Bis Axial Ligation of Simple Imine and Methyleneamido Groups by Ruthenium Porphyrins

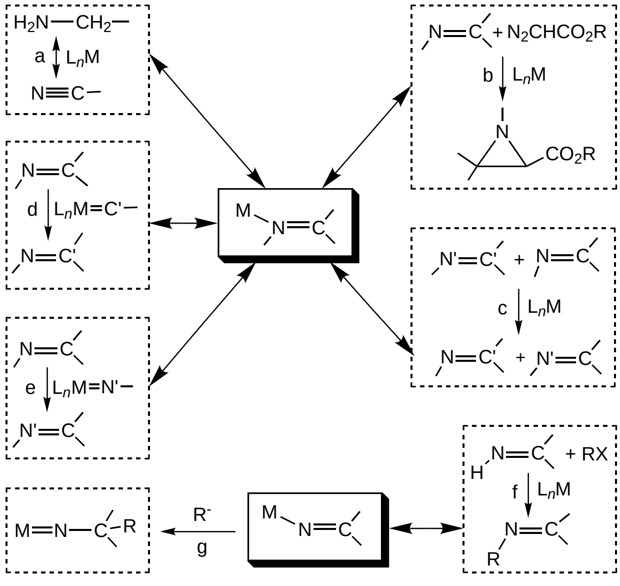
Jie-Sheng Huang, Sarana Ka-Yan Leung, Kung-Kai Cheung, and Chi-Ming Che*[a]

Abstract: Bis(*N*-ethylideneethanamine)ruthenium(II) porphyrins, $[Ru^{II}(Por)(N(Et){=}CHMe)_2]$ (Por = TTP, 4-Cl-TPP), were prepared by the reaction of dioxoruthenium(VI) porphyrins with triethylamine in ≈85% yields. The reaction between dioxoruthenium(VI) porphyrins and benzophenone imine afforded bis(diphenylmethyleneamido)ruthenium(IV) porphyrins, $[Ru^{IV}(Por)(N{=}CPh_2)_2]$ (Por = TTP, 3,4,5-MeO-TPP), in ≈65% yields. These new classes of metalloporphyrins were characterized by ^{1}H NMR, UV/Vis, and IR spectroscopy as well as by mass spectrometry and elemental analysis. The X-ray crystallographic structures of $[Ru^{II}(TTP)(N(Et){=}CHMe)_2]$ and $[Ru^{IV}(3,4,5\text{-}MeO\text{-}TPP)(N{=}CPh_2)_2]$ revealed an axial Ru–N bond length of 2.115(6) Å for the imine complex and 1.896(8) Å for the methyleneamido complex. Each of the $N{=}CPh_2$ axial groups in $[Ru^{IV}(3,4,5\text{-}MeO\text{-}TPP)(N{=}CPh_2)_2]$ adopts a linear coordination mode with a corresponding Ru-N-C angle of 175.9(9)°. Spectral and structural studies revealed essentially single bonding character for the bis(imine) complexes but a multiple bonding character for the bis(methyleneamido) complexes with respect to their axial Ru–N bonds.

Keywords: imines · macrocyclic ligands · methyleneamides · N ligands · ruthenium · structure elucidation

Introduction

Metal complexes with simple imine (N(R″)=CRR′) or methyleneamido (N=CRR′, an alternative and common term: azavinylidene) groups, where R = H, alkyl/aryl, have been observed or proposed to be key intermediates in a number of metal-mediated processes, such as interconversion between amines and nitriles,[1] aziridination of imine by a carbene donor,[2] imine, alkylidene/imine, imide/imine metatheses,[3] and N-arylation of imines[4] (Reactions a–f in Scheme 1). Investigations into the interaction between a metalloporphyrin and a simple imine or methyleneamido group would be of fundamental interest for the application of metalloporphyrins to these processes, which should be attractive because metalloporphyrins that function as catalysts often feature high activity and selectivity[5] and are robust if there are appropriate substituents on the porphyrin rings.[6]



Scheme 1. Reactions involving M–N(R″) = CRR′ and M–N = CRR′ complexes.

However, the binding behavior of metalloporphyrins toward a *simple* imine or methyleneamido group is *hitherto unexplored*. Even their complexes with functionalized monodentate imine or methyleneamido groups are exceedingly rare. In 1974, Lappert and co-workers[7] described the preparation of a cobalt porphyrin with an $N{=}C(CF_3)_2$ axial group (**1**). Recently, Simonneaux and co-workers[8] observed the formation of ruthenium porphyrins that bear an iminoester ($NH{=}CHCO_2Et$) and an aminoester as *mixed* axial ligands (**2**). These species each contain a single iminoester or $N{=}C(CF_3)_2$ group and have only been characterized by spectroscopy. The iminoester and $N{=}C(CF_3)_2$ ligands feature strongly electron-withdrawing groups on the imino-carbon

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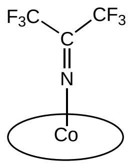

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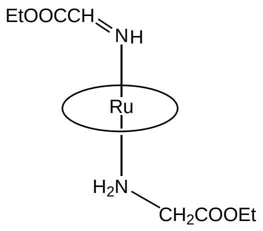

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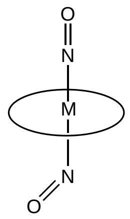
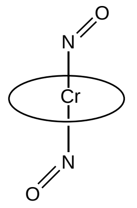


3
(M = Fe, Ru, Os)



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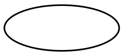
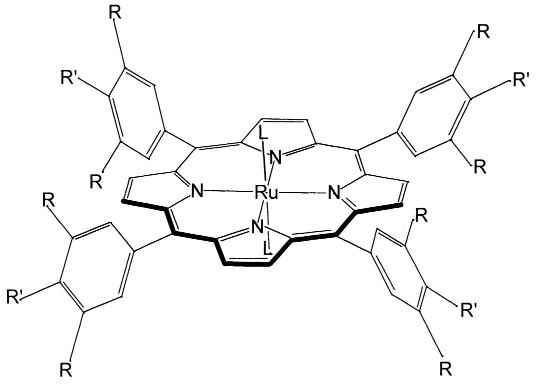


= Por^{2-}
(porphyrinato dianion)



	Ru–L	R	R'
5a	$\mathrm{Ru^{II}{\leftarrow}NEt({=}CHMe)}$	H	Me
5b		H	Cl
6a	$\mathrm{Ru^{IV}{-}\ddot{N}{=}CPh_2}$	H	Me
6b		OMe	OMe

atoms, which may increase their axial ligation to a metalloporphyrin as a result of enhanced backbonding between the metal and the axial ligand. Furthermore, the presence of an electron-withdrawing CO_2Et group is assumed to be responsible for the formation of **2** from its bis(aminoester) counterparts.[8b] Hence, the question whether simple imine or methyleneamido ligands can form stable complexes with a metalloporphyrin remains to be addressed.

