaction from either $(NO_2)(H_2O)Co^{III}TPP$ and/or $(NO_2)(P\phi_3)Co^{III}TPP$ to $P\phi_3$. On the

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[12] Kaduk, J. A.; Scheit, W. R. *Inorg. Chem.* **1974**, *13*, 1875−1880.
[13] Unpublished results.
[14] Hoshino, M.; Kogure, M. *J. Phys. Chem.* **1989**, *93*, 5478−5484.

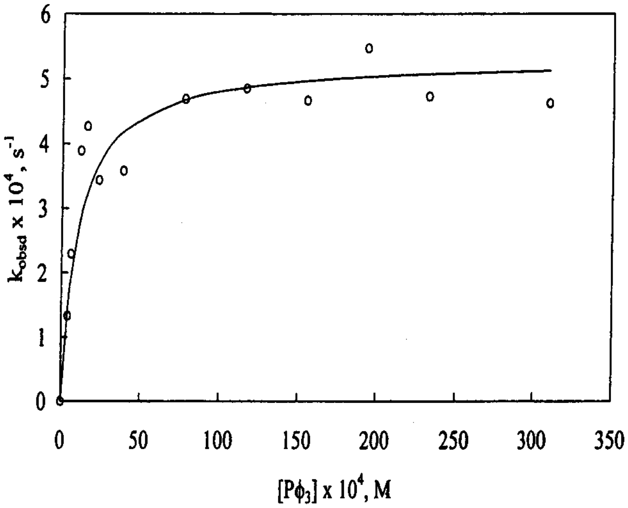

Figure 3. Plot of the rate constants, k_{obsd}, represented as a function of [Pϕ_3]. The solid line is the calculated one according to the reaction scheme (see text).

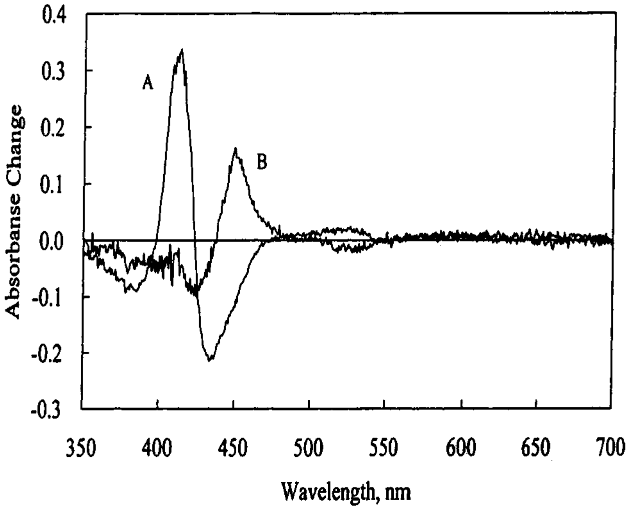

Figure 4. Transient absorption spectra observed for the toluene solution of 1.2×10^{-5} M $(NO)_2(H_2O)Co^{III}TPP$, 1.0×10^{-4} M [Pϕ_3], and 4.4×10^{-3} M H_2O at (A) 30 ns and (B) 1 ms after the 355 nm laser pulse.

basis of the fact that k_{obsd} levels off at higher concentrations of Pϕ_3, $(NO_2)(H_2O)Co^{III}TPP$ is considered to be responsible for the formation of (NO)CoTPP. The reaction mechanism for the formation of (NO)CoTPP is given by

$$(NO_2)(H_2O)Co^{III}TPP + P\phi_3 \xrightarrow{k} (NO)CoTPP + O{=}P\phi_3 + H_2O \quad (4)$$

The IR spectrum of the reaction mixture exhibited intense absorption peaks at 1121 and 1178 cm^{-1} in chloroform due to the formation of O=Pϕ_3.[15]

From eqs 1 and 4, the rate constant, k_{obsd} for the decay of $(NO_2)(P\phi_3)Co^{III}TPP$ is formulated as

$$k_{obsd} = k[P\phi_3]/(1 + K[P\phi_3]/[H_2O]) \quad (5)$$

The $K/[H_2O]$ value in eq 5 has already been determined as 9.8×10^2 M^1 from the absorption spectroscopic measurements. The rate constant k is obtained as 0.52 M^{-1} s^{-1} with curve fitting of k_{obsd} using eq 5, $K/[H_2O]$, and a least-squares fitting program.

