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Tuning the Reactivity of Dioxoruthenium(VI) Porphyrins toward an Arylimine by Altering Porphyrin Substituents

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Reaction of dioxoruthenium(VI) porphyrins [$Ru^{VI}(Por)O_2$] with arylimine $HN{=}CPh_2$ in dichloromethane afforded bis(methyleneamido)ruthenium(IV) porphyrins [$Ru^{IV}(Por)(N{=}CPh_2)_2$] for Por = 4-Cl-TPP and TMP; (methyleneamido)hydroxoruthenium(IV) porphyrins [$Ru^{IV}(Por)(N{=}CPh_2)(OH)$] for Por = TPP and TTP; and bis(arylimine)ruthenium(II) porphyrins [$Ru^{II}(Por)(HN{=}CPh_2)_2$] for Por = 3,5-$Cl_2$TPP and 3,5-$(CF_3)_2$TPP. In dichloromethane solution exposed to air, complex [Ru^{II}(3,5-Cl_2TPP)$(HN{=}CPh_2)_2$] underwent oxidative deprotonation to form [Ru^{IV}(3,5-Cl_2TPP)$(N{=}CPh_2)_2$]. The new ruthenium porphyrins were identified by ^{1}H NMR, UV–vis, IR, and mass spectroscopy, along with elemental analysis. X-ray crystal structure determinations of [Ru^{IV}(4-Cl-TPP)$(N{=}CPh_2)_2$], [Ru^{IV}(TPP)$(N{=}CPh_2)(OH)$], and [Ru^{II}(3,5-$(CF_3)_2$TPP)$(HN{=}CPh_2)_2$] revealed the Ru–N(methyleneamido) or Ru–N(arylimine) distances of 1.897(5) Å (average), 1.808(4) Å, and 2.044(2) Å (average), respectively.

Introduction

Since the first synthesis of [$Ru^{VI}(TMP)O_2$] (TMP = *meso*-tetramesitylporphyrinato dianion) by Groves and Quinn in 1984,[1a] dioxoruthenium(VI) porphyrins, [$Ru^{VI}(Por)O_2$], have received considerable attention.[1−17] This interesting family of high-valent ruthenium porphyrins not only exhibits high reactivity toward oxidation of hydrocarbons,[1b,2b−f,3,5,10,11,14,15] thioethers,[4a] alcohols,[4b] and phosphines,[4d,9a,b] but also serves as unique precursors for preparation of amine,[4c,9d,e,17a−c] nitrosoarene,[17f] hydroxylamine,[17f] amido,[17b,c] hydrazido(1−),[17d] and imido[17c] complexes of ruthenium porphyrins.

Recently, we initiated exploration of the reactivity of [$Ru^{VI}(Por)O_2$] toward imines and obtained the bis-methyl-

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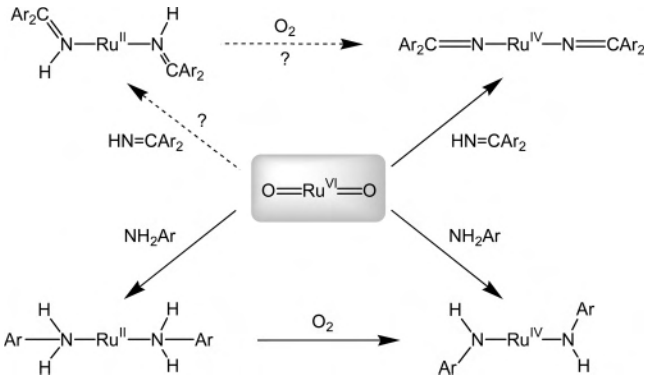
Scheme 1



eneamido (or azavinylidene) metalloporphyrins, $[Ru^{IV}(Por)(N{=}CAr_2)_2]$, from the reaction of $[Ru^{VI}(TTP)O_2]$ (TTP = *meso*-tetrakis(*p*-tolyl)porphyrinato dianion) or $[Ru^{VI}(3,4,5\text{-}(MeO)_3TPP)O_2]$ (3,4,5-$(MeO)_3$TPP = *meso*-tetrakis(3,4,5-trimethoxyphenyl)porphyrinato dianion) with arylimine.[17e] This is similar to the formation of bis(arylamido)ruthenium(IV) porphyrins $[Ru^{IV}(Por)(NHAr)_2]$ or $[Ru^{IV}(Por)(NAr_2)_2]$ from treatment of $[Ru^{VI}(Por)O_2]$ with arylamine (such as $H_2N\text{-}p\text{-}C_6H_4NO_2$ and $HNPh_2$).[17b,c] However, reaction of $[Ru^{VI}(Por)O_2]$ with arylamine (such as $H_2N\text{-}p\text{-}C_6H_4Cl$) can also afford bis(arylamine)ruthenium(II) porphyrins $[Ru^{II}(Por)(NH_2Ar)_2]$, which are readily convertible to bis(arylamido)ruthenium(IV) porphyrins through oxidative deprotonation.[17c,18] It would be of interest to examine whether parallel reactivity of $[Ru^{VI}(Por)O_2]$ toward arylimines, i.e., formation of bis(arylimine)ruthenium(II) porphyrins $[Ru^{II}(Por)(HN{=}CAr_2)_2]$ and oxidative deprotonation of the arylimine complexes to give $[Ru^{IV}(Por)(N{=}CAr_2)_2]$ (Scheme 1), can be observed.

So far there have been no reports (to our knowledge) on bis-arylimine metalloporphyrins, despite previous isolation of the bis-alkylimine analogues $[Ru^{II}(Por)(EtN{=}CHMe)_2]$[17e] and the mono-arylimine complex $[Ru^{II}(Por)(CO)(PhN{=}CH\text{-}p\text{-}C_6H_4Cl)]$.[19] In general, metalloporphyrins with simple imines, i.e., RN=CR′R″ (R,R′R″ = alkyl or aryl), as the sole axial ligands, are rare, and their synthetic route remains elusive (see below), which is in contrast to the facile formation of numerous pyridine, imidazole, or simple amine complexes of metalloporphyrins.[20] Since metal complexes of simple imines are observed/proposed to be the intermediates in metal-mediated imine aziridination,[21] imine/imide/alkylidene metathesis,[22] and amine-nitrile interconversion,[23] isolation of bis-arylimine metalloporphyrins would be essential for examination of their related reactivity, thus facilitating development of metalloporphyrin-mediated arylimine functionalizations or arylamine-nitrile interconversion.

In the course of our continuing studies on the reaction between $[Ru^{VI}(Por)O_2]$ and imines, we have found that bis-arylimine complexes $[Ru^{II}(Por)(HN{=}CAr_2)_2]$ can be formed and isolated in good yields from such reaction by employing benzophenone imine ($HN{=}CPh_2$) and certain porphyrin ligands. Like the bis-arylamine analogues, a $[Ru^{II}(Por)(HN{=}CAr_2)_2]$ complex can undergo oxidative deprotonation, leading to the formation of $[Ru^{IV}(Por)(N{=}CAr_2)_2]$. We have also found that treatment of some $[Ru^{VI}(Por)O_2]$ complexes with an arylimine afforded a (methyleneamido)hydroxoruthenium(IV) complex, $[Ru^{IV}(Por)(N{=}CAr_2)(OH)]$. All these findings are reported herein.

Results and Discussion

Dioxoruthenium(VI) porphyrins $[Ru^{VI}(Por)O_2]$ can be readily prepared by treatment of the carbonyl precursors $[Ru^{II}(Por)(CO)]$ with excess *m*-chloroperoxybenzoic acid.[1,2a,b] It has been well documented that these ruthenium(VI) complexes exhibit high reactivity toward a variety of alkyl- or arylamines,[4c,9d,e,17a−c] affording, in most cases, bis(amine)ruthenium(II) porphyrins such as $[Ru^{II}(Por)(H_2NR)_2]$ in high yields. In contrast, much less is known about the reactivity of $[Ru^{VI}(Por)O_2]$ toward alkyl- or arylimines; only the reactions of a few $[Ru^{VI}(Por)O_2]$ complexes with 2,2,4,4-tetramethylpentan-3-one imine ($HN{=}CBu^t_2$)[24] and $HN{=}CPh_2$[17e] have been reported.