Our interest in methyleneamido metalloporphyrins also stems from the following considerations: 1) tosylimido ruthenium porphyrins are reactive towards aziridination of alkenes and amidation of saturated C–H bonds.[9] In order to extend the scope of such reactions, it is essential to develop synthetic routes to produce metalloporphyrins that contain other imido groups. Methyleneamido metalloporphyrins might be unique precursors to these species by means of C-hydrogenation or alkylation of the ligated methyleneamido groups (Reaction g in Scheme 1).[10] 2) Because the methyleneamido group is *isoelectronic* with the nitrosyl (NO) group, it is known to resemble the behavior of NO in binding metal ions.[11] Both linear and bent coordination modes have been observed for a terminal methyleneamido ligand.[11] Since metalloporphyrins usually bind a single NO axial group,[12] and the rare examples of bis(nitrosyl) ruthenium,[13a] iron,[13b,c] osmium,[13d–f] and chromium[13g] porphyrins **3** and **4** (*none have been structurally characterized*) are proposed to bear either linear/bent or bent/bent NO groups, we are interested in examining whether bis(methyleneamido)metalloporphyrins can also be prepared and, if so, which coordination mode(s) the methyleneamido groups would adopt.

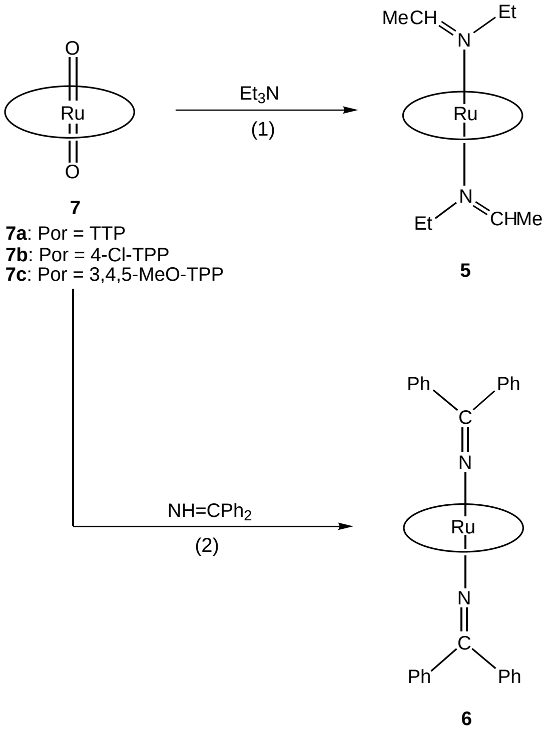
Herein we report on ruthenium porphyrins $[\mathrm{Ru^{II}(Por)(N(Et){=}CHMe)_2}]$ (Por = TTP, **5a**; 4-Cl-TPP, **5b**) and $[\mathrm{Ru^{IV}(Por)(N{=}CPh_2)_2}]$ (Por = TTP, **6a**; 3,4,5-MeO-TPP, **6b**)[14] that bear *simple* imine and methyleneamido axial groups, respectively. Complexes **5a** and **5b** were obtained through an *unprecedented* N-dealkylation of triethylamine by an isolated oxo metalloporphyrin. The structure of complex **6b** features interesting linear/linear methyleneamido axial groups, in contrast to the NO analogues **3** and **4**.

Results and Discussion

Synthesis: Despite a *vast* number of metal complexes with *chelating* imines reported in the literature,[15] complexes with *simple* monodentate imines are still rare and have attracted considerable attention only recently.[16–26] Metal-methyleneamido (M–N=CRR′) complexes[11, 27] have also attracted less attention than metal nitrosyl (M–NO),[11b, 28] imido (M=NR),[29] and amido (M–NRR′)[30] complexes. To our knowledge, there is only one mononuclear ruthenium methyleneamido complex reported in the literature that bears a *single* methyleneamido group.[21b,c] While M–NO, M=NR, and M–NRR′ compounds with a macrocyclic auxiliary ligand have all been prepared and their importance has been recognized,[31, 32] *no metallomacrocyles that bear simple imine or methyleneamido ligands have yet been reported.*

Bis(imine) complexes: Simple imines are usually weaker bases than their amine analogues. In contrast to the facile syntheses of metal amine complexes, metal complexes with simple imines are rather *elusive*. We have demonstrated that the reaction of dioxoruthenium(VI) porphyrins $[\mathrm{Ru^{VI}O_2(Por)}]$ (**7**) with a wide variety of amines provides a simple and general route to bis(amine)ruthenium(II) porphyrins.[32a–c] However, treatment of **7** with commercially available, simple imines, such as $NH{=}CR_2$ (R = *t*Bu, Ph), afforded neither mono- nor bis(imine) adducts of ruthenium porphyrins. Instead, bis(methyleneamido) complexes were obtained in the case of $NH{=}CPh_2$ (vide infra). Furthermore, James and Bailey[33a] observed the catalytic dehydrogenation of amine to imine and nitrile by a ruthenium complex with a TMP[33b] macrocycle. Nevertheless, only a bis(amine)ruthenium(II) porphyrin was isolated from the reactions.

The bis(imine) complexes **5** were prepared, in a special manner, by the reaction of the corresponding dioxo complexes **7** with triethylamine (Et_3N) (Reaction (1) in Scheme 2). A mixture of **7a** or **7b** in *highly purified* Et_3N



Scheme 2. Reactions of **7** with Et_3N and $NH{=}CPh_2$ to give complexes **5** and **6**, respectively.

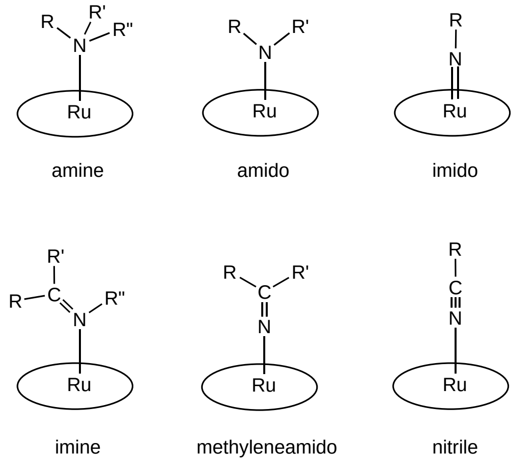
was stirred for 0.5 h at ambient temperature to give a brown solution. Removal of Et_3N followed by recrystallization from dichloromethane/*n*-hexane afforded analytically pure **5a** or **5b** as a dark purple solid in ≈85% yield. The purified Et_3N contained no primary or secondary amine impurities, as revealed by ^1H NMR measurements. We expected that the presence of these impurities would cause the products to be contaminated by bis(amine)ruthenium(II) porphyrins. Indeed, when Et_3N containing 0.3 wt% diethylamine (Et_2NH) was used, a mixture of **5a**, $[Ru^{II}(TTP)(NHEt_2)_2]$ (**8**),[34] and perhaps $[Ru^{II}(TTP)(N(Et){=}CHMe)(NHEt_2)]$ was isolated in about 1:1:0.8 molar ratio (based on ^1H NMR measurements).