Continuous Photolysis and Laser Photolysis of $(NO_2)(H_2O)Co^{III}TPP$ and $(NO_2)(P\phi_3)Co^{III}TPP$. The 355-nm laser photolysis of $(NO_2)(H_2O)Co^{III}TPP$ was carried out in the presence of Pϕ_3 at low ([Pϕ_3] < 2.0×10^{-4} M) and high ([Pϕ_3] > 4.0×10^{-3} M) concentration range. $(NO_2)(H_2O)Co^{III}TPP$ is a major species (>91%) when [Pϕ_3] < 1.2×10^{-4} M. However, $(NO_2)(P\phi_3)Co^{III}TPP$ becomes predominant (>80%) when [Pϕ_3] > 4.0×10^{-3} M.

Figure 4 shows the transient absorption spectra observed for the toluene solution of 1.2×10^{-5} M $(NO_2)(H_2O)Co^{III}TPP$ and 1.0×10^{-4} M Pϕ_3 at 30 ns and 1.0 ms after the pulse. The transient spectrum detected at 30 ns is in good accord with the difference spectrum ($Co^{II}TPP$ minus $(NO_2)(H_2O)Co^{III}TPP$). Thus, the initial photochemical event is the dissociation of NO_2 from $(NO_2)(H_2O)Co^{III}TPP$. At 1.0 ms after the pulse, the transient spectrum exhibits a positive peak at 450 nm and negative one at 425 nm. Since the spectrum agrees well with the difference spectrum ($(NO_2)(P\phi_3)Co^{III}TPP$ minus $(NO_2)(H_2O)Co^{III}TPP$), the transient species is ascribed to $(NO_2)(P\phi_3)Co^{III}TPP$. The transient detected at 1 ms decays according to first-order kinetics to regenerate $(NO_2)(H_2O)Co^{III}TPP$.

The decay of $Co^{II}TPP$ monitored at 410 nm follows second-order kinetics, indicating that $Co^{II}TPP$ principally reacts with NO_2 to give $(O{=}NO)Co^{III}TPP$.[9] The second-order rate constant between $Co^{II}TPP$ and NO_2 is obtained as $(2.6 \pm 0.2) \times 10^9$ M^{-1} s^{-1}, invariant to the triphenylphosphine concentration in the range 0 < [Pϕ_3] < 1.0×10^{-4} M.

Thus, the chemical reactions of the present system are represented as follows:

$$(NO_2)(H_2O)Co^{III}TPP \xrightarrow{h\nu} Co^{II}TPP + NO_2 + H_2O \quad (6)$$

$$Co^{II}TPP + NO_2 \rightarrow (O{=}N{-}O)Co^{III}TPP \quad (7)$$

$$(O{=}N{-}O)Co^{III}TPP + P\phi_3 \rightarrow (NO_2)(P\phi_3)Co^{III}TPP \quad (8)$$

$$(NO_2)(P\phi_3)Co^{III}TPP \underset{k_b}{\overset{k_f}{\rightleftarrows}} (NO_2)Co^{III}TPP + P\phi_3 \quad (9)$$

$$(NO_2)Co^{III}TPP + H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} (NO_2)(H_2O)Co^{III}TPP \quad (10)$$

$Co^{II}TPP$ produced by photolysis of $(NO_2)(H_2O)Co^{III}TPP$ reacts with NO_2 to yield coordinately unsaturated nitritocobalt(III) tetraphenylporphyrin, $(O{=}NO)Co^{III}TPP$.[9] The coordination of Pϕ_3 to $(O{=}NO)Co^{III}TPP$ presumably accelerates the intramolecular rearrangement of the O=NO moiety, resulting in the facile formation of $(NO_2)(P\phi_3)Co^{III}TPP$. Equations 9 and 10 indicate that $(NO_2)(P\phi_3)Co^{III}TPP$ decays via a coordinately unsaturated intermediate, $(NO_2)Co^{III}TPP$, which eventually regenerates $(NO_2)(H_2O)Co^{III}TPP$ by the axial coordination of H_2O.