Reaction of $[Ru^{VI}(Por)O_2]$ with Arylimine. Following our previous work on the reaction of $[Ru^{VI}(TTP)O_2]$ or $[Ru^{VI}(3,4,5\text{-}(MeO)_3TPP)O_2]$ with $HN{=}CPh_2$,[17e] we examined the reaction of $[Ru^{VI}(Por)O_2]$ with the same arylimine by employing a series of other porphyrin ligands, including TPP (*meso*-tetraphenylporphyrinato dianion) and its derivatives 4-Cl-TPP (*meso*-tetrakis(*p*-chlorophenyl)porphyrinato dianion), TMP, 3,5-Cl_2TPP (*meso*-tetrakis(3,5-dichlorophenyl)porphyrinato dianion), and 3,5-$(CF_3)_2$TPP (*meso*-tetrakis(3,5-

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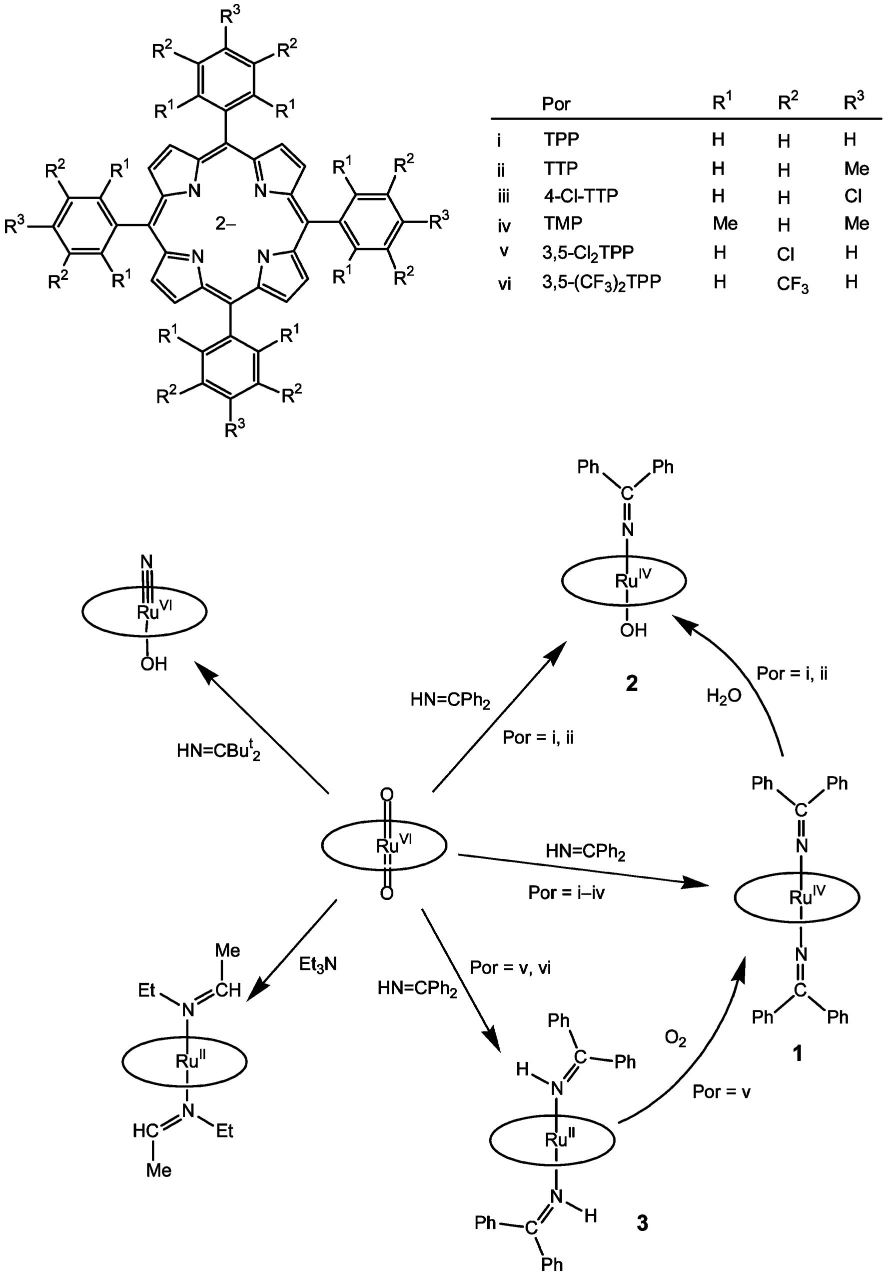
Scheme 2



	Por	R^1	R^2	R^3
i	TPP	H	H	H
ii	TTP	H	H	Me
iii	4-Cl-TTP	H	H	Cl
iv	TMP	Me	H	Me
v	3,5-Cl_2TPP	H	Cl	H
vi	3,5-$(CF_3)_2$TPP	H	CF_3	H

(trifluoromethyl)phenyl)porphyrinato dianion). This led to the isolation of three types of ruthenium porphyrin products: [Ru^{IV}(Por)$(N{=}CPh_2)_2$] (Por = 4-Cl-TPP: **1a**, TMP: **1b**), [Ru^{IV}(Por)$(N{=}CPh_2)(OH)$] (Por = TPP: **2a**, TTP: **2b**), and [Ru^{II}(Por)$(HN{=}CPh_2)_2$] (Por = 3,5-Cl_2TPP: **3a**, 3,5-$(CF_3)_2$TPP: **3b**) (Scheme 2).

The isolation of bis(methyleneamido)ruthenium(IV) porphyrins **1** for Por = 4-Cl-TPP and TMP is similar to that for Por = TTP and 3,4,5-$(MeO)_3$TPP reported previously.[17e] In these cases, treatment of in situ formed [Ru^{VI}(Por)O_2] with excess $HN{=}CPh_2$ in dichloromethane at room temperature followed by addition of ethanol to the reaction mixture and subsequent evaporation of dichloromethane readily gave **1** in about 65% yield as a dark purple, crystalline solid.

However, the same procedure for Por = TPP led to the isolation of a mixture of [Ru^{IV}(TPP)$(N{=}CPh_2)_2$] and [Ru^{IV}(TPP)$(N{=}CPh_2)(OH)$] (**2a**); the former was identified by its ^1H NMR signals similar to those of [Ru^{IV}(TTP)$(N{=}CPh_2)_2$].[25] Attempts to obtain pure [Ru^{IV}(TPP)$(N{=}CPh_2)_2$] were unsuccessful. In an effort to purify the product by chromatography on an alumina column, we found that [Ru^{IV}(TPP)$(N{=}CPh_2)_2$] was transformed to **2a**, which was isolated in 70% yield.

Complex **2a** is a unique metalloporphyrin bearing both methyleneamido and hydroxo axial groups. The facile conversion of [Ru^{IV}(TPP)$(N{=}CPh_2)_2$] to **2a** during the chromatography prompted us to examine the stability of previously reported [Ru^{IV}(TTP)$(N{=}CPh_2)_2$][17e] toward similar

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(25) ^1H NMR spectral data for [Ru^{IV}(TPP)$(N{=}CPh_2)_2$] (300 MHz, $CDCl_3$): H_β 8.46 (s, 8H), H_o 7.91 (d, J = 7.8 Hz, 8H), H_m, H_p 7.67 (m, 12H), H'_p 6.67 (t, J = 7.5 Hz, 4H), H'_m 6.44 (t, J = 7.7 Hz, 8H), H'_o 4.03 (d, J = 7.1 Hz, 8H). The signals of pyrrolic protons (H_β) and axial methyleneamido phenyl protons (H'_p, H'_m, and H'_o) are very similar to those reported for [Ru^{IV}(TTP)$(N{=}CPh_2)_2$]: H_β 8.47 (s, 8H), H'_p 6.66 (t, 4H), H'_m 6.43 (t, 8H), H'_o 4.01 (d, 8H).[17e]

treatment, which resulted in almost complete conversion of $[\mathrm{Ru^{IV}(TTP)(N{=}CPh_2)_2}]$ to $[\mathrm{Ru^{IV}(TTP)(N{=}CPh_2)(OH)}]$ (**2b**). The ^{1}H NMR spectrum of **2b** turned out to be virtually identical to that of "$[\mathrm{Ru^{IV}(TTP)(N{=}CPh_2)}]_2\mathrm{O}$" previously observed in solution;[17e] accordingly, the latter species should be reformulated as $[\mathrm{Ru^{IV}(TTP)(N{=}CPh_2)(OH)}]$ (see the spectral and X-ray structural characterization of **2** described below). Complexes **1a**,**b** were found to be stable during the chromatography.

