For the CNA–TCNE EDA complex, CT excitation produced transient absorption bands near 460 and 750 nm. Both appeared within 20 ps and decayed simultaneously within ~60 ps after excitation (Figure 2). We assign the band near 750 nm to the cyanoanthracene cation ($CNA^{+}\cdot$) and that near 460 nm to a composite of the tetracyanoethylene anion ($TCNE^{-}\cdot$) and $CNA^{+}\cdot$. Such an assignment follows from the absorption spectra (Figure 1) of $CNA^{+}\cdot$ ($\epsilon_{715} \approx 7700\ M^{-1}\ cm^{-1}$)[14] and $TCNE^{-}\cdot$ ($\epsilon_{435} \approx 7100\ M^{-1}\ cm^{-15}$)[15] generated electrochemically from CNA[16] and TCNE,[17] respectively, and from consideration of a superposition of these absorptions and the negative absorption arising from depopulation of the ground-state EDA complex ($\epsilon_{615} \approx 250\ M^{-1}\ cm^{-1}$).[18] The picosecond absorption data thus suggest the occurrence of the CT process:

$$\mathrm{CNA} + \mathrm{TCNE} \rightleftarrows [\mathrm{CNA\,TCNE}] \overset{h\nu_{CT}}{\rightleftarrows} [\mathrm{CNA}^{+}\cdot \mathrm{TCNE}^{-}\cdot]$$

where [CNA TCNE] is the ground-state EDA complex and $[CNA^{+}\cdot TCNE^{-}\cdot]$ is the radical-ion pair. Such a formulation represents in this study a confirmation of Mulliken theory, in which CT band excitation of the relatively nonpolar ground state produces an ion pair. Electron transfer within the EDA complex effectively occurs with the absorption of a photon. No evidence exists from the picosecond absorption data for an excited-state intermediate of the EDA complex.

The short lifetime observed for the transient absorptions in Figure 2 indicates that the radical-ion pair is formed and resides within the ground-singlet-state manifold during its lifetime.[19] The decay time is consistent with vibrational and solvent relaxation phenomena.[20] Since the transient absorption bands return to $\Delta A = 0$ within 60 ps after excitation, the radical-ion pair must react via rapid back electron transfer to regenerate the original EDA complex.

The IN–TCNE EDA complex also was investigated. CT band excitation (Figure 1) afforded two absorption bands (Figure 3) near 460 and 600 nm, which were assigned to $TCNE^{-}\cdot$ and the indene cation ($IN^{+}\cdot$),[21] respectively, and which appeared within the time duration of the laser pulse. No transient absorptions were apparent in the region between 640 and 770 nm within 0–500 ps after excitation. As the absorption bands of $TCNE^{-}\cdot$ and $IN^{+}\cdot$ disappeared within ~60 ps, the negative absorption arising from depopulation of the ground-state EDA complex became quite apparent in the spectral region from 420 to ~650 nm.[22] We detected no product that was irreversibly formed. The original EDA complex ultimately was regenerated to its initial concentration because the difference absorption spectrum returned to $\Delta A = 0$ within 500 ps.

The rapid decay of the $IN^{+}\cdot/TCNE^{-}\cdot$ pair indicates that it resides in the singlet manifold, but unlike the $CNA^{+}\cdot/TCNE^{-}\cdot$ pair, the appearance of negative absorption is evidence for an intermediate that subsequently regenerates the original EDA complex. This species does not absorb between 420 and 770 nm and could result from a one-bond formation between $IN^{+}\cdot$ and $TCNE^{-}\cdot$ to generate a metastable biradical or zwitterion.[23] We currently are investigating the absorption spectrum at $\lambda < 420$ nm in an effort to observe and identify the intermediate spectroscopically.

Acknowledgment. J.M.M., C.A., and J.K.K. thank the National Science Foundation for financial support.

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[17] See: Matsuzaki, S.; Mitsuishi, T.; Toyoda, K. *Chem. Phys. Lett.* **1982**, *91*, 296.