The decay of $(NO_2)(P\phi_3)Co^{III}TPP$ monitored at 450 nm strictly follows first-order kinetics with a rate constant k_r.

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(15) *The Aldrich Library of FT-IR Spectra*, 2nd ed.; Aldrich Chemical: Milwaukee, WI, 1997; Vol. 2, p 559.

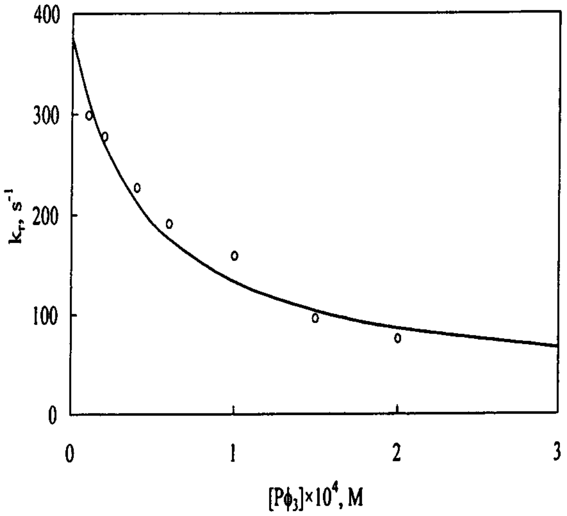


Figure 5. Rate constants, k_r, represented as a function of $[P\phi_3]$.

Scheme 1

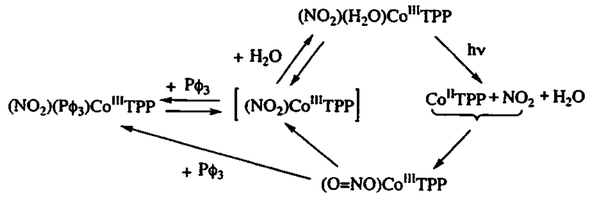


Figure 5 shows the rate constant k_r represented as a function of $[P\phi_3]$. The k_r values gradually decrease with an increase in $[P\phi_3]$. From eqs 9 and 10 and the steady-state approximation with regard to $(NO_2)Co^{III}TPP$, the rate constant k_r for the decay of $(NO_2)(P\phi_3)Co^{III}TPP$ is expressed as

$$k_r = (k_2k_b[P\phi_3] + k_fk_1[H_2O])/(k_b[P\phi_3] + k_1[H_2O]) \tag{11}$$

Further, the equilibrium constant K in eq 1 is rewritten as

$$K/[H_2O] = (k_b/k_f)(k_2/k_1[H_2O]) = 9.8 \times 10^2\ M^{-1} \tag{12}$$

Thus, eq 11 is transformed to

$$k_r = (k_fk_1[H_2O])\ (1 + 9.8 \times 10^2[P\phi_3])/(k_b[P\phi_3] + k_1[H_2O]) \tag{13}$$

From the curve fitting of k_r with the use of eq 13 and a least-squares fitting program, the rate constant, k_f, and the ratio, $k_b/k_1[H_2O]$, are determined as $k_f = 3.76 \times 10^2$ s^{-1} and $k_b/k_1[H_2O] = 2.1 \times 10^4$ M^{-1}, respectively. From k_f, $k_b/k_1[H_2O]$, and eq 12, we obtain $k_2 = 17.5$ s^{-1}, which gives $k_f/k_2 = 2.1 \times 10$. The ratio k_b/k_1 is calculated as 9.2×10 from $k_b/k_1[H_2O] = 2.1 \times 10^4$ M^{-1} and $[H_2O] = 4.4 \times 10^{-3}$ M in toluene used in this study. These results are summarized as (1) $P\phi_3$ reacts with the coordinately unsaturated (NO_2)-$Co^{III}TPP$ ca. 10^2 times faster than H_2O and (2) the rate constant for the dissociation of $P\phi_3$ from $(NO_2)(P\phi_3)$-$Co^{III}TPP$ is ca. 20 times larger than that of H_2O from $(NO_2)(H_2O)Co^{III}TPP$. In Scheme 1 are described the photochemical reaction processes of $(NO_2)(H_2O)Co^{III}TPP$ in the presence of low concentrations of $P\phi_3$.

