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Synthesis and Characterization of Tetrakis(2,6-difluorophenyl)porphinato Ruthenium(II)(CO)(N-MeIm); Oxidation Reaction of Hydrocarbon Catalyzed by the Ruthenium Porphyrin

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Abstract

Synthesis, characterization and properties of a new ruthenium porphyrin, tetrakis(2,6-difluorophenyl)porphinato ruthenium(II)(CO)(N-MeIm), Ru2FP(CO)(N-MeIm), are described. The complex catalyzes the oxidation of hydrocarbons by use of t-BuOOH or hypochlorite as oxidant. To styrene and α-methylstyrene oxidation, Ru2FP(CO)(N-MeIm)–oxidant systems favor the cleavage of the C=C double bond over the formation of the epoxide. Cyclooctene epoxidation and cyclohexane hydroxylation are efficiently performed by the use of TBHP oxidant. On the contrary, hypochlorite oxidant demonstrates only a low catalytic ability for cyclooctene and cyclohexene oxidations.

Introduction

Over the last decade, the search for the cytochrome P-450 family of monooxygenase enzymes has attracted chemists because of the versatility of its catalyses, i.e. aliphatic hydroxylation, alkene epoxidation and heteroatom dealkylation [1]. An understanding of the redox chemistry mediated by this enzyme has been increased using a variety of model systems including metalloporphyrins [2]. In these models, the oxygen source for oxygenation was iodosylbenzene [3–6], hypochlorite [7–9], alkyl hydroperoxide [10–13] or molecular dioxygen [14, 15], and the oxygenation catalyst has often been iron or manganese porphyrin. We previously reported the powerful catalytic system of olefin epoxidation using various protected porphyrin complexes [16–18], and the details of the oxygenation mechanism in these protected porphyrin–hypochlorite systems have been described [19, 20].

In recent years, the range of metalloporphyrins has been expanded by the synthesis of species containing second- and third-row transition metal ions. In particular, the structural and coordination chemistry of the ruthenium porphyrin in the various oxidation states (II, III, IV, VI) has been developed by many inorganic chemists [21–24]. On the other hand, there has been a growing interest in the oxidation chemistry of oxo–ruthenium complexes, which are potential catalysts for aerobic and selective oxidative reactions [25–27]. The oxygenation reaction of hydrocarbon [28] or phosphine [29] using the ruthenium OEP complex was performed by James and coworkers. Groves *et al.* reported the isolation of *trans*-dioxoruthenium(VI)porphyrin and subsequently demonstrated that such a species was a competent catalyst for the aerobic epoxidation of olefins [30, 31]. The relationship of iron and ruthenium in the periodic table suggests that the latter might be able to provide more stable examples of high-valent intermediate species in the oxygenation reaction. However, only a few examples of the catalytic oxygenation system using ruthenium porphyrin have been reported so far [28–33].

5,10,15,20-Tetrakis(2,6-difluorophenyl)porphyrin (abbr. 2FP, Fig. 1) is substituted by eight fluorine atoms for degradative protection during the catalytic oxygenation reaction. The iron(III) and manganese(III) complexes of 2FP have demonstrated a highly efficient catalytic ability for the olefin epoxidation reaction [16]. Therefore, the ruthenium complex of 2FP is expected to show a sufficient capability for the oxygenation reaction. Apart from being a catalyst for oxidation, the character of Ru2FP is supposed to be different from other ruthenium porphyrins,

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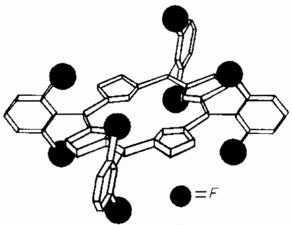

(2F)P

Fig. 1. Tetrakis-(2,6-difluorophenyl)porphyrin (2FP).

such as ruthenium octaethylporphyrin (abbr. RuOEP), ruthenium tetraphenylporphyrin (abbr. RuTPP), and ruthenium tetramesitylporphyrin (abbr. RuTMP), because of the electronegativity of the fluorine atoms which have a drastic influence on the electronic state of the porphyrin metal center. We report here on the synthesis and characterization of a new ruthenium complex, Ru2FP(CO)(N-MeIm) and on its catalytic oxidation reaction of hydrocarbon using t-butylhydroperoxide (TBHP) or sodium hypochlorite as oxidant.