It is interesting that reaction of $[\mathrm{Ru^{VI}(3,5\text{-}Cl_2TPP)O_2}]$ or $[\mathrm{Ru^{VI}(3,5\text{-}(CF_3)_2TPP)O_2}]$ with $\mathrm{HN{=}CPh_2}$, through a procedure similar to that for preparation of **1a**,**b**, afforded bis(arylimine)ruthenium(II) porphyrins **3a**,**b**, which were isolated in about 65% yield. This is parallel to the formation of bis(amine)ruthenium(II) porphyrins from $[\mathrm{Ru^{VI}(Por)O_2}]$ and amines.[4c,9e,17a−c]

Besides **3a**,**b**, the other known metalloporphyrins with simple imine as the sole axial ligands are the bis-alkylimine complexes $[\mathrm{Ru^{II}(Por)(EtN{=}CHMe)_2}]$,[17e] which were prepared through apparent *N*-dealkylation of triethylamine by $[\mathrm{Ru^{VI}(Por)O_2}]$ (Scheme 2). Attempts to prepare bis(alkylimine)ruthenium(II) porphyrins from reaction of $[\mathrm{Ru^{VI}(Por)O_2}]$ with alkylimine $\mathrm{HN{=}CBu^t_2}$ were not successful; this reaction was found to result in cleavage of the C═N bond and gave, unexpectedly, nitridoruthenium(VI) complexes $[\mathrm{Ru^{VI}(Por)(N)(OH)}]$[24] (Scheme 2).

Complexes **1a**,**b**, **2a**,**b**, and **3b** are moderately stable to air both in the solid state and in solution, but complex **3a** can be handled only for a short time in solutions exposed to air, although it is stable to air for weeks in the solid state. Interestingly, when a solution of **3a** in dichloromethane or chloroform exposed to air was left standing for 1 day, this complex was completely converted to the bis-methyleneamido complex $[\mathrm{Ru^{IV}(3,5\text{-}Cl_2TPP)(N{=}CPh_2)_2}]$, as revealed by ^{1}H NMR and UV−vis spectroscopy.[26]

The reason for the marked dependence of the reactivity of $[\mathrm{Ru^{VI}(Por)O_2}]$ toward $\mathrm{HN{=}CPh_2}$ on the porphyrin substituents is not yet clear. It seems that electron-donating substituents such as Me and MeO favor methyleneamido ruthenium(IV) complexes whereas electron-withdrawing substituents such as $\mathrm{CF_3}$ favor arylimine ruthenium(II) complexes. Indeed, electron-withdrawing substituents would stabilize metal complexes in a lower oxidation state by reducing the electron density of metal atoms. The conversion of $[\mathrm{Ru^{IV}(TPP)(N{=}CPh_2)_2}]$ and $[\mathrm{Ru^{IV}(TTP)(N{=}CPh_2)_2}]$ to **2a**,**b** through chromatography is probably due to the presence of water in the alumina or solvents: we found that $[\mathrm{Ru^{IV}(TTP)(N{=}CPh_2)_2}]$ gradually converted to **2b** in chloroform solution exposed to air and addition of water to the solution significantly speeded up the conversion. The higher stability of **2a**,**b** than $[\mathrm{Ru^{IV}(TPP)(N{=}CPh_2)_2}]$ and $[\mathrm{Ru^{IV}(TTP)(N{=}CPh_2)_2}]$ may be attributed to the stronger *trans* effect of the methyleneamido group than the hydroxo group.

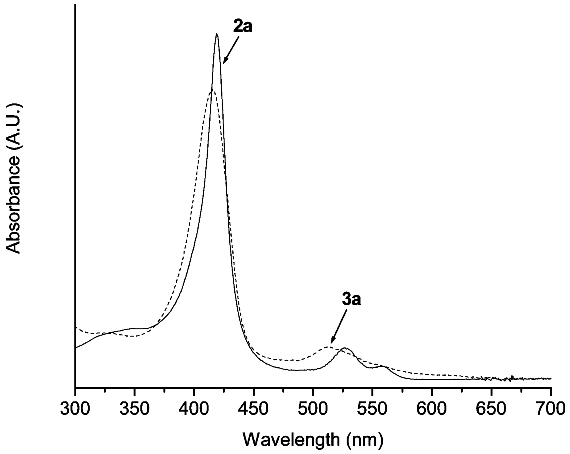

Figure 1. UV−vis spectra of $[\mathrm{Ru^{IV}(TPP)(N{=}CPh_2)(OH)}]$ (**2a**) and $[\mathrm{Ru^{II}(3,5\text{-}Cl_2TPP)(HN{=}CPh_2)_2}]$ (**3a**) in $\mathrm{CH_2Cl_2}$.

Spectral Characterization of Reaction Products. Bis(methyleneamido)ruthenium(IV) porphyrins **1a**,**b** show UV−vis spectra featuring Soret and β bands at about 420 and 530 nm, respectively, similar to those of $[\mathrm{Ru^{IV}(TTP)(N{=}CPh_2)_2}]$ and $[\mathrm{Ru^{IV}(3,4,5\text{-}(MeO)_3TPP)(N{=}CPh_2)_2}]$.[17e] In the ^{1}H NMR spectra, all these methyleneamido complexes exhibit the axial $[\mathrm{N{=}CPh_2}]^-$ signals at $\delta \approx 6.7$ (t, H'_p), 6.4 (t, H'_m), and 4.0 ppm (d, H'_o), with the signal of pyrrolic protons (H_β) appearing at $\delta \approx 8.5$ ppm. The appearance of a single set of the axial $[\mathrm{N{=}CPh_2}]^-$ phenyl signals arises from the linear C═N−Ru−N═C arrangement in these methyleneamido ruthenium(IV) porphyrins.[17e]

Complexes **2a**,**b** exhibit UV−vis spectra (Soret: ca. 420 nm, β: 527 nm) that are very similar to those of **1a**,**b** and $[\mathrm{Ru^{IV}(TTP)(N{=}CPh_2)_2}]$ but dramatically different from those of previously reported dinuclear μ-oxo ruthenium(IV) porphyrins such as $[\mathrm{Ru^{IV}(TPP)X}]_2\mathrm{O}$ ($\mathrm{X} = \mathrm{Cl^-}, \mathrm{ArO^-}$).[27] The spectrum of **2a** is shown in Figure 1 as an example. In the ^{1}H NMR spectra of **2a**,**b** (see, for example, Figure 2), all the signals are located at normal fields and well resolved, like those of diamagnetic complexes $[\mathrm{Ru^{IV}(Por)(N{=}CPh_2)_2}]$,[17e] indicating the diamagnetic character of the (methyleneamido)hydroxoruthenium(IV) porphyrins. Because each $[\mathrm{Ru^{IV}(Por)}]$ moiety in **2a**,**b** is unsymmetrically coordinated at the axial sites, the *ortho* or *meta* protons of the *meso*-phenyl groups in the porphyrin ligands give two well-separated sets of peaks, in contrast to the single set of peaks observed for such protons in $[\mathrm{Ru^{IV}(TPP)(N{=}CPh_2)_2}]$[25] and $[\mathrm{Ru^{IV}(TTP)(N{=}CPh_2)_2}]$.[17e] Also, the H_β signals of **2a**,**b** ($\delta \approx 8.6$ ppm) are appreciably downfield from those of the two bis-methyleneamido complexes. Since only a single set of the axial $[\mathrm{N{=}CPh_2}]^-$ phenyl signals was observed for **2a**,**b**, both the complexes should contain linear axial Ru−N═C moieties.

The UV−vis spectra of the bis(arylimine)ruthenium(II) porphyrins **3a**,**b** (see, for example, Figure 1) show Soret and β bands at about 415 and 510 nm, respectively, which are considerably blue shifted from those of **1a**,**b**, but similar to those of bis(amine)ruthenium(II) porphyrins.[17a−c] In the IR

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[26] Spectral data for $[\mathrm{Ru^{IV}(3,5\text{-}Cl_2TPP)(N{=}CPh_2)_2}]$, ^{1}H NMR (300 MHz): H_β 8.52 (s, 8H), H_o 7.80 (d, $J = 1.7$ Hz, 8H), H_p 7.77 (t, $J = 1.8$ Hz, 4H); H'_p 6.79 (t, $J = 7.4$ Hz, 4H), H'_m 6.51 (t, $J = 7.9$ Hz, 8H), H'_o 4.01 (d, $J = 7.1$ Hz, 8H). UV−vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$/nm 419 (Soret), 527 (β).

[27] Collman, J. P.; Barnes, C. E.; Brothers, P. J.; Collins, T. J.; Ozawa, T.; Gallucci, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 5151.