[18] For related arene–TCNE complexes, see: Figeys, H. P.; Wilmet-Devos, B. *Bull. Soc. Chim. Belg.* **1970**, *79*, 459.

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[22] Unlike the TCNE–CNA complex,[18] the extinction coefficient of the TCNE–IN complex ($\epsilon \approx 2000\ M^{-1}\ cm^{-1}$) is in the range of that of $TCNE^{-}\cdot$.[15] See Toncheva, V.; Velichkova, R.: Panaiotov, I. M. *Bull. Soc. Chim. Fr.* **1974**. 1033.

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NMR Studies of Ruthenium(II) Porphyrin π-Cation Radicals with Relevance to Horseradish Peroxidase Compound I

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Higher oxidation states of metalloporphyrins have been investigated[1] because they have structural relevances to the reaction intermediates formed in the oxidation of peroxidase and catalase by H_2O_2, compounds I and II, in the electron transfer reactions of cytochromes and in the photooxidattion of chlorophyll. As to the compound I of HRP (horseradish peroxidase), it is now described as ferryl (Fe^{IV}) porphyrin π-cation radical in which the electron spins on the iron d-orbitals and porphyrin π-orbitals are coupled to give a strongly broadened ESR spectrum[2] and, in contrast, the well-defined proton NMR spectrum[3,4] in the paramagnetically shifted region. One of the prevalent arguments on the electronic structures of compound I and related porphyrin π-cation radicals is the electron spin distribution on the porphyrin ring, especially at the meso carbon, from which the symmetry of the π-cation radical orbital (a_{1u} or a_{2u}) is readily discerned.[5] However, there have been quite limited studies on determination of spin distribution at the meso carbon in porphyrin π-cation radical.[1,5] We wish to report here the first NMR studies[6] of porphyrin π-cation radicals with $^2A_{1u}$ or $^2A_{2u}$ state and of these radicals incorporated into HRP. Resulting isotropic paramagnetic shifts for the porphyrin peripheral protons allowed us to determine

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[6] The NMR studies of *iron* porphyrin π-cation radicals where the paramagnetic center is placed at both metal (iron) and porphyrin ring have been reported. (a) Groves, J. T.; Haushalter, R. C.; Nakamura. M.; Nemo, T. E.; Evans. B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884–2886. (b) Phillippi, M. A.; Goff, H. M. *Ibid.* **1982**, *104*, 6026–6034.