Experimental

Diethyleneglycolmonomethylether was freshly distilled from drying agents and anhydrous stannous chloride. Other solvents used for syntheses were reagent grade. Solvents for physical measurements were purified by the literature methods [34]. All porphyrin free bases, 2FP, OEP [35] and TMP [36] were prepared by the Rothemund or literature methods.

Preparation of Ru(Por)(CO)(N-MeIm)

The typical reaction conditions of the ruthenium insertion experiment were as follows [37]. A 1.0 g portion of the porphyrin free base (2FP; 1.4 mmol) was added to 300 cm^3 of diethyleneglycolmonomethylether, and the resulting suspension was heated to reflux under a carbon monoxide atmosphere. A 3.2 g portion of ruthenium trichloride dissolved in 200 cm^3 of diethyleneglycolmonomethylether was added dropwise to the suspension of porphyrin free base over 4 h. The suspension was refluxed for 24 h. After refluxing, the solvent was reduced to *c.* 80 cm^3. After cooling to room temperature, 200 cm^3 of water was added. The precipitate was filtered by suction, washed by water and subsequently by methanol. The crude material was dried *in vacuo*, and redissolved in 300 cm^3 of dichloromethane. A 0.4 g portion of DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone) was added to the dichloromethane solution and then the resulting solution was refluxed for 5 h. After cooling to ambient temperature, excess DDQ was decomposed by use of sodium hydrosulphite. The crude material was purified on a silica gel column (Wako gel C-200; eluent chloroform–dichloromethane). The eluate was concentrated to *c.* 30 cm^3, and then 6 cm^3 of methanol was added. The complex Ru(2FP)(CO)(MeOH) was precipitated from the resulting solution. Ru(2FP)(CO)(MeOH) was redissolved in 30 cm^3 of dichloromethane and 3 cm^3 of 1-methylimidazole (N-MeIm) was added. The resulting solution was concentrated to *c.* 3 cm^3 and left overnight. The precipitate was filtered by suction and purified on a silica gel column (eluent; benzene:dichloromethane = 1:1). The desired complex Ru(2FP)(CO)(N-MeIm) was recrystallized from dichloromethane/methanol and dried *in vacuo*. Yield; 0.58 g (0.61 mmol, 44%).

Ru2FP(CO)(MeOH)·$2H_2O$. *Anal.* Calc. for $C_{46}H_{28}N_4O_4F_8Ru$: C, 57.93; H, 2.96; N, 5.87. Found: C, 58.01; H, 2.64; N, 5.75%. UV–Vis ($CHCl_3$): λ (nm) 406, 523, 556. IR (KBr disk) νCO = 1955 cm^{-1}. Ru2FP(CO)(N-MeIm). *Anal.* Calc. for $C_{49}H_{26}N_6OF_8Ru$: C, 60.80; H, 2.71; N, 8.68. Found: C, 60.70; H, 2.75; N, 8.75%. UV–Vis (CH_2Cl_2) λ (nm) (ϵ (M^{-1} cm^{-1})), 408(3.3×10^5), 528(1.6×10^3), 562(4.0×10^2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.06 (1H, s, N-MeIm), 1.34 (1H, s, N-MeIm), 2.06 (3H, s, CH_3 of N-MeIm), 4.59 (1H, s, N-MeIm), 7.26 (12H, m, *meso*-phenyl), 8.57 (8H, s, pyrrole β-H). IR (CH_2Cl_2 solution) νCO = 1949 cm^{-1}.

RuOEP(CO)(N-MeIm) and RuTMP(CO)(N-MeIm) were prepared by a similar procedure and characterized by elemental analyses and spectroscopic methods.

Electrochemical and IR Spectra Measurement

Cyclic voltammetric measurements of the ruthenium porphyrins, Ru(Por)(CO)(N-MeIm), were carried out in a 2 M dichloromethane solution containing tetrabutylammonium hexafluorophosphate as supporting electrolyte. The working electrode was a glassy carbon. The reference electrode was a Ag/AgCl electrode. Voltammograms were measured at sweep rates of 0.1 V/s. The IR spectra of the ruthenium porphyrin solutions were measured by means of a thallium chloride liquid cell whose optical path was 0.1 mm.