The observation that $(NO_2)(H_2O)Co^{III}TPP$ in toluene at low concentrations of $P\phi_3$ slowly changes to $(NO)Co^{III}TPP$ by continuous photolysis suggests that, as will be mentioned later, NO_2 in eq 6 is partly reduced by $P\phi_3$ to NO, which reacts with $Co^{II}TPP$ to produce $(NO)Co^{III}TPP$.

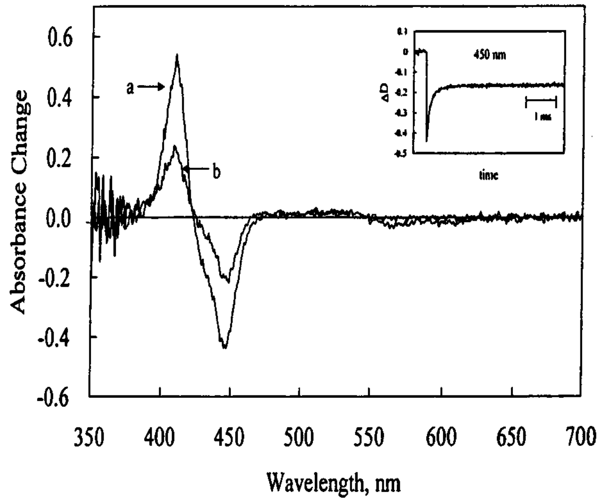


Figure 6. Transient absorption spectra observed for the toluene solution of 1.2×10^{-5} M $(NO)_2(P\phi_3)Co^{III}TPP$ and 1.9×10^{-2} M $[P\phi_3]$ at (a) 30 ns and (b) 600 μs after the 355 nm laser pulse. The inset presents the absorbance change, ΔD, measured at 450 nm after the laser pulse.

Continuous photolysis of $(NO_2)(P\phi_3)Co^{III}TPP$ in toluene at higher concentrations of $P\phi_3$ ($>4 \times 10^{-3}$ M) was carried out with the mercury lamp. As described above, the thermal reaction takes place to yield (NO)CoTPP. Thus, the photochemical reaction of $(NO_2)(P\phi_3)Co^{III}TPP$ in toluene was examined immediately after mixing $(NO_2)Co^{III}TPP$ and $P\phi_3$ to minimize the effects of the thermal reaction.

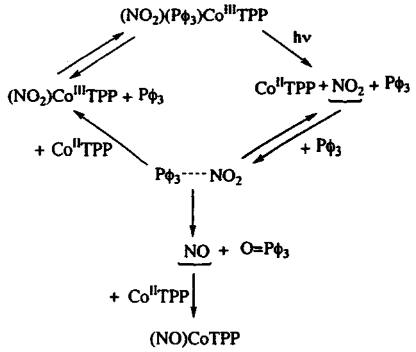
Figure 3S of the Supporting Information shows the absorption spectral changes observed for a toluene solution of 1.2×10^{-5} M $(NO_2)(P\phi_3)Co^{III}TPP$ in the presence of 1.9×10^{-2} M $P\phi_3$ upon irradiation with the mercury lamp. The absorption peaks of $(NO_2)(P\phi_3)Co^{III}TPP$ located at 450, 560, and 600 nm decrease in intensity with an increase in the irradiation time, and new peaks appear at 410 and 540 nm with isosbestic points at 370, 440, and 550 nm. The photochemical reaction completed within 10 s irradiation. The absorption spectrum of the photoproduct is identical with that of (NO)CoTPP. Since the thermal reaction of (NO_2)-$(P\phi_3)Co^{III}TPP$ in toluene is negligible at 10 s, the observed spectral changes in Figure 3S are concluded to be mostly caused by the photochemical reaction.