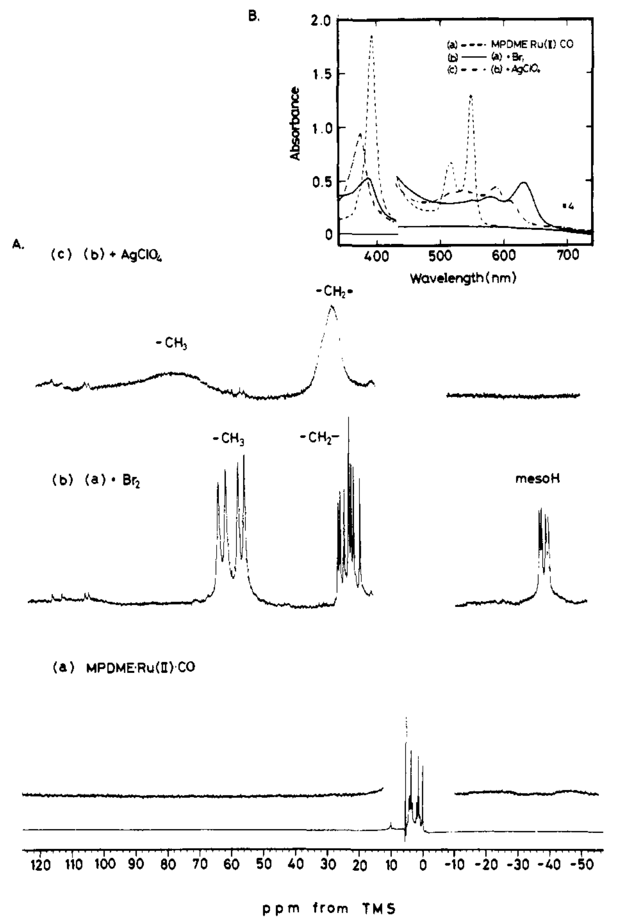

Figure 1. (A) Proton NMR spectra (300 MHz, 22 °C) of the CD_2Cl_2 solution of (MPDME)$Ru^{II}CO$ (ca. 5 mM) in diamagnetic state (a), its one-electron-oxidized π-cation radical [(MPDME)$Ru^{II}CO]^{+}\cdot Br^{-}$ (b), and [(MPDME)$Ru^{II}CO]^{+}\cdot ClO_4^{-}$ (c). (B) UV–visible spectra of the above compounds.

electron spin density distributions with sign on the prophyrin ring.

Ruthenium(II) porphyrin electrochemically undergoes the ring oxidation to form the π-cation radical for its monocarbonyl complex, while the metal oxidation occurs for the pyridine-ligated complex.[7] These oxidation processes and characterization of the oxidized products have been studied by UV–visible absorption, cyclic voltammetry, and ESR spectroscopic method.[7] We are concerned here with the NMR studies of the Ruthenium(II) porphyrin π-cation radical of which ESR spectrum is not detectable at room temperature. The π-cation radical was formed by the Br_2 oxidation of the CO complex of Ruthenium(II) mesoporphyrin IX dimethyl ester ((MPDME)$Ru^{II}CO$) in methylene chloride solution.[8] This process was followed by the characteristic UV–visible spectrum (Figure 1B) with absorption maxima at 626 and 386 nm, which resembles the spectra of the $^2A_{1u}$ type porphyrin π-cation radicals of other metalloporphyrin complexes.[1] A single ESR signal with $g = 2.003$ and 11-G peak to peak width was obtained at 77 K. The proton NMR spectrum of this radial, [(MPDME)$Ru^{II}CO]^{+}\cdot Br^{-}$, is illustrated in Figure 1A, spectrum b.[9,10] The paramagnetically shifted proton peaks are surprisingly sharp and well-resolved, presumably due to very short electron spin relaxation time.[11] This finding appears to correspond to the observation that the ESR spectrum was beyond detection at room temperature due to too much broadening. Br_2 oxidation of the octaethylporphyrin analogue (OEP)$Ru^{II}CO$ also yielded sharp proton resonances at 24 and 30 ppm, readily assignable to the CH_2 protons, and sharp single peak at −35 ppm arising from the meso protons. The unambiguious signal assignments for methyl and meso proton resonances of mesoporphyrin π-cation radical can be made as shown in Figure 1A.

Addition of ClO_4^- ion to the CD_2Cl_2 solution of [(MPDME)$Ru^{II}CO]^{+}\cdot Br^{-}$ or [(OEP)$Ru^{II}CO]^{+}\cdot Br^{-}$ afforded substantially broadened proton spectrum in the downfield region as exemplified in Figure 1A, spectrum c, and a single-line ESR spectrum with $g = 2.000$ and 12 G peak to peak width at room temperature and with 8-G width at 77 K. The UV-visible spectrum (Figure 1B) was characteristic of an $^2A_{2u}$ type porphyrin π-cation radical, which is formulated as [(MPDME)-$Ru^{II}CO]^{+}\cdot ClO_4^{-}$.[1d,e] It is to be noted in Figure 1A, spectrum c, that the meso proton signals were not detected in the upfield or downfield region, in sharp contrast to the spectrum of [(MPDME)$Ru^{II}CO]^{+}\cdot Br^{-}$. This was also confirmed by the NMR spectrum of [(OEP)$Ru^{II}CO]^{+}\cdot ClO_4^{-}$, which showed a broad CH_2 resonance at 33 ppm and the meso proton peak was beyond detection in the ±2000-ppm spectral region.