Oxidation Reaction

In controlled experiments of oxidation, the reaction conditions were as follows. The porphyrin (0.012 mmol), substrate (7.6 mmol) and internal standard (*p*-dichlorobenzene; 1.4 mmol) were dissolved in 20 cm^3 of dichloromethane. When hypochlorite solution was used as the oxidant, the phase-transfer reagent (benzyldimethyltetradecylammonium chloride) was added to the dichloromethane solution. Then, 15 cm^3 of sodium hypochlorite solution (8.7 mmol) or 2 cm^3 of 70% TBHP solution (14.4 mmol) were poured into the dichloromethane solution. The oxidation reaction was started just at the point where TBHP was added, while in the case of hypochlorite, vigorous stirring was needed for the initiation of the oxidation reaction. The reaction temperature was maintained at 285 K during the oxidation reaction. The products were analyzed by means of gas chromatography.

Results and Discussion

cis and trans Influences of Ruthenium Porphyrins

cis or *trans* influences observed in the CO stretching frequencies of carbonyl hemes have been ascribed by Caughey and coworkers to the metal–carbonyl π-bonding [38]. The '*cis* influence' in Ru(Por)(CO)L is brought about by changing the porphyrin ligands. The π-acceptor properties of the TPP derivatives are stronger than that of octaethylporphyrin, since the four aryl groups of the TPP derivatives produce an additional withdrawal of d electrons [39]. The *ortho* replacements of the *meso*-phenyl moieties in the TPP derivatives induce a change in the π-acceptor capabilities of the porphyrin ligands. If highly electron-withdrawal fluorine atoms are introduced, the π-acceptor property is increased in comparison with non-substituted TPP. On the other hand, the substitution of electron donative methyl groups to the *meso*-phenyl moieties decreases the π-acceptor character. In this way, the π-acceptor properties of the porphyrin ligands should be conceptionally summarized in the order 2FP > TMP > OEP.

The CO stretching frequencies obtained in IR measurements are listed in Table 1. The CO stretching frequencies vary in the range of 1918 to 1949 cm^{-1} with the change in the porphyrin ligand. The observed trend of CO stretching frequencies is in good agreement with the order of π-acceptor properties. The increase of the π-acceptor capability of the porphyrin ligand brings about the increase of the CO stretching frequency. Thus the *cis* influence is definitely demonstrated by our experiments with Ru(Por)(CO)L.

TABLE 1. The CO stretching frequencies of ruthenium porphyrins

Compound	Solvent	Frequency (cm^{-1})
Ru2FP(CO)(MeOH) [a]	CH_2Cl_2	1949
	DMF	1936
Ru2FP(CO)(N-MeIm)	CH_2Cl_2	1949
	DMF	1942
RuTMP(CO)(MeOH)	KBr disk	1933
RuTMP(CO)(N-MeIm)	CH_2Cl_2	1933
	DMF	insoluble
RuOEP(CO)(MeOH) [a]	CH_2Cl_2	1922
	DMF	1918
RuOEP(CO)(N-MeIm)	CH_2Cl_2	1922
	DMF	1922

[a] Ru(Por)(CO)(MeOH) reversibly loses MeOH in dichloromethane solution and changes into the five coordinated species Ru(Por)(CO).

The '*trans* influence' indicates the π-backdonating strength of an axial ligand L *trans* to Ru–CO. In CH_2Cl_2 solution, the CO stretching frequencies of Ru(Por)(CO)L are independent of the kind of ligand L (L = MeOH or N-MeIm). The compound Ru(Por)(CO)(MeOH) reversibly loses the MeOH ligand in dichloromethane solution and changes into Ru(Por)(CO) [40]. The five coordinated Ru(Por)(CO) and six coordinated Ru(Por)(CO)(N-MeIm) have almost the same νCO values as a result. Our results show that the axial ligand N-MeIm has a negligible '*trans* influence'.

The solvents (CH_2Cl_2 or DMF) have no influence on the CO stretching frequency of RuOEP(CO)(N-MeIm). On the contrary, the CO stretching frequency of Ru2FP(CO)(N-MeIm) is decreased by changing the solvent from CH_2Cl_2 to DMF. This reduction of the νCO value is caused by the polar solvent effect of DMF. The polar solvent effect of DMF on the CO stretching frequency is also observed in Ru2FP(CO)(MeOH)*.