In view of the fact that **7a** and **7b** can quantitatively react with trimethylamine (Me_3N) to form bis(amine) complexes $[Ru^{II}(Por)(NMe_3)_2]$,[32a] the formation of bis(imine) complexes from Reaction (1) in Scheme 2 deserves attention. Probably, Et_3N as an axial ligand is too bulky to form a stable adduct with a ruthenium porphyrin. Reaction (1) (Scheme 2) provided useful information on the reactivity of dioxo complexes **7** toward a tertiary amine. When we previously reported the reaction of **7a** or **7b** with Me_3N, the fate of Me_3N was unclear. In this work, it appeared that Et_3N was oxidized by **7a** or **7b** to form the imine $N(Et){=}CHMe$, which was trapped by the intermediate $[Ru^{II}(Por)]$ to form **5a** or **5b**. This type of *N*-dealkylation of Et_3N has not been reported for *isolated* oxo metalloporphyrins;[35a] however, it is known for an oxo ruthenium(V) complex with a nonporphyrinato ligand.[35b]

Although **5a** and **5b** were prepared by a rather special method, their ready formation and isolation revealed that the axial ligation of a simple imine to a metalloporphyrin could be fairly robust. Complexes **5a** and **5b** are rare examples of mononuclear metal complexes with *multiple* simple imine ligands. Prior to this work, only a few mononuclear metal complex *cations* that contain two or three simple imine ligands have been reported.[21e, 23, 25, 26]

Bis(methyleneamido) complexes: There are a number of synthetic routes to metal methyleneamido complexes, of which the halide–methyleneamido exchange method is the most frequently used.[11, 27] Keene and co-workers had previously reported the preparation of a highly oxidizing dimethylmethyleneamido ruthenium(IV) complex by means of the oxidative deprotonation of an imine precursor.[21b,c] In this work, complexes **6** were prepared in ≈65% yield by the treatment of the corresponding **7** with benzophenone imine ($HN{=}CPh_2$) in dichloromethane (Reaction (2) in Scheme 2). This is the first demonstration of the preparation of metal methyleneamido complexes from the reaction of a metal–oxo complex with a simple imine. Reaction (2) formally resembles the reactions between dioxoruthenium(VI) porphyrins and arylamines to form arylamido complexes.[32a,b] This implies that the $N{=}CPh_2$ groups might be similar to arylamido groups in their coordination to metal ions; a similarity not well recognized previously. In fact, although arylamido, nitrosyl, and methyleneamido ligands are all potential three-electron donors, only the similarity between methyleneamido and nitrosyl ligands in binding metal ions is widely known.[11]

Remarkably, the isolation of **5** and **6** marked the synthesis of ruthenium porphyrins that bear a complete set of simple acyclic *N*-donating axial ligands with C–N, C=N, and C≡N bonds, that is, amine (NRR′R″),[32a–c, 33] amido (NRR′),[32a,b] imido (NR),[32a,c] imine (N(R″)=CRR′), methyleneamido (N=CRR′), and nitrile (N≡C–R)[36] complexes.



Spectral features

^1H NMR spectroscopy: As expected for ruthenium(II) porphyrins, complexes **5a** and **5b** are diamagnetic. All their proton resonances appear at normal fields and are well resolved. The spectral data are summarized in Table 1. For comparison, the data for complex **8**, $[Ru^{II}(TTP)(Py)_2]$ (**9**),[37] and free $N(Et){=}CHMe$ and Py are also included in the Table.

Table 1. ^{1}H NMR spectral data (δ, $CDCl_3$) for bis(imine)ruthenium(II) porphyrins **5a** and **5b**. The data for bis(diethylamine) analogue **8**, bis(pyridine) analogue **9**, and free N(Et)=CHMe and Py are also included for comparison.

	H_β (s, 8H)	H_o (d, 8H)	H_m (d, 8H)	*p*-Me (s, 12H)	$CH_3CH{=}NCH_2CH_3$ $CH_3\mathit{CH}$ (q, 2H)	 $\mathit{CH_3}CH$ (d, 6H)	 $CH_3\mathit{CH_2}$ (q, 4H)	 $\mathit{CH_3}CH_2$ (t, 6H)
5a	8.09	7.90	7.43	2.63	1.45	− 0.34	− 1.25	− 1.88
5b	8.07	7.94	7.62	–	1.44	− 0.34	− 1.26	− 1.88
N(Et)=CHMe[a]					7.63 (qxt)	1.90 (dt)	3.33 (qt)	1.16 (t)
					Et_2NH[b] NH (br, 2H)	 CH_a (m, 4H)	 CH_b (m, 4H)	 CH_3 (t, 12H)
8	8.08	7.90	7.43	2.63	− 6.40[c]	− 2.12	− 2.39	− 1.59
					Py H'_o (d, 4H)	 H'_m (t, 4H)	 H'_p (t, 2H)	
9	8.18	7.90	7.42	2.63	2.47	5.11	5.97	
Py					8.61	7.28	7.67	

[a] From ref. [38]. [b] The methylene protons of the coordinated Et_2NH groups in complex **8** are diastereotopic. [c] Disappeared upon addition of D_2O.

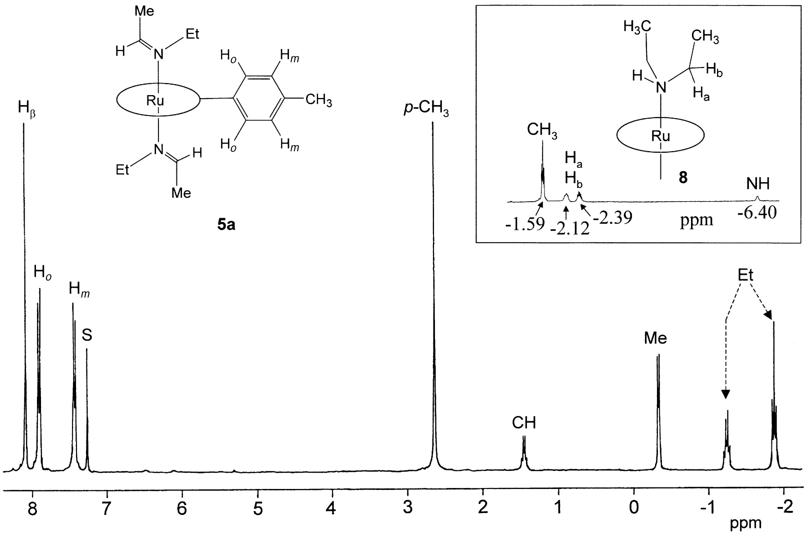
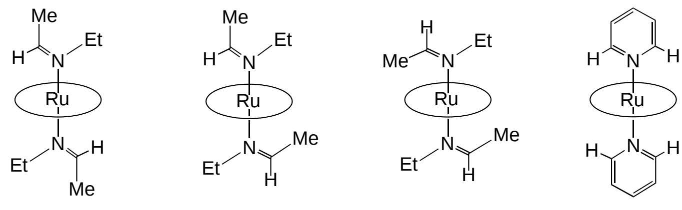