We have also examined the proton NMR of the π-cation radicals of other metalloporphyrin complexes. $OEPCo^{II}$ in CD_2Cl_2 solution generates the $^2A_{1u}$ type π-cation radical [(OEP)-$Co^{III}]^{2+}\cdot 2Br^{-}$ by Br_2 oxidation.[1] This radical did not afford the ESR signal at room temperature, while replacement of $2Br^-$ by $2ClO_4^-$ produced the $^2A_{2u}$ type radical, which was ESR detectable at room temperature.[1] The proton NMR of [(OEP)$Co^{III}]^{2+}\cdot 2Br^{-}$ exhibited a relatively sharp methylene proton signal at 23 ppm with half-line width of 900 Hz and a broad meso proton peak at −81 ppm.

An isotropic shifts of −45 ppm (upfield) at 275 K for the meso proton of [(OEP)$Ru^{II}CO]^{+}\cdot Br^{-}$ and −91 ppm for [(OEP)-$Co^{III}]^{2+}\cdot 2Br^{-}$ are translated into spin densities of 0.027 and 0.054, respectively, at the meso carbon π-orbital, which are more than 10 times as much as the corresponding value (0.0012) calculated by SCF–CI MO method for the metal-free porphyrin π-cation radical ($^2A_{1u}$).[1c] An absolute value of a meso proton ESR coupling constant, 1.48 G, measured[1c] for [(OEP)$Mg^{II}]^{+}\cdot ClO_4^{-}$ corresponds to a π-spin density of 0.066, comparable to the present NMR results. Since an a_{1u} π-cation orbital has a node at the meso

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(8) The equimolar amount of Br_2 was added to the CD_2Cl_2 solution of (MPDME)$Ru^{II}CO$ to yield a one-electron-oxidized species, which was readily reduced to the starting material by KI. With the excess Br_2, further oxidized species was formed and was not reduced by KI.

(9) Proton NMR spectra were obtained at 300 MHz on a Nicolet NT-300 spectrometer equipped with a 1280 computer system. There was no noticable concentration dependence on the line width of the proton spectrum of this radical. The visible spectrum persisted after the NMR spectrum was recorded.

(10) The hyperfine shift pattern for the species in Figure 1A, spectrum b, and for [(OEP)$Ru^{II}CO]^{+}\cdot Br^{-}$ appears to resemble that for the ferric high-spin porphyrin complexes. This may allow one to expect that Ru^{III} high-spin state could be responsible for the NMR hyperfine shifts. This possibility is, however, ruled out on a basis of the observations that the ESR spectrum is characteristic of the doublet free radical, the visible spectrum matches that expected for a porphyrin π-cation radical and that the magnetic susceptibility measurement by the Evans method shows the $S = {}^1/_2$ state ($\mu_{eff} = \sim 1.8\mu_B$). Collman et al., reported the NMR spectrum of a (OEP)Ru^{II} dimer ($S = 1$), which has a CH_2 signal near that shown in Figure 1A, spectrum b, (Collman, J. P.; Barnes, C. E.; Collins, T. J.; Brothers, P. J.; Gallucci, J.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 7030–7032.). However, the meso H of this dimer is located at 10 ppm in the downfield region, which contrasts to the upfield shift in Figure 1A, spectrum. The possibility of Ru^{III} low-spin state is also ruled out by the NMR measurement of the low-spin complex (OEP)$Ru^{III}(py)_2$, which afforded single methyl resonance at 23 ppm (Shiro and Morishima, unpublished results). The finding that the one-electron-oxidized species of (MPDME)$Ru^{II}CO$ and (OEP)$Ru^{II}CO$ is readily reduced by a mild reducing reagent, KI, may also support that one electron is extracted from the porphyrin ring rather than the metal.

(11) The reason for short electron spin relaxation time is not clear at the present stage. Quite a normal value of $g = 2.003$ for these radicals may allow us to expect that a spin–orbit coupling at metal atom may not be responsible for enhanced electron spin relaxation. Coupling of metal orbitals and π-levels or counteranion and π-radical could cause the short electron spin relaxation.[1d,e] Degenerate or nearly degenerate radicals may also exhibit enhanced relaxation caused by electron exchange between two states. The unusual non-Curie law behavior of the meso proton resonance of the $OEPRu^{II}CO$ π-cation radical could be due to this cause.