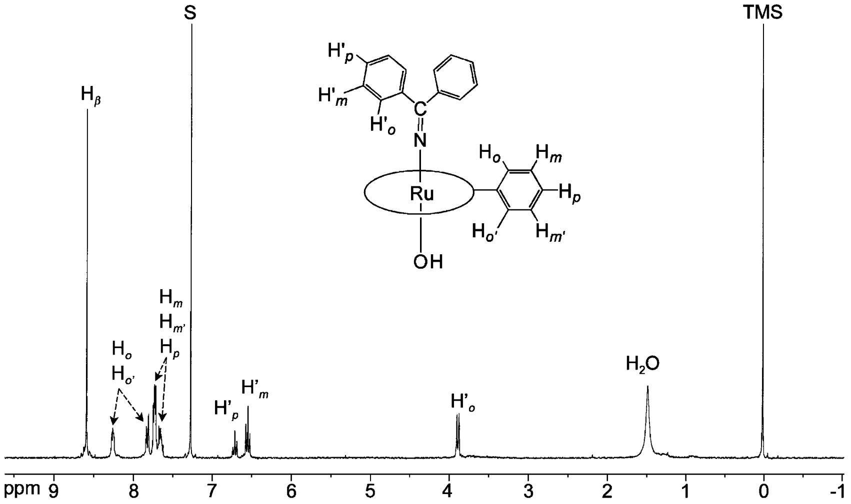

Figure 2. ^{1}H NMR spectrum of [Ru^{IV}(TPP)(N=CPh$_2$)(OH)] (**2a**) in CDCl$_3$ (the water came from the deuteriochloroform solvent).

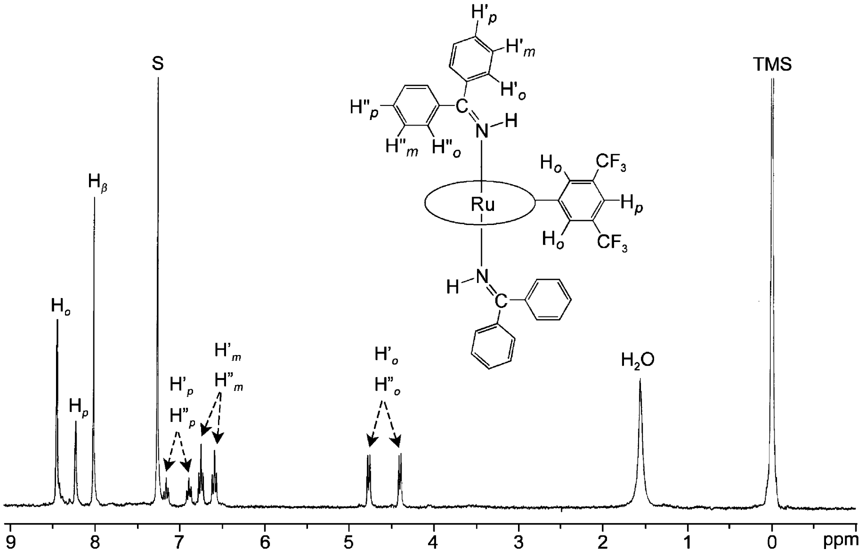

Figure 3. ^{1}H NMR spectrum of [Ru^{II}(3,5-(CF$_3$)$_2$TPP)(HN=CPh$_2$)$_2$] (**3b**) in CDCl$_3$ (the water came from the deuteriochloroform solvent).

spectra of **3a**,**b**, the oxidation state marker bands[1c,17a] appear at frequencies of 1005 and 1002 cm^{-1}, respectively, again similar to those observed for the bis(amine)ruthenium(II) porphyrins,[17a−c] but considerably lower than those of the methyleneamido ruthenium(IV) porphyrins **1a**,**b** and **2a**,**b** (1010−1012 cm^{-1}) and bis(arylamido)ruthenium(IV) porphyrins.[17b,c] The weak and sharp bands at 3258 (**3a**) and 3250 cm^{-1} (**3b**) in the IR spectra are absent in the methyleneamido complexes and can be attributed to the NH stretching vibrations of the axial HN=CPh$_2$ ligands.

Since the axial Ru−N=C moieties in **3a**,**b** must be bent and rotation of the CPh$_2$ moiety of HN=CPh$_2$ about its C=N bond is prohibited, the two phenyl groups in each of the axial HN=CPh$_2$ ligands of **3a**,**b** should give different signals in the ^{1}H NMR spectra. This is indeed found to be the case (see, for example, the spectrum of **3b** shown in Figure 3), with one set of axial phenyl signals located at $\delta \approx 7.2$ (*p*-H), 6.7 (*m*-H), and 4.7 ppm (*o*-H), and the other at $\delta \approx 6.9$ (*p*-H), 6.6 (*m*-H), and 4.3 ppm (*o*-H). Consistent with the lower oxidation state of ruthenium in **3a** than in [Ru^{IV}(3,5-Cl$_2$TPP)(N=CPh$_2$)$_2$], the H$_\beta$ signal of the former ($\delta = 8.11$ ppm) is significantly upfield from that of the latter ($\delta = 8.52$ ppm).[26]

In the mass spectra of **3a**,**b**, three cluster peaks assignable to the parent ion [M]$^+$, and the fragments [M − HN=CPh$_2$]$^+$ and [M − 2HN=CPh$_2$]$^+$ were observed in each case. For **1a**,**b**, their mass spectral features are similar to the previously reported analogues such as [Ru^{IV}(TPP)(N=CPh$_2$)$_2$].[17e] Complexes **2a**,**b** each exhibit a mass spectrum that is dominated by the cluster peak ascribable to [M − OH]$^+$; a cluster peak assignable to [Ru^{IV}(Por)(N=CPh$_2$)]$_2$O (which might be generated under the mass spectroscopic conditions) is also present.

X-ray Crystal Structures. We have determined the crystal structure of each type of the reaction products by employing diffraction-quality crystals of **1a**, **2a**, and **3b**·0.5CH$_2$Cl$_2$. The crystal data are summarized in Table 1. Selected bond distances and angles are given in Table 2.

The structure of **1a** (Figure 4) resembles that of [Ru^{IV}(3,4,5-(MeO)$_3$TPP)(N=CPh$_2$)$_2$] reported earlier,[17e] featuring a planar

Table 1. Crystallographic Data for [Ru^{IV}(4-Cl-TPP)(N=CPh$_2$)$_2$] (**1a**), [Ru^{IV}(TPP)(N=CPh$_2$)(OH)] (**2a**), and [Ru^{II}(3,5-(CF$_3$)$_2$TPP)(HN=CPh$_2$)$_2$]·0.5CH$_2$Cl$_2$ (**3b**·0.5CH$_2$Cl$_2$)

	1a	**2a**	**3b**·0.5CH$_2$Cl$_2$
formula	$C_{70}H_{44}Cl_4N_6Ru$	$C_{57}H_{39}N_5ORu$	$C_{78}H_{42}F_{24}N_6Ru\cdot 0.5CH_2Cl_2$
cryst syst	monoclinic	monoclinic	monoclinic
fw	1211.98	911.00	1662.71
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	12.145(2)	12.934(1)	16.597(1)
b, Å	20.470(4)	30.942(4)	17.904(2)
c, Å	23.446(5)	11.181(1)	25.811(2)
α, deg	90.00	90.00	90.00
β, deg	102.48(3)	101.492(3)	93.517(2)
γ, deg	90.00	90.00	90.00
V, Å^3	5691(2)	4384.9(8)	7656(1)
Z	4	4	4
ρ_{calc}, g cm^{-3}	1.415	1.380	1.443
2θ range, deg	50.90	55.12	55.20
GOF	0.98	1.01	1.02
$R1/wR2$	0.051/0.14	0.063/0.12	0.078/0.20

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Ru^{IV}(4-Cl-TPP)(N=CPh$_2$)$_2$] (**1a**), [Ru^{IV}(TPP)(N=CPh$_2$)(OH)] (**2a**), and [Ru^{II}(3,5-(CF$_3$)$_2$TPP)(HN=CPh$_2$)$_2$]·0.5CH$_2$Cl$_2$ (**3b**·0.5CH$_2$Cl$_2$)