Figure 1. ^{1}H NMR spectrum (300 MHz) of complex **5a** in $CDCl_3$ (note that the $CDCl_3$ used in this case contained no TMS). The inset shows the ^{1}H NMR spectrum of complex **8** in the axial ligand region.

Figure 1 shows the spectrum of **5a** in deuteriochloroform. This spectrum features H_β (the pyrrole protons of the porphyrinato ligand), H_o, and H_m signals almost identical to those of the bis(amine) complex **8** (see Table 1). For both complexes **5a** and **8**, the signals of axial ligands have substantial upfield shifts relative to the corresponding free ligands on account of the porphyrin ring-current effect. However, the signal patterns of these axial ligands are dramatically different. Assignment of the ethyl and ethylidene signals of N(Et)=CHMe in **5a** is facilitated by their different coupling constants (Et: $J = 7.2$ Hz, CHMe: $J = 5.7$ Hz), as well as by their unique multiplicity and intensity ratio. The Et_2NH signals in **8** feature NH proton resonances with large upfield shifts and a clear splitting of the methylene proton resonances (H_a and H_b in the inset to Figure 1). Such a splitting stems from the diastereotopy of these protons in complex **8**.

Although the monodentate coordination of two N(Et)=CHMe molecules to a [Ru(Por)] moiety would result in three geometric isomers (**I**–**III** in Figure 2), it seems that only isomer **I** exists in solution, since the porphyrin ring-current effect on the ethylidene CH proton resonances in **5a** is almost identical to that on the *ortho* proton resonances of pyridine in **9**.[38] Note that only in isomer **I** are the distances to the porphyrin ring from both ethylidene CH protons similar to those from the *ortho* protons of pyridine for **9** (Figure 2). Probably, isomers **II** and **III** are destabilized by the repulsion between the ethylidene methyl groups and the porphyrinato ligand.

The methyleneamido ruthenium(IV) complexes **6a** and **6b** also exhibit diamagnetic ^{1}H NMR spectra, similar to bis(arylamido)ruthenium(IV) porphyrins.[32a,b] Figure 3 shows the spectrum of **6b** in deuteriochloroform as an example. The sharp singlet observed for either H_o or *m*-OMe protons indicates the presence of a pseudomirror plane through the porphyrinato ring. The signal patterns of the phenyl proton resonances of axial $N{=}CPh_2$ groups (H'_o, H'_m and H'_p) deserve special attention. Since a *single* set of these signals appears in Figure 3, both the methyleneamido axial groups must be linear. As shown in Figure 4, the coordination of a bent $N{=}CPh_2$ group would render its two phenyl groups nonequivalent as a result of the prohibited rotation of the CPh_2 moiety about the N=C double bond.



I **II** **III** **9**

Figure 2. Possible geometric isomers of complexes **5a** and **5b** as compared with their bis(pyridine) analogue **9**.

Table 2 summarizes the spectral data for complexes **6a** and **6b**. The H_β chemical shifts of **6a** ($\delta = 8.47$) and **6b** ($\delta = 8.61$) are larger than those of the ruthenium(II) complexes **5a**, **5b**, **8**,

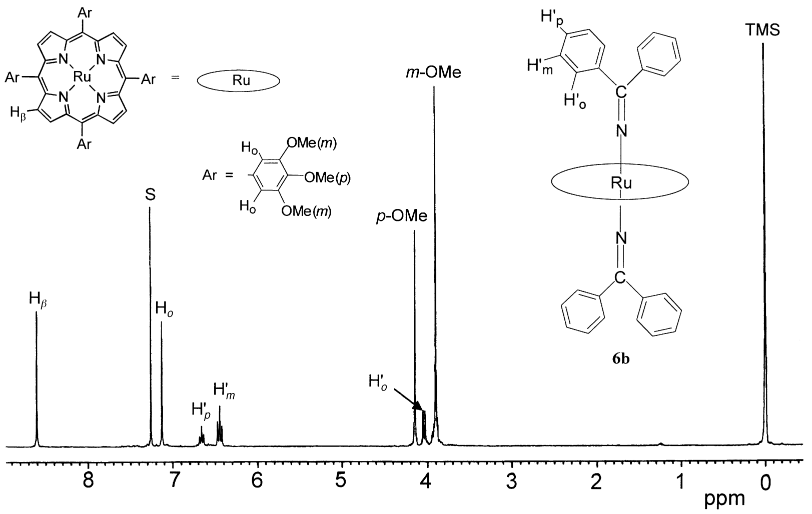


Figure 3. ^{1}H NMR spectrum (300 MHz) of complex **6b** in CDCl$_3$.

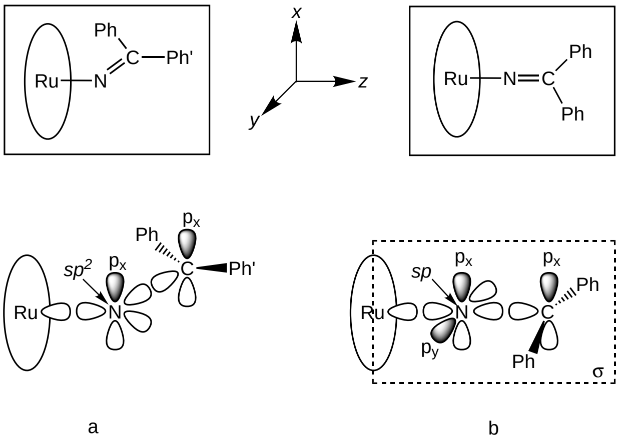


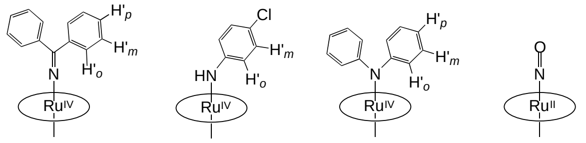
Figure 4. Schematic diagram showing a) bent and b) linear Ru–N=CPh$_2$ geometry. One of the two phenyl groups in (a) is considerably closer to the porphyrin ring and therefore the proton resonances are expected at higher fields. The two phenyl groups in (b) are identical owing to the dotted mirror plane.