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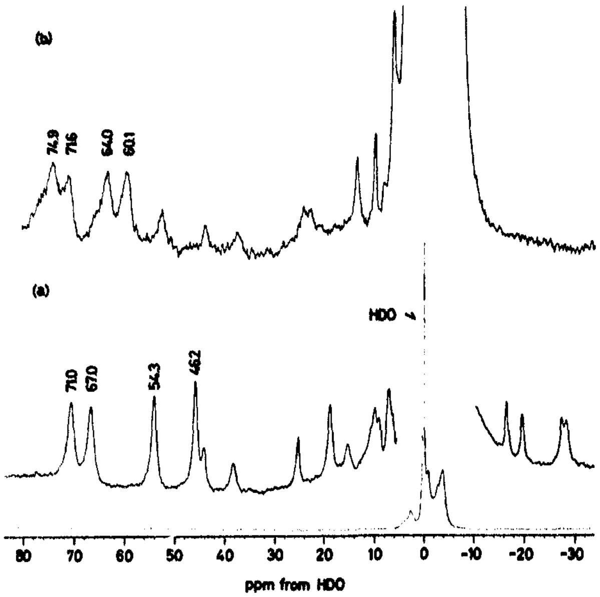

Figure 2. Proton NMR spectra (300 MHz) of (a) HRP compound I and (b) the π-cation radical formed by the one-electron oxidation of the CO complex of Ruthenium(II) mesoporphyrin incorporated into HRP in a 0.1 M phosphate buffer at pH 7.0 and 22 °C.

carbon, a negative spin density due to electron correlation effect was expected at the meso position.[6b] The present NMR results show that this is not the case, which could probably be interpreted if configuration interaction were performed for a Ru porphyrin or, alternatively, if we assume that mixing of an $^2A_{2u}$ radical which to some extent places positive spin density at the meso position is caused by a fast electron exchange between nearly degenerate a_{1u} and a_{2u} orbitals.

It is now of interest to see the proton NMR of Ruthenium(II) porphyrin π-cation radical reconsitituted in HRP. (MP)Ru^{II}CO incorporated into HRP was readily oxidized by K_2IrCl_6 to form a one-electron-oxidized species, which was identified as (MP)-Ru^{II}CO π-cation radical on the basis of the visible spectrum ($^2A_{2u}$ type)[13] and the ESR spectrum at 77 K. The proton NMR spectrum of Ru^{II}(HRP)CO π-cation radical is shown in Figure 2 and is compared with that of HRP compound I. Compound I is now formulated as ferryl low-spin ($S = 1$) porphyrin π-cation radical (a_{2u}) and large hyperfine shifts[3,4] of the heme peripheral protons may result mostly from the π-radical center rather than from the paramagnetic metal center, because the ferryl low-spin leads to very small hyperfine shifts as much as 18 ppm, as was evidenced by the previously reported proton NMR spectrum of HRP compound II with ferryl low-spin state.[3,12] It is therefore reasonable to see comparable hyperfine shifts of the heme methyl protons in Ru(II)HRP·CO π-cation and compound I, both of which have a_{2u} type porphyrin π-cation radicals. Lack of the meso proton resonances in the upfield region in these two spectra is also explained by referring the proton spectra of the model Ruthenium(II) porphyrin π-cation radical ($^2A_{2u}$) in Figure 1A, spectrum c.

It is also worth noting that oxidation of the Ru-substituted myoglobin–CO complex did not yield the corresponding π-cation radical, in accord with the fact that myoglobin does afford compound II but not compound I. The same conclusion was obtained by the use of Zn- or Mg-substituted HRP's and myoglobins.[14]

This implies that a characteristic heme environmental structure of HRP may serve to stabilize the porphyrin π-cation radical through the heme proximal or distal side or combination of both. To gain further insight into structural origins in stabilizing compound I, studies on porphyrin π-cation radicals having a variety of ligands are in progress in our laboratory.