Electrochemical Measurements

The redox properties of the ruthenium porphyrins, Ru(Por)(CO)(N-MeIm) have been studied by cyclic voltammetry. The half-wave potentials ($E_{1/2}$) for each redox couple obtained from cyclic voltammetry are listed in Table 2. The redox reactions at the first and second oxidative potentials and at the reductive potential are shown in eqns. (1), (2) and (3), respectively [40, 41].

$$\mathrm{Ru(II)(Por)(CO)} \rightleftharpoons [\mathrm{Ru(II)(Por^{+\bullet})(CO)}]^{+} + e^{-} \tag{1}$$

$$[\mathrm{Ru(II)(Por^{+\bullet})(CO)}]^{+} \rightleftharpoons [\mathrm{Ru(III)(Por^{+\bullet})(CO)}]^{2+} + e^{-} \tag{2}$$

$$\mathrm{Ru(II)(Por)(CO)} + e^{-} \rightleftharpoons [\mathrm{Ru(II)(Por^{-\bullet})(CO)}]^{-} \tag{3}$$

Each cyclic voltammogram is illustrated in Fig. 2. In each ruthenium porphyrin, the first and second one-electron oxidations are reversible. However, as far as Ru2FP(CO)(N-MeIm) is concerned, the second one-electron oxidation is irreversible. The data of $E_{1/2}$ using various *p*-substituted Ru(II)TPP(CO) derivatives by Meyer *et al.* are also listed in Table 2

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*The CO frequency of RuOEP(CO)(MeOH) was reduced to 4 cm^{-1} by changing the solvent from CH_2Cl_2 to DMF (Table 1). It is not clear that DMF ligation might give rise to this reduction of νCO.

TABLE 2. The half wave potentials (V vs. Ag/AgCl) for Ru(Por)(CO)L

Compound	1st oxidation		2nd oxidation		Reduction		Reference
	E_p	I_{pa}/I_{pc}	E_p	I_{pa}/I_{pc}	E_p	I_{pa}/I_{pc}	
RuOEP(CO)(N-MeIm)	0.585	1.00	1.130	0.96			this work
RuTMP(CO)(N-MeIm)	0.668	1.03	1.325	1.02	−1.810	0.68	this work
Ru2FP(CO)(N-MeIm)	0.980	0.97	1.505	1.44	−1.480	0.50	this work
Ru(*p*-MeTPP)(CO) [a]	0.75		1.20		−1.35		41
RuTPP(CO) [a]	0.79		1.20		−1.32		41
Ru(*p*-FTPP)(CO) [a]	0.85		1.25		−1.28		41

[a] The measurements were made vs. the saturated sodium chloride calomel electrode (SSCE).

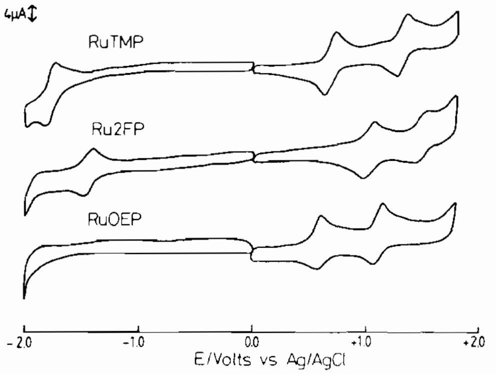

Fig. 2. Cyclic voltammograms of Ru(Por)(CO)(N-MeIm).

[41]. The potentials are affected by the substituent bound to the phenyl ring. Reduction and oxidation potentials show a cathodic shift together with an increase of the electron-withdrawing power of the substituent Me < H < F. Meyer *et al.* also reported that the carbonyl stretching frequencies of *p*-substituted RuTPP(CO) remained fairly constant; Ru(*p*-MeTPP)(CO), 1918 cm^{-1}; RuTPP(CO), 1922 cm^{-1}; Ru(*p*-FTPP)(CO), 1922 cm^{-1} [41]. Their results suggest that the substituent effect is primarily a σ-effect and does not greatly perturb the π-system of the metal–carbonyl bond. In our results, the $E_{1/2}$ values for the first and second oxidation reactions have shifted cathodically in the order of Ru2FP > RuTMP > RuOEP. This order is consistent with the idea that a series of porphyrin ligands have the weaker σ-basicity in the sequence of 2FP > TMP > OEP.

Oxidation Reaction

The results of the oxidation reaction using Ru(Por)(CO)(N-MeIm) and Fe(Por)Br are listed in Tables 3–6.