and **9** ($\delta = 8.07-8.18$), in agreement with the +4 oxidation state of ruthenium in complexes **6**.[39, 40] In order to compare **6** with the closely related bis(arylamido)ruthenium(IV) and nitrosylruthenium(II) *meso*-tetraarylporphyrins, the spectral data of [Ru^{IV}(TTP)(NH-*p*-C$_6$H$_4$Cl)$_2$] (**10**),[32a] [Ru^{IV}(3,4,5-MeO-TTP)(NPh$_2$)$_2$] (**11**),[32b] and [Ru^{II}(TPP)(NO)(OH)] (**12**)[41, 42] are also included in Table 2. Apparently, the H$_\beta$ chemical shifts of complexes **6a** and **6b** are more similar to those of the bis(arylamido) species **10** and **11**. Notably, the signals of the axial phenyl groups in **6a** and **6b** appear at lower fields than those of **10** and **11**. This is consistent with the greater distances between these phenyl groups and the porphyrin rings that are expected for the methyleneamido complexes with linear N=CPh$_2$ axial groups.

UV/Vis spectrophotometry: Bis(imine) complexes **5a** and **5b** exhibit bands at about $\lambda = 412$ (Soret), 507 (β), and 532 (α) nm; a spectrum characteristic of ruthenium(II) porphyrins with σ-donating ligands, such as amines[32a–c] and nitriles.[36] The spectrum of **5a** is almost identical to that of its pyridine analogue **9**.[37] In contrast, bis(methyleneamido) complexes **6a** and **6b** show bands at about $\lambda = 422$ (Soret), 526 (β), and 557 (α) nm, which are all red-shifted relative to the bis(imine) complexes **5a** and **5b**. The spectrum of **6b** is depicted in Figure 5 as an example. As is evident from the inset in Figure 5 , the spectrum of the methyleneamido complex is similar to that of the diphenylamido complex **11**; however, it is significantly different from that of the nitrosyl complex **12**.

IR spectroscopy and MS spectrometry: The IR spectra of the imine complexes **5a** and **5b** show "oxidation state marker" bands[32a] at about $\tilde{\nu} = 1000$ cm^{-1}, which are identical to that observed for the pyridine complex **9**.[37] The "oxidation state marker" bands of the methyleneamido complexes **6a** and **6b** ($\tilde{\nu} = 1011$ cm^{-1}) are also similar to those of the arylamido complexes **10** and **11** ($\tilde{\nu} = 1009-1012$ cm^{-1}). The positive-ion FAB mass spectra of **5a**, **5b**, **6a**, and **6b** each exhibit a set of three prominent signals that can be attributed to the parent ion [M]$^+$, and the fragments [M – L]$^+$ and [M – 2L]$^+$, where L is the respective imine and methyleneamido ligand (see the Experimental Section).

Table 2. ^{1}H NMR spectral data (δ, CDCl$_3$) of complexes **6a** and **6b** as compared with those of bis(arylamido)ruthenium(IV) and nitrosylruthenium(II) porphyrins.

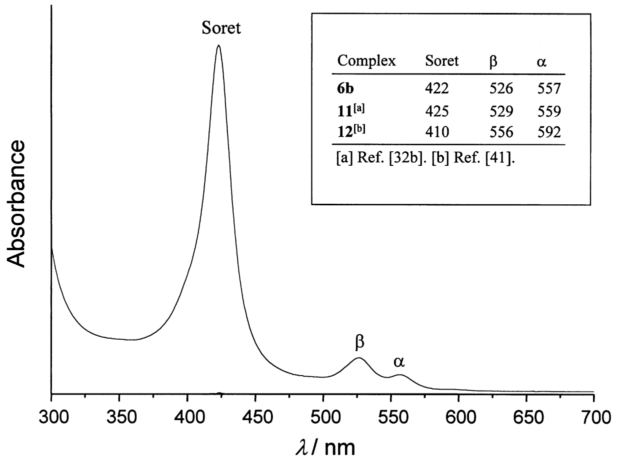


6 **10** **11** **12**

	H$_\beta$ (s, 8H)	H$_o$ (d, 8H)	H$_m$ (d, 8H)	p-Me (s, 12H)	Axial Ph		
					H'$_o$ (d, 8H)	H'$_m$ (t, 8H)	H'$_p$ (t, 4H)
6a	8.47	7.80	7.45	2.66	4.01	6.43	6.66
6b	8.61	7.13	3.90[a]	4.15[b]	4.04	6.45	6.66
10[c]	8.41	7.88	7.49	2.67	2.85[d]	5.84[d]	–
11[e]	8.37	7.04	4.02[a]	4.15[b]	2.71	5.92	6.23
12[f]	8.98	8.28[g]	7.80[h]	–	–	–	–

[a] m-MeO (s, 24H). [b] p-MeO (s, 12H). [c] Ref. [32a]. [d] (d, 4H). [e] Ref. [32b]. [f] Ref.[41]. [g] (m, 8H). [h] H$_m$ and H$_p$ (m, 12H).

Metal → N (axial) backbonding: It is noteworthy that both the simple imine and the meth-



Complex	Soret	β	α
6b	422	526	557
11[a]	425	529	559
12[b]	410	556	592

[a] Ref. [32b]. [b] Ref. [41].

Figure 5. UV/Vis spectrum of complex **6b** in chloroform. A comparison of the spectral data with those of the diphenylamido complex **11** and nitrosyl complex **12** is shown in the inset.

yleneamido ligands distinguish themselves from amine and arylamido ligands with their characteristic C=N double bonds, which may have low-lying unoccupied π* orbitals for M → N=C backbonding. Examination of the contribution of such backbonding to the overall Ru–imine or Ru–methyleneamido axial ligation for complexes **5a**, **5b**, **6a**, and **6b** would be interesting.

In general, for a given metal ion, the strength of the M → L backbonding increases with increasing π-acidity of the ligand L. Buchler, Gouterman and co-workers[13f, 43] have observed that, for iron, ruthenium, and osmium octaethylporphyrins, both the β band wavelength in the UV/Vis spectrum and the H_{meso} chemical shift in the ^{1}H NMR spectrum systematically decrease as the π-acidity of the axial ligands decreases. Our recent work demonstrates that a similar trend also exists for osmium(II) *meso*-tetraarylporphyrins.[44] Provided that the ruthenium analogues also observe these rules, it is possible to estimate the strength of the Ru → N=C axial backbonding in the imine and methyleneamido complexes on the basis of the spectral features described above.