Figure 6 shows the transient absorption spectra observed for the toluene solution of 1.2×10^{-5} M $(NO_2)(P\phi_3)$-$Co^{III}TPP$ and 1.9×10^{-2} M $P\phi_3$. The transient spectrum detected at 30 ns after the pulse is identical with the difference spectrum ($Co^{II}TPP$ minus $(NO_2)(P\phi_3)Co^{III}TPP$). The photochemical reaction occurring within the duration of the laser pulse (20 ns) is represented by

$$(NO_2)(P\phi_3)Co^{III}TPP + h\nu \rightarrow Co^{II}TPP + NO_2 + P\phi_3 \tag{14}$$

On the other hand, the transient spectrum observed at 0.6 ms is in good agreement with the difference spectrum ((NO)CoTPP minus $(NO_2)(P\phi_3)Co^{III}TPP$). This result sug-

Scheme 2



gests that NO_2 is reduced by $P\phi_3$ to yield NO. Subsequently, the recombination reaction of $Co^{II}TPP$ and NO forms (NO)CoTPP.

$$NO_2 + P\phi_3 \rightarrow NO + O{=}P\phi_3 \tag{15}$$

$$NO + Co^{II}TPP \rightarrow (NO)CoTPP \tag{16}$$

The absorption spectrum of $(NO_2)(P\phi_3)Co^{III}TPP$ has a characteristic peak at 450 nm. Thus the absorbance change, ΔD_{450}, at 450 nm after the pulse is monitored for investigation of the formation mechanism of (NO)CoTPP. As shown in the inset of Figure 6, the initial bleaching, $\Delta D_{450}(L,0)$, at 450 nm immediately after the pulse exhibits the recovery of the absorbance change to give $\Delta D_{450}(L,\infty)$ at an “infinite” time. From $\Delta D_{450}(L,0)$ and $\Delta D_{450}(L,\infty)$, we can determine the initial concentration of $Co^{II}TPP$, $[Co^{II}TPP]_0$, and the final concentration of (NO)CoTPP, $[(NO)CoTPP]_\infty$. The ratio, $R = [(NO)CoTPP]_\infty/[Co^{II}TPP]_0$, is expressed as

$$R = \{\Delta D_{450}(L,\infty)/\Delta D_{450}(L,0)\}\{(\epsilon_{PCo} - \epsilon_{Co^{II}})/(\epsilon_{PCo} - \epsilon_{NOCo})\} \tag{17}$$

Here ϵ_{PCo}, $\epsilon_{Co^{II}}$, and ϵ_{NOCo} are the molar absorption coefficients at 450 nm of $(NO_2)(P\phi_3)Co^{III}TPP$, $Co^{II}TPP$, and (NO)CoTPP, respectively: $\epsilon_{PCo} = 1.3 \times 10^5$ M^{-1} cm^{-1}; $\epsilon_{Co^{II}} = 9.7 \times 10^3$ M^{-1} cm^{-1}; $\epsilon_{NOCo} = 3.0 \times 10^4$ M^{-1} cm^{-1}. With an increase in $[P\phi_3]$, the ratio, R, asymptotically increases to a limiting value 0.60 (Figure 4S of the Supporting Information). This fact indicates that $Co^{II}TPP$ partly (ca. 40%) returns to $(NO_2)(P\phi_3)Co^{III}TPP$ even at an “infinite” concentration of $P\phi_3$. The following reaction is assumed to occur:

$$P\phi_3 + NO_2 \rightleftarrows P\phi_3 \cdots NO_2 \rightarrow P\phi_3{=}O + NO \tag{18}$$

NO_2 molecules are trapped by $P\phi_3$ to form a complex, $P\phi_3 \cdots NO_2$, which gives NO and $O{=}P\phi_3$. The assumption that the complex $P\phi_3 \cdots NO_2$ reacts with $Co^{II}TPP$ explains the regeneration of $(NO_2)(P\phi_3)Co^{III}TPP$.

$$P\phi_3 \cdots NO_2 + Co^{II}TPP \rightarrow (NO_2)Co^{III}TPP + P\phi_3 \tag{19}$$

The coordinately unsaturated $(NO_2)Co^{III}TPP$ in eq 19 readily reacts with $P\phi_3$, returning to $(NO_2)(P\phi_3)Co^{III}TPP$. The photochemistry of $(NO_2)(P\phi_3)Co^{III}TPP$ is represented in Scheme 2.