	1a		
Ru−N1	2.072(4)	Ru−N2	2.051(4)
Ru−N3	2.060(4)	Ru−N4	2.049(4)
Ru−N5	1.887(5)	Ru−N6	1.906(4)
N5−C45	1.198(6)	N6−C58	1.204(6)
N1−Ru−N2	89.1(2)	N2−Ru−N3	90.7(2)
N3−Ru−N4	89.4(2)	N1−Ru−N4	90.8(2)
N1−Ru−N3	179.8(2)	N2−Ru−N4	179.8(2)
N5−Ru−N1	90.0(2)	N5−Ru−N2	90.1(2)
N5−Ru−N3	90.0(2)	N5−Ru−N4	89.7(2)
N6−Ru−N1	90.3(2)	N6−Ru−N2	90.3(2)
N6−Ru−N3	89.8(2)	N6−Ru−N4	89.9(2)
N5−Ru−N6	179.5(2)	C45−N5−Ru	175.3(4)
C58−N6−Ru	174.1(4)		
	2a		
Ru−N1	2.039(4)	Ru−N2	2.045(4)
Ru−N3	2.051(4)	Ru−N4	2.045(3)
Ru−N5	1.808(4)	Ru−O1	1.971(3)
N5−C45	1.274(5)		
N1−Ru−N2	90.0(1)	N2−Ru−N3	89.9(1)
N3−Ru−N4	90.5(1)	N1−Ru−N4	89.5(1)
N1−Ru−N3	177.2(1)	N2−Ru−N4	175.8(1)
N5−Ru−N1	93.0(2)	N5−Ru−N2	93.0(2)
N5−Ru−N3	89.8(2)	N5−Ru−N4	91.2(1)
O1−Ru−N1	88.6(1)	O1−Ru−N2	87.7(1)
O1−Ru−N3	88.6(1)	O1−Ru−N4	88.1(1)
N5−Ru−O1	178.3(2)	C45−N5−Ru	175.0(4)
	3b·0.5CH$_2$Cl$_2$		
Ru−N1	2.045(2)	Ru−N2	2.042(2)
Ru−N3	2.046(2)	Ru−N4	2.040(2)
Ru−N5	2.035(2)	Ru−N6	2.053(2)
N5−C53	1.291(3)	N6−C66	1.310(3)
N1−Ru−N2	89.96(7)	N2−Ru−N3	90.40(6)
N3−Ru−N4	89.96(7)	N1−Ru−N4	89.71(7)
N1−Ru−N3	178.06(7)	N2−Ru−N4	178.98(7)
N5−Ru−N1	81.69(7)	N5−Ru−N2	94.93(7)
N5−Ru−N3	96.39(7)	N5−Ru−N4	85.99(7)
N6−Ru−N1	97.46(7)	N6−Ru−N2	82.04(7)
N6−Ru−N3	84.47(7)	N6−Ru−N4	97.04(7)
N5−Ru−N6	176.87(7)	C53−N5−Ru	143.2(2)
C66−N6−Ru	142.6(2)		

porphyrin ring (mean deviation: 0.033 Å) and a linear axial C=N−Ru−N=C moiety (C−N−Ru: 174.1(4)°, 175.3(4)°; N−Ru−N: 179.5(2)°) with mean Ru−N distance of 1.897(5) Å and mean C=N distance of 1.201(6) Å (the corresponding bond distances for [Ru^{IV}(3,4,5-(MeO)$_3$TPP)(N=CPh$_2$)$_2$] are 1.896(8) and 1.25(1) Å[17e]).

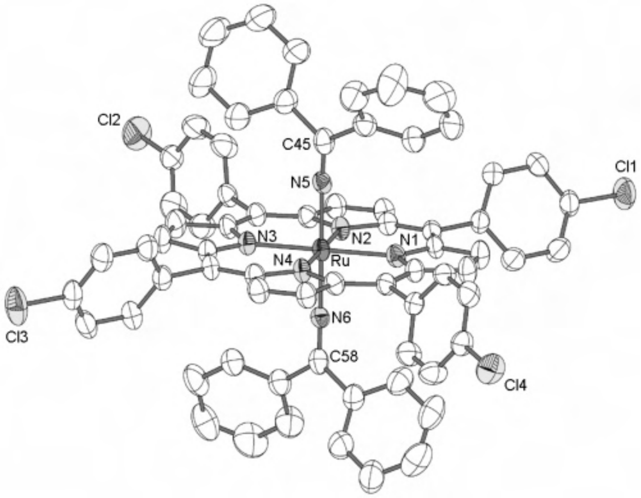

Figure 4. Structure of [Ru^{IV}(4-Cl-TPP)(N=CPh$_2$)$_2$] (**1a**) with omission of hydrogen atoms (thermal ellipsoid probability: 30%).

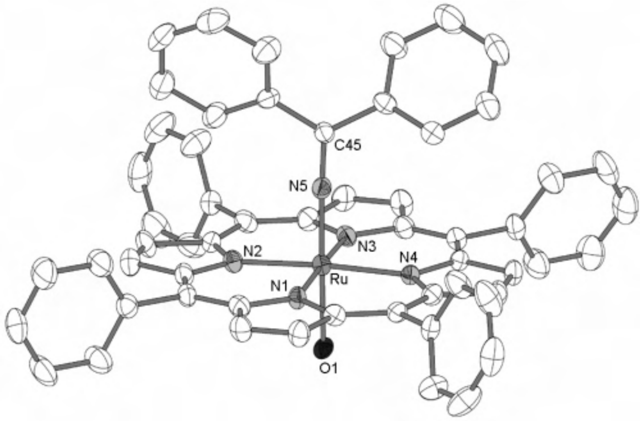

Figure 5. Structure of [Ru^{IV}(TPP)(N=CPh$_2$)(OH)] (**2a**) with omission of hydrogen atoms (thermal ellipsoid probability: 30%).

Complex **2a** (Figure 5) contains a linear axial Ru−N=C moiety (Ru−N−C 175.0(4)°) similar to that in **1a** and [Ru^{IV}(3,4,5-(MeO)$_3$TPP)(N=CPh$_2$)$_2$], but shows appreciably shorter Ru−N(axial) distance (1.808(4) Å) and longer methyleneamido N=C distance (1.274(5) Å) than those of the bis-methyleneamido complexes. This might arise from a smaller *trans* influence of OH$^-$ than the methyleneamido group, which results in the formation of stronger Ru−N(axial) bond in the (methyleneamido)hydroxo complex. The porphyrin ring in **2a** is also planar, with a mean deviation of 0.019 Å. The axial O−Ru−N=C moiety is linear (O−Ru−N 178.3(2)°) and shows a Ru−O distance of 1.971(3) Å.

Note that a methyleneamido group is isoelectronic with the nitrosyl group, resembling the latter in binding metal ions.[28] In this context, the methyleneamido complexes [Ru(Por)(N=CPh$_2$)$_2$] and [Ru(Por)(N=CPh$_2$)(OH)] may be considered analogous to the nitrosyl complexes [Ru(Por)(NO)$_2$] and [Ru(Por)(NO)(OH)], respectively. Since no [Ru-

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(28) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988; p 371. (b) Johnson, B. F. G.; Haymore, B. L.; Dilworth, J. R. In *Comprehensive Coordination Chemistry, Vol. 2*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; p 99.

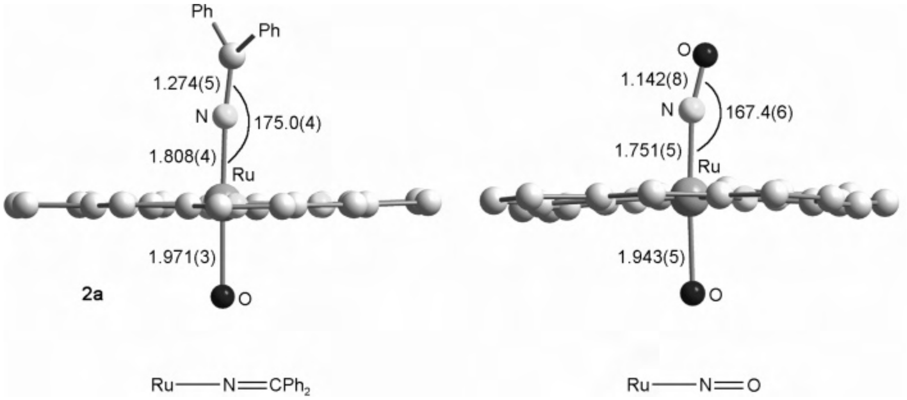

Figure 6. Comparison of the key bond distances (Å) and angles (deg) between [Ru(TPP)(N=CPh$_2$)(OH)] (**2a**) and [Ru(TTP)(NO)(OH)].[29] For clarity, the *meso*-aryl groups of the porphyrin ligands are not shown.

(Por)(NO)$_2$] species have been structurally characterized, nor have structurally characterized methyleneamido complexes of non-ruthenium metalloporphyrins been known, the structure determination of **2a**, together with that of [Ru(TTP)(NO)(OH)],[29] provides a unique opportunity to compare the key structure features of methyleneamido- and nitrosylmetalloporphyrins.

As shown in Figure 6, there is indeed some similarity between the structures of **2a** and [Ru(TTP)(NO)(OH)]. Accordingly, an alternative formulation of **2a** would be [Ru$^{\mathrm{II}}$(TPP)(N=CPh$_2$)(OH)] if one considers the methyleneamido group as [N=CPh$_2$]$^+$, like the NO$^+$ group in the nitrosyl complex (which is usually formulated as [Ru$^{\mathrm{II}}$(TTP)(NO)(OH)]). Figure 6 also shows that **2a** exhibits slightly longer Ru—N(axial) and Ru—O distances, along with a smaller distortion (from planarity) of the porphyrin ring, than the nitrosyl complex, and the Ru—N=C moiety in **2a** has a better linearity than the Ru—N=O moiety in [Ru(TTP)(NO)(OH)].