Inasmuch as the β band wavelengths for ruthenium(II) porphyrins with $NHEt_2$ (**8**), N(Et)=CHMe (**5a** and **5b**), and Py (**9**) are nearly identical, the Ru → L axial backbonding interactions in these complexes are hardly distinguishable in terms of this criterion. The H_β chemical shifts seem more sensitive to the Ru → L axial backbonding. A comparison of the H_β chemical shifts of the ruthenium(II) complexes **5a**, **8**, and **9** (Table 1), which all contain the TTP macrocycle, reveals that while there might be weak Ru → Py backbonding in **9**, the Ru → N=C backbonding in **5a** is negligible. In the case of complexes **6a** and **6b**, both their β band wavelengths and H_β chemical shifts are significantly smaller than the corresponding values for complex **12** (Figure 5 and Table 2). This suggests that the Ru → L axial backbonding, if it is present, in the methyleneamido complexes **6a** and **6b**, should be weaker than that in the nitrosyl complex **12**.

X-ray structural determinations: The formulation of both the imine and methyleneamido complexes has been confirmed by X-ray crystallographic studies. Table 3 gives the crystal data and structure refinement for complexes **5a** and **6b**. Selected bond lengths and angles are listed in Table 4. The ORTEP drawings and atomic numbering schemes are depicted in Figure 6 for **5a** and Figure 7 for **6b**. Both the complexes have *trans* axial ligands, with the ruthenium ions located at the center of symmetry. The orientations of their axial ligands with respect to the porphyrin rings are shown in Figure 8.

The structure of **5a** does correspond to the isomer **I** shown in Figure 2, as suggested from the solution ^{1}H NMR studies described above. The Ru1–N3 bond length of 2.115(6) Å is similar to the Ru–N(benzylamine) bond length of 2.129(2) Å in $[Ru^{II}(TMP)(NH_2CH_2Ph)_2]$ (**13**),[33] but slightly longer than the Ru–N(imine) bond in *cis*-$[Ru^{II}(bpy)_2(NH{=}CMe_2)_2](PF_6)_2$ (**14**, bpy = 2,2′-bipyridine) (average bond length = 2.07(1) Å).[21e] The C=N bond length of the axial imine ligands in **5a** (1.30(1) Å, C1–N3 and C1*–N3*) is also similar to the corresponding bond lengths found for other metal complexes of simple imines, although significantly larger than that of **14** (1.16(2) Å). Notably, complex **5a** is the first

Table 3. Crystal data and structure refinement for complexes **5a** and **6b**.

	Complex **5a**	Complex **6b**·$2CH_2Cl_2$
formula	$C_{56}H_{54}N_6Ru$	$C_{82}H_{72}N_6O_{12}Ru\cdot 2CH_2Cl_2$
M_r	912.15	1604.44
λ [Å]	0.71073	0.71073
T [K]	301	301
crystal system	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$
a [Å]	20.951(3)	10.467(4)
b [Å]	13.339(2)	12.291(7)
c [Å]	20.199(3)	15.687(7)
α [°]	90.00(3)	94.34(4)
β [°]	99.15(2)	107.63(4)
γ [°]	90.00(3)	94.91(4)
V [Å^3]	9384(2)	1905(1)
Z	4	1
ρ_{calcd} [Mg m^{-3}]	1.087	1.398
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.318	0.413
$F(000)$	1904	830
$2\theta_{max}$ [°]	51.0	50
index ranges	$0 \leq h \leq 25, 0 \leq k \leq 18, -24 \leq l \leq 24$	$-12 \leq h \leq 12, 0 \leq k \leq 14, -18 \leq l \leq 18$
reflections collected	26901	7084
independent reflections	5096	6694
refinement method	full-matrix least-squares on F	full-matrix least-squares on F
parameters	286	484
goodness-of-fit on F^2	2.85	2.53
final R indices [$I > 3\sigma(I)$]	R[a] = 0.078, R_w[b] = 0.115	R = 0.080, R_w = 0.108
largest diff. peak hole [e Å^{-3}]	0.97/ – 0.51	1.04/ – 0.86

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 4. Selected bond lengths [Å] and angles [°] for complexes **5a** and **6b**.

	Complex **5a**		
Ru1–N1	2.047(5)	Ru1–N3	2.115(6)
Ru1–N2	2.052(5)	C1–N3	1.30(1)
C3–N3	1.44(1)		
		N1-Ru1-N3	90.7(2)
N1-Ru1-N2	89.5(2)	N2-Ru1-N3	90.2(2)
N1-Ru1-N2*	90.5(2)	N1*-Ru1-N3	89.3(2)
N3-Ru1-N3*	180.0	N2*-Ru1-N3	89.8(2)
Ru1-N3-C1	121.9(6)	N3-C1-C2	129.5(10)
Ru1-N3-C3	121.8(6)	N3-C3-C4	111(1)
	Complex **6b**		
Ru1–N1	2.064(7)	Ru1–N3	1.896(8)
Ru1–N2	2.064(7)	C1–N3	1.25(1)
N1-Ru1-N2	90.6(3)	N1-Ru1-N3	90.3(3)
N1-Ru1-N2*	89.4(3)	N2-Ru1-N3	90.2(2)
N3-Ru1-N3*	180.0	N1*-Ru1-N3	88.9(3)
Ru1-N3-C1	175.9(9)	N2*-Ru1-N3	91.1(3)
N3-C1-C2	119(1)	N3-C1-C8	120(1)

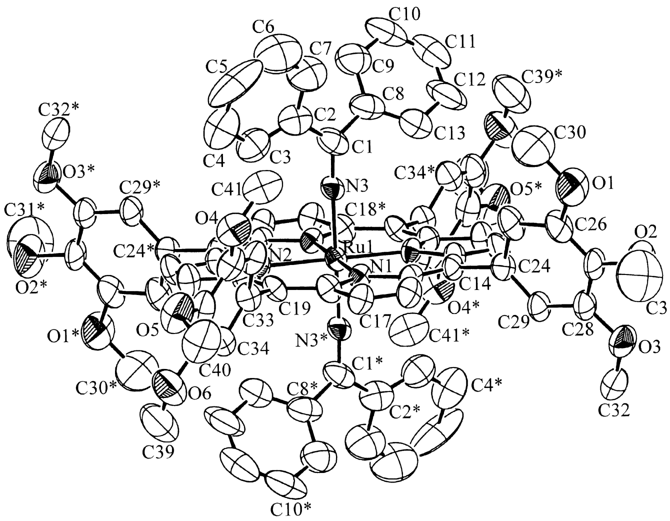


Figure 7. ORTEP drawing with the atomic numbering scheme for complex **6b**. Hydrogen atoms and solvent molecules are omitted. Thermal ellipsoids are drawn on the 40% probability level.