The quantum yield for the photodissociation of NO_2 from $(NO_2)(P\phi_3)Co^{III}TPP$ was measured with the use of the 355 nm laser photolysis technique.[16] The yield, ϕ, for the formation of $Co^{II}TPP$ is represented as

$$\phi = \Delta D_a(\Delta\epsilon_a)^{-1}(I_{abs})^{-1} \tag{20}$$

where ΔD_a and $\Delta\epsilon_a$ are respectively the absorbance change measured at 410 nm immediately after the pulse and the difference in the molar absorption coefficient between $(NO_2)(P\phi_3)Co^{III}TPP$ and $Co^{II}TPP$ at 410 nm and I_{abs} stands for the number of photons absorbed. For determination of I_{abs}, we used a benzene solution of zinc(II) tetraphenylporphyrin, ZnTPP, which has the absorbance identical with that of the toluene solution of $(NO_2)(P\phi_3)Co^{III}TPP$ at 355 nm. The triplet yield, ϕ_T, of ZnTPP is expressed as

$$\phi_T = \Delta D_T(\Delta\epsilon_T)^{-1}(I_{abs})^{-1} \tag{21}$$

Here ΔD_T and $\Delta\epsilon_T$ are respectively the absorbance change at 470 nm immediately after the pulse and the molar absorption coefficient of the triplet ZnTPP at 470 nm. From eqs 20 and 21, the quantum yield ϕ is formulated as

$$\phi = \phi_T(\Delta D_a/\Delta D_T)(\Delta\epsilon_T/\Delta\epsilon_a) \tag{22}$$

The yield for the formation of $Co^{II}TPP$ from $(NO_2)(P\phi_3)Co^{III}TPP$ is determined as 0.56 with the use of eq 22, $\phi_T = 0.83$, and $\Delta\epsilon_T = 7.3 \times 10^4$ M^{-1} cm^{-1} for ZnTPP.[17]

Discussion

The molecular structures of nitrocobalt(III) porphyrins reported hitherto have axial nitrogenous bases, and the bond lengths $Co{-}N_{NO_2}$ are 1.897−1.948 Å.[8,12,18] These values are much shorter than that (2.000(7) Å) obtained with $(NO_2)(P\phi_3)Co^{III}TPP$. The bond length $Co{-}P_{P\phi_3}$ in $(NO_2)(P\phi_3)Co^{III}TPP$ is determined as 2.424(2) Å, moderately in good accord with those of metalloporphyrins having axial tertiary phosphines: 2.425 Å for $Os^{II}{-}P$;[19] 2.523 Å for $V^{II}{-}P$;[20] 2.428 Å for $Ru^{II}{-}P$;[21] 2.415 Å for $Ru^{III}{-}P$;[22] 2.284 Å for $Fe^{II}{-}P$.[23]

The thermal reaction of $(Cl_2Py)CoTPP(NO_2)$ (Cl_2Py = 3,5-dichloropyridine) with $P\phi_3$ in dichloromethane containing $LiClO_4$ gives (NO)CoTPP and $O{=}P\phi_3$.[8] The coordination of pyridine derivatives has been found to decrease markedly the oxo-transfer reactivity of nitrocobalt(III) porphyrins. However, because of the complexity of the reaction system,

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(16) Hoshino, M.; Sonoki, H.; Miyazaki, Y.; Iimura, Y.; Yamamoto, K. *Inorg. Chem.* **2000**, *39*, 4850−3857.

(17) Hurley, J. K.; Sinai, N.; Linschitz, H. *Photochem. Photobiol.* **1983**, *38*, 9−14.

(18) Jene, P. G.; Ibers, J. A. *Inorg. Chem.* **2000**, *39*, 3823−3827.

(19) Che, C.-M.; Lai, T.-F.; Chung, W.-C.; Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1987**, *26*, 3907−3911.

(20) Oumous, H.; Lecomte, C.; Protas, J.; Poncet, J. L.; Barbe, J. M.; Guilard, R. *J. Chem. Soc., Dalton Trans.* **1984**, 2677−2682.

(21) Ariel, S.; Dolphin, D.; Domazetis, G.; James, B. R.; Leung, T. W.; Rettig, S. J.; Trotter, J.; Williams, G. M. *Can. J. Chem.* **1984**, *62*, 755−762.

(22) James, B. R.; Dolphin, D.; Leung, T. W.; Einstein, F. W. B.; Willis, A. C. *Can. J. Chem.* **1984**, *62*, 1238−1245.