Our previous work[17e] demonstrated that bis-methyleneamido ruthenium porphyrins [Ru(Por)(N=CPh$_2$)$_2$] resemble bis-arylamido ruthenium(IV) complexes [Ru$^{\mathrm{IV}}$(Por)(NAr$_2$)$_2$] or [Ru$^{\mathrm{IV}}$(Por)(NHAr)$_2$]. It seems that a methyleneamido group has both the characters of nitrosyl and arylamido groups. All these N-donor ligands can form Ru—N bonds having significant multiple bonding characters.[17e] The shorter Ru—N distance of Ru—NO in [Ru(TTP)(NO)(OH)] than that of Ru—N=CPh$_2$ in **2a**, and the shorter Ru—N distances of Ru—N=CPh$_2$ in **1a** than those of Ru—NHAr in [Ru$^{\mathrm{IV}}$(TTP)(NHAr)$_2$][17c] reflect the order of Ru—N multiple bonding characters: Ru—NO > Ru—N=CPh$_2$ > Ru—NHAr.

In contrast to the linear axial Ru—N=C moieties in methyleneamido complexes **1a** and **2a**, the bis-arylimine complex **3b** features bent axial Ru—N=C moieties (Figure 7) with average Ru—N—C angle of 142.9(2)°. The Ru—N(axial) distances of 2.035(2) and 2.053(2) Å in **3b** are substantially longer than those in **1a** and **2a**, but slightly shorter than those of bis-alkylimine complex [Ru$^{\mathrm{II}}$(TTP)(EtN=CHMe)$_2$] (2.115(6) Å)[17e] and non-porphyrin arylimine complex [Ru$^{\mathrm{II}}$(Tp)(PEt$_3$)$_2$(HN=CPh$_2$)]BPh$_4$ (2.095(5) Å, Tp = hydrotris(pyrazolyl)borate).[30] A considerably longer Ru—N(axial) distance of 2.203 Å was observed for [Ru$^{\mathrm{II}}$(Por)(CO)(PhN=CH-*p*-C$_6$H$_4$Cl)].[19] All these alkyl- or arylimine ruthenium complexes, including **3b**, display the imine C=N distances within the narrow range 1.291(3)−1.310(3) Å.

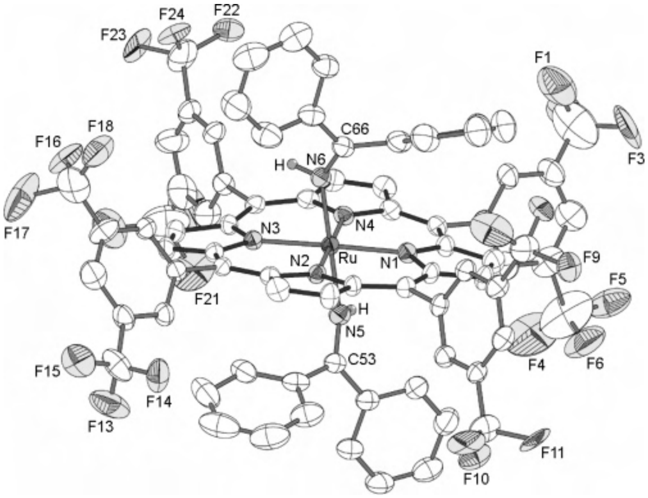

Figure 7. Structure of [Ru$^{\mathrm{II}}$(3,5-(CF$_3$)$_2$TPP)(HN=CPh$_2$)$_2$]·0.5CH$_2$Cl$_2$ (**3b**·0.5CH$_2$Cl$_2$) with omission of hydrogen atoms, except those on the arylimine nitrogen atoms, and solvent molecule (thermal ellipsoid probability: 30%).

The two phenyl groups in each of the axial ligands of **3b** make dihedral angles of about 20° and 89° with the porphyrin plane, with one of the two phenyl groups being almost perpendicular to the porphyrin plane, unlike the cases of **1a** and **2a** (whose corresponding dihedral angles are about 48−72°) but similar to the case of bis(hydrazido(1−))ruthenium(IV) porphyrin [Ru$^{\mathrm{IV}}$(TTP)(HNNPh$_2$)$_2$] (which shows such dihedral angles of about 10° and 85°).[17d] Moreover, the porphyrin ring in **3b** exhibits a marked saddle distortion with mean deviation of 0.125 Å, a value considerably larger than those of [Ru$^{\mathrm{II}}$(TTP)(EtN=CHMe)$_2$] (0.0241 Å) and the foregoing methyleneamido complexes. Such a significant distortion of the porphyrin ring in **3b** might result from the interaction between the phenyl groups of the arylimine and the *meso*-aryl groups of the porphyrin ligand, analogous to the case of [Ru$^{\mathrm{IV}}$(TTP)(HNNPh$_2$)$_2$] (whose axial phenyl groups are closer to the porphyrin ring and the porphyrin ring atoms show a larger mean deviation of 0.167 Å from

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(29) Bohle, D. S.; Hung, C.-H.; Smith, B. D. *Inorg. Chem.* **1998**, *37*, 5798.

(30) Jiménez-Tenorio, M. A.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Inorg. Chim. Acta* **2000**, *300−302*, 869.

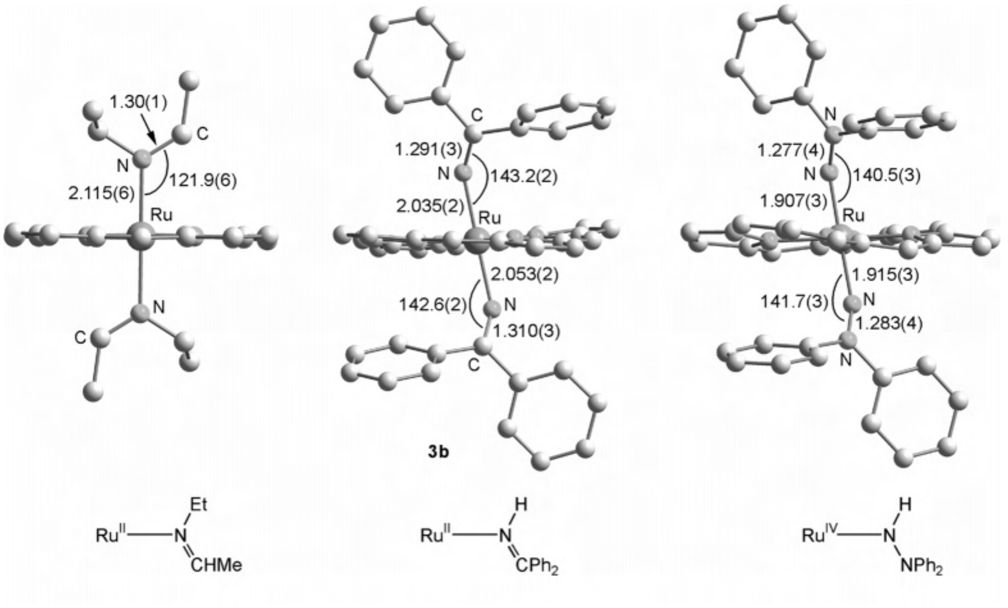

Figure 8. Comparison of the key bond distances (Å) and angles (deg) among [Ru^{II}(TTP)(EtN═CHMe)$_2$],[17e] [Ru^{II}(3,5-(CF$_3$)$_2$TPP)(HN═CPh$_2$)$_2$] (**3b**), and [Ru^{IV}(TTP)(HNNPh$_2$)$_2$].[17d] For clarity, the *meso*-aryl groups of the porphyrin ligands are not shown.

the mean plane).[17d] A comparison of the key structural features among [Ru^{II}(TTP)(EtN═CHMe)$_2$], **3b**, and [Ru^{IV}(TTP)(HNNPh$_2$)$_2$] is depicted in Figure 8.