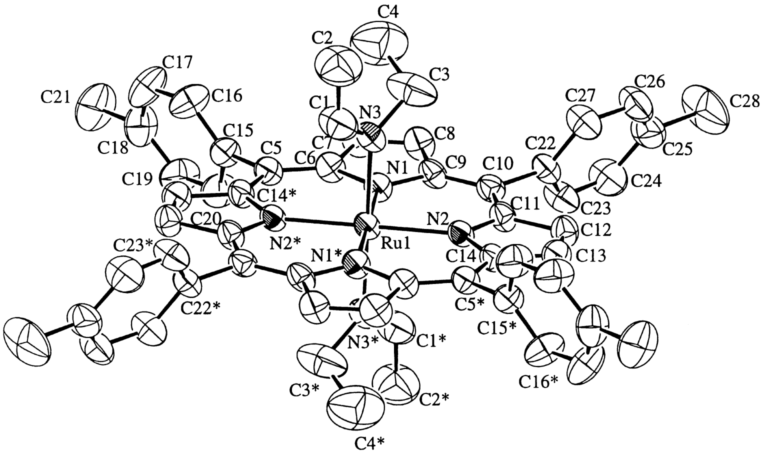


Figure 6. ORTEP drawing with the atomic numbering scheme for complex **5a**. Hydrogen atoms are omitted. Thermal ellipsoids are drawn on the 40% probability level.

structurally characterized metalloporphyrin that contains an acyclic imino N-donating axial ligand.

In view of the spectral similarities between complexes **5a** or **5b**, and **9**, it would be of interest to compare the core structures of the bis(imine) complexes with those of structurally characterized bis(pyridine) metalloporphyrins, such as [Ru^{II}(OEP)(Py)$_2$] (**15**)[37a, 45] and [Fe^{II}(TPP)(Py)$_2$] (**16**),[46] (Table 5). Evidently, the key bond lengths and angles of **5a** are remarkably similar to those of complexes **15** and **16**. Although the C–N bond lengths (d_2 and d_3) in **5a** are different owing to the lack of π-bond delocalization; their average value is almost identical to the C–N bond lengths in **15** and **16**. These observations should be important as they shed light on the relative contribution of the M → Py backbonding to the overall M–Py axial ligation in bis(pyridine)metalloporphyrins. Note that, while a large number of metalloporphyrins with axial pyridine ligands have been reported,[12, 47] it is not totally clear whether the intrinsic stability of these complexes stems from the backdonation of metal d electrons to the delocalized empty π*-orbitals of pyridine. Previously, Buchler, Gouterman, and co-workers[13f] addressed this issue on the basis of theoretical calculations and concluded that this backdonation is not important. Alternatively, the issue can be addressed in a synthetic way, namely to examine whether a metalloporphyrin, [Ru^{II}(Por){N(Me)=CH$_2$}$_2$] (**17**), which binds only the "head" of the pyridine that has no delocalized π-bonding, is sufficiently stable to be isolated. Complexes **5a** and **5b**, the isolated metal

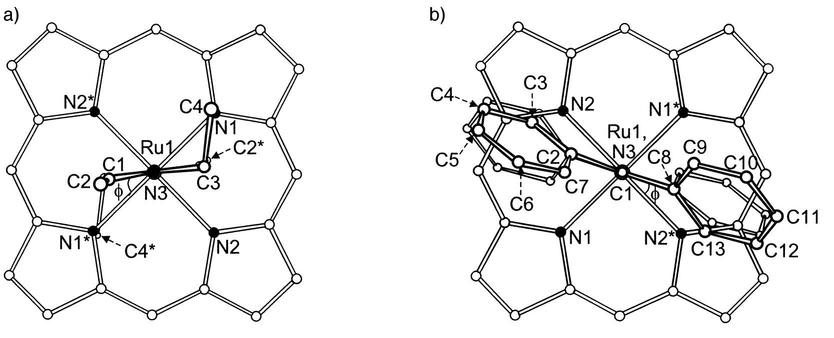
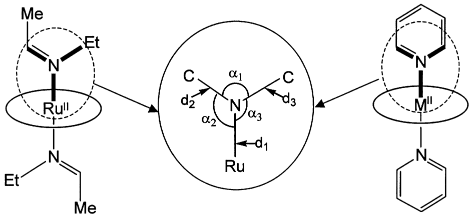


Figure 8. Ball-and-stick drawings showing the orientations of the axial ligands in a) complex **5a** and b) complex **6b** with respect to the porphyrinato rings. The φ angle is defined as described in ref. [47].

Table 5. Comparison of the key bond lengths and angles between complex **5a** and its pyridine analogues **15** and **16**.



5a

15, 16

	d_1 [Å]	d_2 [Å]	d_3 [Å]	α_1 [°]	α_2 [°]	α_3 [°]	ϕ [°]
5a	2.115(6)	1.30(1)	1.44(1)	116.2(8)	121.9(6)	121.8(6)	35
15[a]	2.100	1.34	1.35	[b]	[b]	[b]	[b]
16[c]	2.039(1)	1.341(2)	1.345(2)	115.5(1)	122.2(1)	122.2(1)	34.4

[a] Ref. [37a]. [b] Not reported. [c] Ref. [46].

complexes closest to complex **17**, strongly resemble complex **9**, as described above, and have a stability comparable to complex **9**.[48] This also demonstrates that the Ru → Py backbonding in the bis(pyridine) complex is unimportant.

The structure of complex **6b** (Figure 7) features two linear, axial $N{=}CPh_2$ groups (Ru1-N3-C1 175.9(9)°) with a linear $C{=}N{-}Ru{-}N{=}C$ backbone, consistent with the solution ^1H NMR spectrum of **6b**. The ϕ angle in Figure 8b is ≈29°. The C1–N3 bond length (1.25(1) Å) falls in the range of 1.24(2)–1.39(6) Å found for the C=N bonds of other metal methyleneamido complexes.[11b, 27] The Ru–N(methyleneamido) bond of 1.896(8) Å is slightly longer than that in $[Ru^{IV}(tpy)(bpy)(N{=}CMe_2)]^{2+}$ (1.831(10) Å),[21c, 49] and slightly shorter than the Ru–N(arylamido) bond of 1.956(7) Å observed for complex **10**,[32a] but considerably longer than the Ru–N(NO) bond of 1.726(9) Å reported for complex **12** that contains a linear NO group.[41] These observations further support the formulation of **6a** and **6b** as ruthenium(IV) species with formal $(N{=}CPh_2)^-$ groups that resemble an arylamido group $(NRR')^-$. The *linear* coordination mode of $(N{=}CPh_2)^-$ is in contrast to the usual *bent* coordination mode of the NO^- group.