(23) Sodano, P.; Simonneaux, G, Toupet, L. *J. Chem. Soc., Dalton Trans.* **1988**, 2615−2620.

the detailed mechanistic study has not yet been done.[8] We have carried out the kinetic studies on the reaction between $(NO_2)(H_2O)Co^{III}TPP$ and $P\phi_3$. The results are interpreted by assuming that (1) $P\phi_3$ thermally abstracts an oxygen atom from $(NO_2)(H_2O)Co^{III}TPP$ to yield (NO)CoTPP and $O{=}P\phi_3$ and (2) such oxo transfer does not occur from $(NO_2)(P\phi_3)Co^{III}TPP$. Presumably, the coordination of an electron-rich $P\phi_3$ molecule to the central cobalt(III) atom effectively reduces the oxidation ability of the NO_2 moiety in $(NO_2)(P\phi_3)Co^{III}TPP$, and thus, $(NO_2)(P\phi_3)Co^{III}TPP$ is unable to oxidize $P\phi_3$.

The laser photolysis studies of $(NO_2)(H_2O)Co^{III}TPP$ in toluene at the low concentrations of $P\phi_3$ ($<1.0 \times 10^{-4}$ M) revealed that $Co^{II}TPP$ was produced immediately after the pulse decays with the concomitant formation of $(NO_2)(P\phi_3)Co^{III}TPP$, which further reacts with water to regenerate $(NO_2)(H_2O)Co^{III}TPP$. From the kinetic studies, the substitution reaction of $P\phi_3$ in $(NO_2)(P\phi_3)Co^{III}TPP$ with H_2O is established to occur via a coordinately unsaturated $(NO_2)Co^{III}TPP$. The similar substitution reaction has been observed for the six-coordinate chromium(III) porphyrin: a coordinately unsaturated chromium(III) porphyrin is also a key intermediate in the ligand exchange reaction.[24−26]

The quantum yield for the formation of $Co^{II}TPP$ from $(NO_2)(P\phi_3)Co^{III}TPP$ is determined as 0.56. This value is much larger than the quantum yield (0.07) obtained with the photolysis of $(NO_2)(H_2O)Co^{III}TPP$ in benzene.[9] Probably, the photodissociation of NO_2 from $(NO_2)(P\phi_3)Co^{III}TPP$ becomes facile more than that from $(NO_2)Co^{III}TPP$ owing to the effects of the axial $P\phi_3$. It is suggested that the bond dissociation energy of $Co-N_{NO_2}$ in $(NO_2)(P\phi_3)Co^{III}TPP$ is smaller than that in $(NO_2)(H_2O)Co^{III}TPP$. In fact, the bond distance $Co-N_{NO_2}$ in $(NO_2)(P\phi_3)Co^{III}TPP$ is markedly longer than that in $(NO_2)(H_2O)Co^{III}TPP$.

Continuous photolysis of $(NO_2)(P\phi_3)Co^{III}TPP$ gives (NO)CoTPP as the photoproduct. From the laser photolysis studies, NO_2 produced by photolysis of $(NO_2)(P\phi_3)Co^{III}TPP$ is assumed to interact with $P\phi_3$ to form the complex $NO_2\cdots P\phi_3$, which undergoes intracomplex oxygen atom transfer to give NO and $O{=}P\phi_3$. The nitric oxide molecule, thus produced, was concluded to react with $Co^{II}TPP$, resulting in the formation of (NO)CoTPP.

Supporting Information Available: Table 1S, listing atomic parameters for the absolute structure analysis, a CIF file, listing details of crystallographic experiments, atomic coordinates, anisotropic displacement parameters, bond lengths, and bond angles, and Figures 1S−4S, presenting the external shape of the crystal, absorption spectra of $(NO_2)(H_2O)Co^{III}TPP$ in toluene containing $P\phi_3$, spectral changes observed for a mixture of $(NO_2)(H_2O)Co^{III}TPP$ and $(NO_2)(P\phi_3)Co^{III}TPP$ in toluene upon continuous photolysis, and the plot of R vs $[P\phi_3]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Yamaji, M.; Hama, Y.; Hoshino, M. *Chem. Phys. Lett.* **1990**, *165*, 309−314.

(25) Inamo, M.; Nakaba, H.; Nakajima, K.; Hoshino, M. *Inorg. Chem.* **2000**, *39*, 4417−4423.

(26) Inamo, M.; Hoshino, M. *Photochem. Photobiol.* **1999**, *70*, 596−601.