Recently TBHP has been used considerably in organic synthesis. Although TBHP performs a highly selective oxidation of organic compounds with high

TABLE 3. The products of styrene oxidation reaction (yields are represented by turnover numbers)

Catalyst	Oxidant	Time	Styrene oxide	Phenylacetaldehyde	Benzaldehyde	Total
Ru2FP(CO)(N-MeIm)	NaClO	24 h	12	20	150	182
	TBHP	24 h	37	0	99	136
Fe2FPBr	NaClO	7 min	533	0	7	540
	TBHP	24 h	25	0	103	128
RuOEP(CO)(N-MeIm)	NaClO	24 h	15	19	184	218

TABLE 4. The products of α-methylstyrene oxidation (yields are represented by turnover numbers)

Catalyst	Oxidant	Time	α-Methylstyreneoxide	α-Phenylpropionaldehyde	Acetophenone	Total
Ru2FP(CO)(N-MeIm)	NaClO	24 h	8	2	102	112
	TBHP	24 h	36	18	424	478
Fe2FPBr	NaClO	7 min	311	81	0	392
	TBHP	24 h	22	0	432	454

TABLE 5. The results of cyclooctene epoxidation catalyzed by Ru2FP(CO)(N-MeIm) (yields are represented by turnover numbers)

Oxidant	Time	Epoxide
TBHP	6 h	119
	24 h	176
NaClO	6 h	4
	24 h	12

yield, it is unreactive toward most organic compounds in the absence of catalysts [42]. Sharpless *et al.* have described non-radical, metal-catalyzed oxygenations [42, 43]. When TBHP is used as oxidant in a reaction catalyzed by a metalloporphyrin, the major difficulty is to avoid the homolytic breaking of the O–O bond which leads to the formation of the RO radical. In this case, chain radical oxidation, but no epoxidation, is observed [44]. By use of iron and manganese porphyrins, Mansuy and coworkers have shown that interaction with the alkylhydroperoxides has been largely modified by the presence of a strong donor ligand, such as imidazole [45][*]. In the case of oxygenation in the presence of imidazole, the epoxidation of styrene occurred with a yield analogous to that obtained with iodosylbenzene [45]. In our experiments with TBHP, the cleavage of the C=C double bond is favored over the formation of epoxide in both styrene and α-methylstyrene oxidation (see Tables 3 and 4). In the styrene oxidation experiment of the Ru(2FP)(CO)(MeOH)–TBHP system, the products distribution was analogous with the result of the Ru2FP(CO)(N-MeIm)–TBHP system. Addition of an excessive amount of imidazole to the Ru(Por)(CO)(N-MeIm)–TBHP catalytic system was not able to cause the production of epoxide in styrene oxidation. It seems that Ru(Por)(CO)L (L = N-MeIm or MeOH) performs the radical reaction in TBHP oxidation in spite of the presence of imidazole. The result of olefin oxidation differed substantially when cyclooctene was employed as the substrate. An epoxide (cyclooctene oxide) was mainly produced (Table 5). Cyclooctene oxide formation may occur not only via the oxometal route, but also by a free-radical pathway [47]. Dixit and Sinivasan reported that cyclooctene oxide formation has occurred via the free-radical pathway in manganese(III) schiff base catalyzed oxidation with TBHP [48][†]. No UV–Vis spectral change was shown in the treatment of Ru2FP(CO)(MeOH) or Ru2FP(CO)(N-MeIm) solution with TBHP[††]. This spectral data suggests that the high-valent oxometal complex is hardly formed in the Rh2FP(CO)L-TBHP system. Ru(Por)(CO)(N-MeIm), therefore, performs the free radical oxidation reaction by use of TBHP as oxidant. The results of cyclohexane hydroxylation are listed in Table 6. The hydroxylation has been catalyzed more efficiently by Ru2FP(CO)(N-MeIm) than by Fe2FPBr after 3 h. The hydroxylation reaction by Ru2FP(CO)(N-MeIm) was almost completed after 6 h. Accordingly the relative efficiency of the catalyst in cyclohexane oxidation for a 24 h period was Fe > Ru.

In the catalytic oxygenation reaction of olefins using various kinds of metalloporphyrins with hypochlorite, epoxides have been produced mainly in good yields [17]. For example, epoxide was produced in yields of over 90% in styrene oxygenation using iron(III) or manganese(III) porphyrin–hypochlorite systems [18]. The results of styrene and α-methylstyrene oxidation with hypochlorite are listed in Tables 3 and 4, respectively. The products distribution of Ru(Por)(CO)(N-MeIm)–hypochlorite is similar to that of Ru(Por)(CO)(N-MeIm)–TBHP or that of Fe(Por)Br–TBHP. A considerable difference

TABLE 6. The oxidation reaction of cyclohexane using TBHP (yields are represented by turnover numbers)

Catalyst	Time (h)	Cyclohexanone	Cyclohexanol	Total
Ru2FP(CO)(N-MeIm)	3	108	149	257
	24	176	203	379
RuOEP(CO)(N-MeIm)	3	171	224	395
	24	201	242	443
Fe2FPBr	3	30	58	88
	24	193	236	429

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[*] Molybdenum or titanium porphyrin has catalyzed the epoxidation of olefins with TBHP or cumyl hydroperoxide.