Acknowledgment. We are grateful to Dr. T. Kawamura and Mr. T. Sowa for ESR measurements and helpful discussion. We thank Professor I. Yamazaki for a gift of K_2IrCl_6 and discussions. Encouragement by Professor T. Yonezawa is also gratefully acknowledged. This work is supported by a grant from Ministry of Education, Japan (57470119).

Registry No. HRP, 9003-99-0; [(MPDME)Ru^{II}CO]$^+$·Br$^-$, 86846-48-2; [(MPDME)Ru^{II}CO]$^+$·ClO$_4^-$, 86846-50-6; [(OEP)Ru^{II}CO]$^+$·Br$^-$, 86846-51-7; [(OEP)Ru^{II}CO]$^+$·ClO$_4^-$, 86846-52-8; [(OEP)Co^{III}]$^{2+}$·2Br$^-$, 32880-79-8; (MPDME)Ru^{II}CO, 32073-83-9; (OEP)Ru^{II}CO, 41636-35-5.

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[13] $^2A_{1u}$ to $^2A_{2u}$ conversion occurred when (MP)Ru^{II}CO π-cation radical is incorporated into HRP, probably due to the axial ligand effect. See: Fujita, I.; Hanson, L. K.; Walker, F. A.; Fajer, J. *J. Am. Chem. Soc.* **1983,** *105,* 3296–3300. The ligand effect could also be responsible for different feature of electron spin relaxation of the ruthenium porphyrin π-cation radical in its free and liganded forms (Figures 1A, spectrum c and 2, spectrum b), which are both in $^2A_{2u}$ state. In our preliminary experiments, the imidazole-liganded OEPRu^{II}CO π-cation radical afforded the ^{1}H spectrum at −40 °C, which is characteristic of the ^{2}Azu state and with the α-CH$_2$ line width comparable to those for the Ru(II)HRP·CO π-cation radical (the details will be published in a full length paper).

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(Benzene)vanadium, $(C_6H_6)V$: A Half-Sandwich with an η^6-Benzene Ligand

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We report in this communication the synthesis and spectroscopic characterization of the first example of a half-sandwich zerovalent transition-metal complex $(C_6H_6)M$, which can be considered to be the parent in our quest for $(C_6H_6)M_n$ (where $n = 2, 3, ...$) chemisorption models.

Both the mono(benzene)metal stoichiometry as well as the mode of bonding of the metal to the benzene ring were established by UV–visible absorption and EPR spectroscopy. Thus, when V atoms are deposited with either pure benzene or concentrated $C_6H_6/Ar \simeq 1/1$ to $1/10$ matrices at 12 K under mononuclear conditions, V/C_6H_6 or $Ar \simeq 1/10^4$, the UV–visible absorption spectrum displays two prominant bands around 320 (vs) and 450 (w) nm, assigned to the $4e_{2g}{}^4 8a_{1g}{}^1 \rightarrow 4e_{2g}{}^3 8a_{1g}{}^1 4e_{2u}{}^1$, $4e_{2g}{}^4 8a_{1g}{}^0 4e_{2u}{}^1$ metal-to-ligand charge-transfer transitions of the 17-electron bis(η^6-benzene)vanadium(0) complex.[2] The corresponding EPR spectra of $(\eta^6\text{-}C_6H_6)_2V$ under these conditions are those expected for the rigid limit, where the hyperfine splitting is governed by the eight-line vanadium coupling (I, $^{51}V = 7/2$) with $\bar{a}_\perp(^{51}V) = 93.57$ G and $\bar{a}_\parallel(^{51}V) \simeq 10.2$ G, and the proton superhyperfine splitting is never fully resolved.[3] Thus, although the 12 protons in $(\eta^6\text{-}C_6H_6)_2V$ are spatially equivalent, they are magnetically inequivalent in the rigid limit of solid benzene, and the 12 nuclear superhyperfine tensors due to the interaction of the unpaired electron with the nuclear spins of the benzene protons are not all the same. Only when the two benzene rings rotate rapidly with respect to one another or when the molecule as a whole rotates about its C_6 axis, can the superhyperfine tensors axially average, to produce narrow line widths and well-resolved spectra (see later).

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