Conclusion

The reactivity of dioxoruthenium(VI) porphyrins [Ru^{VI}(Por)O$_2$] toward arylimine is affected by the substituents on the *meso*-phenyl groups of the porphyrin ligands. Reaction of in situ formed [Ru^{VI}(TPP)O$_2$] with excess HN═CPh$_2$ in dichloromethane affords a mixture of bis(methyleneamido)ruthenium(IV) porphyrin [Ru^{IV}(TPP)(N═CPh$_2$)$_2$] and (methyleneamido)hydroxoruthenium(IV) porphyrin [Ru^{IV}(TPP)(N═CPh$_2$)(OH)]; the former can be converted to the latter upon chromatography on an alumina column. Introducing 4-chloro, 2,4,6-trimethyl, or 3,4,5-trimethoxy substituents to the *meso*-phenyl groups of the TPP macrocycle effectively prevents formation of [Ru^{IV}(Por)(N═CPh$_2$)(OH)], resulting in the generation of stable [Ru^{IV}(Por)(N═CPh$_2$)$_2$] as the sole isolable products. However, neither [Ru^{IV}(Por)(N═CPh$_2$)$_2$] nor [Ru^{IV}(Por)(N═CPh$_2$)(OH)] is observed when 3,5-di(trifluoromethyl) substituents are introduced; in this case, the reaction product is bis(arylimine)ruthenium(II) porphyrin [Ru^{II}(3,5-(CF$_3$)$_2$TPP)(HN═CPh$_2$)$_2$]. By introducing 3,5-dichloro substituents, the product is a less stable bis-arylimine complex [Ru^{II}(3,5-Cl$_2$TPP)(HN═CPh$_2$)$_2$] which can be isolated but, in solutions exposed to air, readily undergoes oxidative deprotonation to form [Ru^{IV}(3,5-Cl$_2$TPP)(N═CPh$_2$)$_2$], a reactivity resembling the formation of bis-arylamine complex [Ru^{II}(Por)(NH$_2$Ar)$_2$] from [Ru^{VI}(Por)O$_2$] and NH$_2$Ar and the oxidative deprotonation of [Ru^{II}(Por)(NH$_2$Ar)$_2$] to bis-arylamido complex [Ru^{IV}(Por)(NHAr)$_2$] reported earlier.[17c] X-ray crystal structure determination of [Ru(TPP)(N═CPh$_2$)(OH)] reveals that the key structural feature of this methyleneamido complex is similar to that of the nitrosyl complex [Ru(TPP)(NO)(OH)]. The present work demonstrates the resemblance of methyleneamido ruthenium porphyrins to both arylamido and nitrosyl analogues and provides, to our knowledge, the first access to bis-arylimine and (methyleneamido)hydroxo complexes of metalloporphyrins.

Experimental Section

General. Benzophenone imine (97%, Aldrich) and *m*-chloroperoxybenzoic acid (*m*-CPBA; 55%, Merck) were used as received. All solvents were of AR grade and were used without purification. The complexes [Ru^{II}(Por)(CO)] (Por = TPP, TTP, 4-Cl-TPP, TMP, 3,5-Cl$_2$TPP, 3,5-(CF$_3$)$_2$TPP),[31,32] used for in situ generation of [Ru^{VI}(Por)O$_2$][33] (by oxidation with *m*-CPBA in dichloromethane), were synthesized according to the literature method. UV−vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer (interfaced with an IBM-compatible PC). ^{1}H NMR spectra were recorded on a Bruker DPX 300 spectrometer at 298 K with tetramethylsilane (TMS) as internal standard. Chemical shifts (ppm) are reported relative to TMS. IR spectra were obtained on a Bio-Rad FT-IR spectrometer. Fast atom bombardment mass spectra

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[32] Spectral and analytical data for [Ru^{II}(3,5-Cl$_2$TPP)(CO)], ^{1}H NMR (300 MHz, CDCl$_3$): H$_\beta$ 8.72 (s, 8H), H$_o$, H$'_o$ 8.13 (m, 4H), 8.05 (m, 4H), H$_p$ 7.81 (t, $J = 1.8$ Hz, 4H). UV−vis (CH$_2$Cl$_2$): λ_{max}/nm (log ϵ) 413 (5.18), 529 (4.03). IR (Nujol): 1945 (ν_{CO}), 1010 cm^{-1} (oxidation state marker band). Anal. Calcd for C$_{45}$H$_{20}$N$_4$Cl$_8$ORu·H$_2$O: C, 52.20; H, 2.14; N, 5.41. Found: C, 52.65; H, 2.31; N, 5.34. Spectral and analytical data for [Ru^{II}(3,5-(CF$_3$)$_2$TPP)(CO)], ^{1}H NMR (300 MHz, CDCl$_3$): H$_\beta$ 8.79 (s, 8H), H$_o$, H$'_o$ 8.63 (br, 8H), 8.36 (br, 4H). UV−vis (CH$_2$Cl$_2$): λ_{max}/nm (log ϵ) 413 (5.23), 529 (3.96). IR (Nujol): 1921 (ν_{CO}), 1011 cm^{-1} (oxidation state marker band). Anal. Calcd for C$_{53}$H$_{20}$N$_4$F$_{24}$ORu·H$_2$O: C, 48.82; H, 1.70; N, 4.30. Found: C, 49.12; H, 1.78; N, 4.31.

[33] Treatment of [Ru^{II}(Por)(CO)] for Por = 3,5-Cl$_2$TPP and 3,5-(CF$_3$)$_2$-TPP with *m*-CPBA in CH$_2$Cl$_2$ or CDCl$_3$ completely shifted the Soret (413 nm) and β (529 nm) bands (UV−vis spectra) to 421 and 519 nm, respectively, and the H$_\beta$ signal ($\delta \approx 8.7$ ppm, ^{1}H NMR spectra) to $\delta \approx 9.1$ ppm. This is characteristic of the conversion of the carbonyl complexes to [Ru^{VI}(3,5-Cl$_2$TPP)O$_2$] or [Ru^{VI}(3,5-(CF$_3$)$_2$TPP)O$_2$], like the conversion of [Ru^{II}(Por)(CO)] with Por = TPP, TTP, and 4-Cl-TPP to the corresponding [Ru^{VI}(Por)O$_2$] through similar reactions (which shifts the Soret band from ca. 413 to 420 nm, the β band from ca. 530 to 518 nm, and the H$_\beta$ signal from $\delta \approx 8.6$ to $\delta \approx 9.1$ ppm).[2a,b]

(FAB MS) were recorded on a Finnigan MAT 95 mass spectrometer using 3-nitrobenzyl alcohol as matrix. Electrospray mass spectra (ES MS) were measured on a Finnigan LCQ quadrupole ion trap mass spectrometer with HPLC dichloromethane as solvent. Elemental analyses were performed by the Institute of Chemistry, the Chinese Academy of Sciences.

Preparation of Bis(methyleneamido)ruthenium(IV) Porphyrins [Ru^{IV}(Por)(N=CPh$_2$)$_2$] (1). These complexes were isolated as dark purple solids by treating [Ru^{VI}(Por)O$_2$] (in situ formed from [Ru^{II}(Por)(CO)] and *m*-CPBA) with excess HN=CPh$_2$ (*m*-CPBA/HN=CPh$_2$ molar ratio ≈ 1:25) in dichloromethane according to a procedure similar to that for the preparation of [Ru^{IV}(TTP)(N=CPh$_2$)$_2$] and [Ru^{IV}(3,4,5-(MeO)$_3$TPP)(N=CPh$_2$)$_2$].[17e]

[Ru^{IV}(4-Cl-TPP)(N=CPh$_2$)$_2$] (1a). Yield: 65%. ^{1}H NMR (300 MHz, CDCl$_3$): H_β 8.46 (s, 8H), H_o 7.81 (d, $J = 8.4$ Hz, 8H), H_m 7.63 (d, $J = 8.4$ Hz, 8H), H'_p 6.68 (t, $J = 7.5$ Hz, 4H), H'_m 6.43 (t, $J = 7.7$ Hz, 8H), H'_o 3.98 (d, $J = 7.3$ Hz, 8H). UV−vis (3.72×10^{-6} M, CH$_2$Cl$_2$): λ_{max}/nm (log ϵ) 420 (5.37), 529 (4.28), 556 (3.99, sh). IR (KBr pellet): 1010 cm^{-1} (oxidation state marker band). ES MS: *m/z* 1212 [M]$^+$, 1032 [M − L]$^+$, 852 [M − 2L]$^+$ (L = N=CPh$_2$). Anal. Calcd for $C_{70}H_{44}N_6Cl_4Ru$: C, 69.37; H, 3.66; N, 6.93. Found: C, 69.65; H, 3.68; N, 6.68.

[Ru^{IV}(TMP)(N=CPh$_2$)$_2$] (1b). Yield: 68%. ^{1}H NMR (300 MHz, CDCl$_3$): H_β 8.34 (s, 8H), H_m 7.12 (s, 8H), *p*-Me 2.55 (s, 12H), *o*-Me 1.43 (s, 24H), H'_p 6.64 (t, $J = 7.4$ Hz, 4H), H'_m 6.43 (t, $J = 7.7$ Hz, 8H), H'_o 4.01 (d, $J = 7.3$ Hz, 8H). UV−vis (4.94×10^{-6} M, CH$_2$Cl$_2$): λ_{max}/nm (log ϵ) 419 (5.24), 530 (4.27), 555 (3.92, sh). IR (KBr pellet): 1012 cm^{-1} (oxidation state marker band). FAB MS: *m/z* 1242 [M]$^+$, 1062 [M − L]$^+$, 882 [M − 2L]$^+$ (L = N=CPh$_2$). Anal. Calcd $C_{82}H_{72}N_6Ru$: C, 79.26; H, 5.84; N 6.76. Found: C, 79.46; H, 6.03; N, 6.90.