[†] By use of the heterogeneous clay-anchored catalyst with TBHP, cyclooctene epoxidation occurred via the oxometal route.

[††] In the case of treatment of RuOEP(CO)L solution with TBHP, RuOEP(CO)L was oxidated to the Ru(IV) μ-oxo dimer [22].

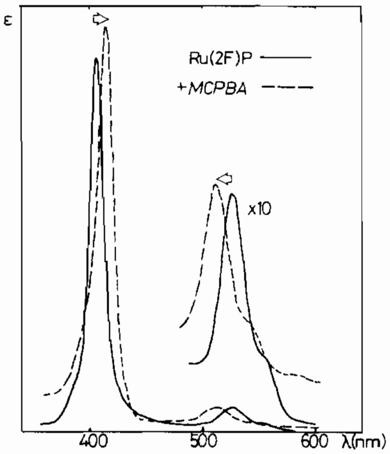

Fig. 3. Spectral changes of Ru2FP(CO)(MeOH).

is, however, shown between TBHP and hypochlorite in cyclooctene and cyclohexane oxidation catalyzed by Ru2FP(CO)(N-MeIm). In the case of cyclooctene epoxidation, the hypochlorite system has a rather low yield compared with the TBHP system (see Table 5). In particular, in cyclohexane oxidation by the Ru2FP(CO)(N-MeIm)–hypochlorite system, only a trace amount of the hydroxylation product was detected.

After styrene oxidation by Ru2FP(CO)(MeOH)–hypochlorite, a new species (compound X) originating from Ru2FP(CO)(MeOH) appeared in CH_2Cl_2 solution, and spectral changes were observed in both UV–Vis and IR*. In the UV–Vis spectra of compound X, the Soret-band was 8 nm red shifted and the Q-band was 15 nm blue shifted compared to Ru2FP(CO)(N-MeIm)**. The peak of CO stretching at 1949 cm^{-1} disappeared in the IR spectra. Addition of MCPBA (*m*-chloroperbenzoic acid) to a CH_2Cl_2 solution of Ru2FP(CO)(MeOH) led to similar UV–Vis spectral changes (Fig. 3). Hence, a treatment of Ru2FP(CO)(MeOH) with MCPBA is supposed to generate the compound X. Owing to the absence of catalytic ability for an aerobic olefin oxygenation†, this compound X is not the Ru(VI) species which was proposed by Groves and Quinn [30]. Meyer and coworkers reported the catalytic oxidation using ruthenium complex [(trpy)(bpy)Ru(OH_2)](ClO_4)$_2$ [49]††. A high percentage of benzaldehyde (benzaldehyde:styreneoxide = 78:22) has been found as a product of the hypochlorite-catalyzed oxidation of styrene [49]. Our Ru(Por)(CO)(N-MeIm)–hypochlorite system is supposed to have a somewhat similar reaction path to [(trpy)(bpy)Ru(OH_2)](ClO_4)$_2$. At the present stage, we cannot account for the reaction mechanism of our Ru porphyrin–hypochlorite system, and it is not clear whether the compound X is an active species of the Ru2FP(CO)L–hypochlorite system or not. We, however, speculate tentatively that compound X is a Ru(III) complex and is not the active species in the Ru2FP(CO)(N-MeIm)–hypochlorite system.

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*This UV–Vis spectra does not agree with the spectra of the μ-oxo dimer.

**The CH_2Cl_2 layer of the Ru2FP(CO)(MeOH)–hypochlorite system was taken out during styrene oxidation, and the UV–Vis spectra were immediately measured. Similar spectral changes were observed.

†Although the aerobic epoxidation reaction was examined in accordance with the report of Groves and Quinn [30], no oxygenation product was detectable after 48 h reaction.

††bpy = 2,2′-bipyridine, py = pyridine, trpy = 2,2′,2″-terpyridine.

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