Preparation of (Methyleneamido)hydroxoruthenium(IV) Porphyrins [Ru^{IV}(Por)(N=CPh$_2$)(OH)] (2). These complexes were prepared according to a similar procedure to that for the preparation of **1**, except that the products obtained were subjected to column chromatography on alumina (aluminum oxide 90, neutral, 70−230 mesh, EM) with dichloromethane−chloroform as eluent followed by removal of the solvents (which afforded **2** as dark purple solids).

[Ru^{IV}(TPP)(N=CPh$_2$)(OH)] (2a). Yield: 70%. ^{1}H NMR (300 MHz, CDCl$_3$): H_β 8.60 (s, 8H), H_o, $H_{o'}$ 8.27 (m, 4H), 7.82 (m, 4H), H_m, $H_{m'}$, H_p 7.73 (m, 8H), 7.66 (m, 4H), H'_p 6.72 (t, $J = 7.4$ Hz, 2H), H'_m 6.55 (t, $J = 7.7$ Hz, 4H), H'_o 3.89 (d, $J = 7.4$ Hz, 4H). UV−vis (6.94×10^{-6} M, CH$_2$Cl$_2$): λ_{max}/nm (log ϵ) 419 (5.29), 527 (4.23), 557 (3.81, sh). IR (KBr pellet): 3605 (ν_{OH}), 1012 cm^{-1} (oxidation state marker band). ES MS: *m/z* 894 [M − OH]$^+$, 1805. Anal. Calcd for $C_{57}H_{39}N_5ORu$: C, 75.15; H, 4.31; N, 7.69. Found: C, 75.55; H, 4.44; N, 7.67.

[Ru^{IV}(TTP)(N=CPh$_2$)(OH)] (2b). Yield: 68%. ^{1}H NMR (300 MHz, CDCl$_3$): H_β 8.61 (s, 8H), H_o, $H_{o'}$ 8.14 (dd, $J = 7.6$, 1.7 Hz, 4H), 7.71 (dd, $J = 7.7$, 1.8 Hz, 4H), H_m, $H_{m'}$ 7.54 (d, $J = 7.5$ Hz, 4H), 7.47 (d, $J = 7.5$ Hz, 4H), *p*-CH$_3$ 2.69 (s, 12H), H'_p 6.69 (t, $J = 7.6$ Hz, 2H), H'_m 6.53 (t, $J = 7.7$ Hz, 4H), H'_o 3.87 (d, $J = 7.8$ Hz, 4H). UV−vis (6.36×10^{-6} M, CH$_2$Cl$_2$): λ_{max}/nm (log ϵ) 421 (5.28), 527 (4.32), 558 (4.11, sh). IR (KBr pellet): 3602 (ν_{OH}), 1011 cm^{-1} (oxidation state marker band). ES MS: *m/z* 950 [M − OH]$^+$, 1917. Anal. Calcd for $C_{61}H_{47}N_5ORu$: C, 75.76; H, 4.90; N, 7.24. Found: C, 76.27; H, 4.84; N, 7.17.

Preparation of Bis(arylimine)ruthenium(II) Porphyrins [Ru^{II}(Por)(HN=CPh$_2$)$_2$] (3). These complexes were isolated as dark purple solids according to the same procedure as that for the preparation of **1a**,**b** except that [Ru^{II}(3,5-Cl$_2$TPP)(CO)] or [Ru^{II}(3,5-(CF$_3$)$_2$TPP)(CO)] was used instead of [Ru^{II}(4-Cl-TPP)(CO)] or [Ru^{II}(TMP)(CO)].

[Ru^{II}(3,5-Cl$_2$TPP)(HN=CPh$_2$)$_2$] (3a). Yield: 63%. ^{1}H NMR (300 MHz, CDCl$_3$): H_β 8.11 (s, 8H), H_o 7.86 (d, $J = 1.9$ Hz, 8H), H_p 7.69 (t, $J = 1.8$ Hz, 4H), H'_p, H''_p 7.16 (t, $J = 7.5$ Hz, 2H), 6.83 (t, $J = 7.5$ Hz, 2H), H'_m, H''_m 6.74 (t, $J = 7.8$ Hz, 4H), 6.58 (t, $J = 7.8$ Hz, 4H), H'_o, H''_o 4.71 (d, $J = 7.2$ Hz, 4H), 4.30 (d, $J = 7.0$ Hz, 4H). UV−vis (9.62×10^{-6} M, CH$_2$Cl$_2$): λ_{max}/nm (log ϵ) 415 (5.09), 512 (4.22). IR (KBr pellet): 3258 (ν_{NH}), 1005 cm^{-1} (oxidation state marker band). FAB MS: *m/z* 1352 [M]$^+$, 1171 [M − L]$^+$, 990 [M − 2L]$^+$ (L = HN=CPh$_2$). Anal. Calcd for $C_{70}H_{42}N_6Cl_8Ru$: C, 62.19; H, 3.13; N, 6.22. Found: C, 62.41; H, 3.19; N, 5.99.

[Ru^{II}(3,5-(CF$_3$)$_2$TPP)(HN=CPh$_2$)$_2$] (3b). Yield: 65%. ^{1}H NMR (300 MHz, CDCl$_3$): H_β 8.03 (s, 8H), H_o 8.45 (s, 8H), H_p 8.23 (s, 4H), H'_p, H''_p 7.16 (t, $J = 7.7$ Hz, 2H), 6.89 (t, $J = 7.7$ Hz, 2H), H'_m, H''_m 6.75 (t, $J = 7.8$ Hz, 4H), 6.59 (t, $J = 7.8$ Hz, 4H), H'_o, H''_o 4.76 (d, $J = 7.3$ Hz, 4H), 4.39 (d, $J = 7.2$ Hz, 4H). UV−vis (4.94×10^{-6} M, CH$_2$Cl$_2$): λ_{max}/nm (log ϵ) 415 (5.24), 510 (4.33). IR (KBr pellet): 3250 (ν_{NH}), 1002 cm^{-1} (oxidation state marker band). ES MS (CH$_2$Cl$_2$): *m/z* 1620 [M]$^+$, 1439 [M − L]$^+$, 1258 [M − 2L]$^+$ (L = HN=CPh$_2$). Anal. Calcd for $C_{78}H_{42}N_6F_{24}Ru$: C, 57.82; H, 2.61; N, 5.19. Found: C, 57.61; H, 2.90; N, 5.04.

X-ray Crystal Structural Determination of 1a, 2a, and 3b·0.5CH$_2$Cl$_2$. Diffraction-quality crystals were grown by slow evaporation of a solution in dichloromethane−hexane (1:5 v/v) at room temperature for about 3 days (**1a** and **2a**) or by slow evaporation of a solution in dichloromethane−ethanol (1:5 v/v) at room temperature for a week (**3b**·0.5CH$_2$Cl$_2$). Data were collected using graphite-monochromatized Mo Kα radiation at 28 °C on a MAR diffractometer with a 300-mm image plate detector for **1a** (dimensions $0.40 \times 0.25 \times 0.20$ mm^3) and at 21 °C on a Bruker SMART CCD diffractometer for **2a** (dimensions: $0.18 \times 0.14 \times 0.08$ mm^3) and **3b**·0.5CH$_2$Cl$_2$ (dimensions: $0.20 \times 0.16 \times 0.14$ mm^3). In the case of **1a**, the data collection was made with 2° oscillation step of φ, 600-second exposure time, and 120-mm scanner distance, and 100 images were collected. The structures were solved by direct methods employing SIR-97[34] program (**1a**) or SHELXS-97[35] program (**2a** and **3b**·0.5CH$_2$Cl$_2$) and refined by full-matrix least-squares on F^2 employing SHELXL-97[36] program on PC. For **3b**·0.5CH$_2$Cl$_2$, the F atoms of the CF$_3$ groups in the 3,5-(CF$_3$)$_2$TPP ligand are disordered. In the least-squares refinements, all non-hydrogen atoms, except some of the disordered F atoms, were refined anisotropically, and the H atoms at calculated positions were not refined.

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Supporting Information Available: Positional and thermal parameters and bond lengths and angles for [Ru^{IV}(4-Cl-TPP)(N=CPh$_2$)$_2$] (**1a**), [Ru^{IV}(TPP)(N=CPh$_2$)(OH)] (**2a**), and [Ru^{II}(3,5-(CF$_3$)$_2$TPP)(HN=CPh$_2$)$_2$]·0.5CH$_2$Cl$_2$ (**3b**·0.5CH$_2$Cl$_2$) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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