Note that the axial Ru–N bonds in **6b** (1.896(8) Å) are considerably shorter than Ru–N single bonds, such as those in complex **13** (2.129(2) Å)[33a]. This indicates a multiple bonding character for the axial Ru–N bonds in **6b**. Consequently, the diamagnetism of **6a** and **6b** can be rationalized in a manner analogous to that for the diphenylamido complex **11**,[32b] namely the axial $N(p_y)$-$Ru(d_{yz})$-$N(p_y)$ π-bonding (Figure 9a) splits the originally degenerate d_{xz} and d_{yz} orbitals of the d^4 ruthenium ion and causes the ruthenium ion to adopt a $(d_{xy})^2(d_{xz})^2$ configuration. This bonding mode requires the axial ligands to assume an eclipsed conformation, which indeed is the case in the structure of **6b** (Figure 8b). However, the difference in the hybridization of the axial nitrogen atoms in the methyleneamido (*sp*) and arylamido complexes (*sp*^{2}) raises a new issue for the M–L axial bonding in ruthenium(IV) porphyrins. Since the occupied d_{xz} orbital of the ruthenium ion matches the empty π* orbital of the axial N=C bond in symmetry (Figure 9b), $Ru \rightarrow N{=}CPh_2$ backbonding might exist in complexes **6a** and **6b** as mentioned above. Provided that the $p_y(N)$ orbital of $N{=}CPh_2$ has a lower energy, while the π* orbital of $N{=}CPh_2$ has a higher energy than the d_{xz} and d_{yz} orbitals of ruthenium, both the $N(p_y)$-$Ru(d_{yz})$-$N(p_y)$ π-bonding and $Ru \rightarrow N{=}CPh_2$ backbonding are expected to increase the energy gap between the d_{xz} and d_{yz} orbitals. The presence of $Ru \rightarrow N{=}CPh_2$ backbonding in **6** is consistent with the shorter Ru–N(axial) distance and larger H_β chemical shift for **6b** relative to the arylamido complex **10**. We noted that the difference of the H_β chemical shifts between the methyleneamido and arylamido complexes with TTP macrocyle (**6a** and **10**) is smaller than that between the complexes with 3,4,5-MeO-TPP (**6b** and **11**) (see Table 2). This is not surprising, as M → L axial backbonding should be more important for metal complexes with a more electron-rich porphyrinato ligand.

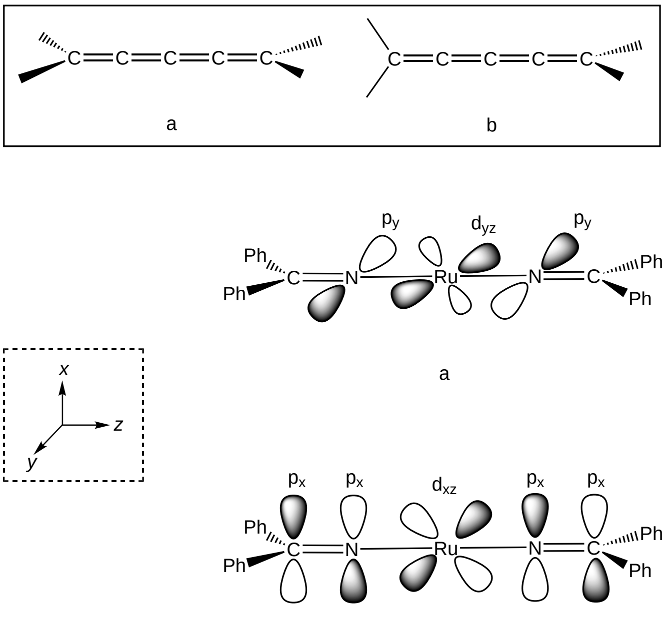
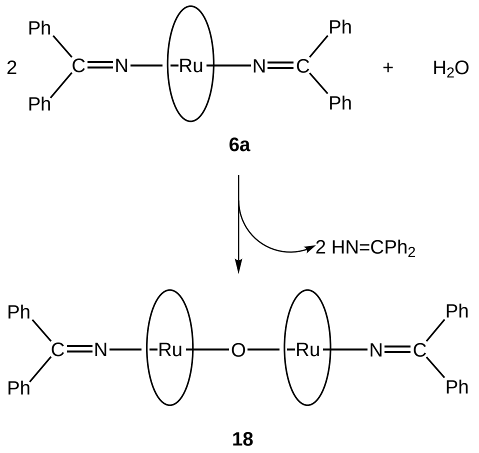


Figure 9. Schematic diagrams showing a) $N(p_y)$-$Ru(d_{yz})$-$N(p_y)$ π-bonding and b) $Ru \rightarrow N{=}CPh_2$ backbonding in complexes **6a** and **6b**. The inset shows a) unobserved and b) observed configurations of [4] cumulene.

Interestingly, the linear axial $Ph_2C{=}N{-}Ru{-}N{=}CPh_2$ moiety and its Ru–N multiple bonding character, coupled with the co-planarity of its four C–C(Ph) terminal bonds, endow complex **6b** with an *unprecedented hetero[4]cumulene* backbone that corresponds to an *unobserved* configuration of [4]cumulenes (pentatetraenes) depicted in the inset (a) of Figure 9. In contrast, all the [4]cumulenes reported in the literature adopt a configuration in which the two terminal planes are perpendicular to each other on account of the orthogonal π-planes of the C=C=C=C=C backbone (inset (b) in Figure 9).[50]

Stability: Complexes **5a**, **5b**, **6a**, and **6b** are stable towards moist air for months in the solid state. In aerobic chloroform solutions at room temperature, the bis(imine) complexes **5a** and **5b** were oxidized to unknown paramagnetic ruthenium porphyrins within one day, whereas the bis(methyleneamido) complex **6a** gradually degraded into diamagnetic dinuclear ruthenium(IV) porphyrins $[Ru^{IV}(TTP)(N{=}CPh_2)]_2O$ (**18**), probably as a result of partial hydrolysis of the axial methyleneamido ligands (Scheme 3). Indeed, such degrada-



Scheme 3. Proposed partial hydrolysis of complex **6a** into the diamagnetic dinuclear ruthenium(IV) porphyrin $[\mathrm{Ru^{IV}(TTP)(N{=}CPh_2)}]_2\mathrm{O}$ (**18**).

tion of **6a** became more rapid if water was deliberately added to the solution. The ^{1}H NMR spectrum of **18**[51] features a Ru(TTP):N=CPh$_2$ ratio of 1:1 and a considerable splitting of the *meta* and especially the *ortho* proton resonances of the *meso* tolyl groups on the TTP macrocycle. The latter is the result of the unsymmetrical coordination at the axial sites for each Ru(TTP) subunit of **18**. The positive-ion electrospray mass spectrum of **18** exhibits a prominent cluster peak at *m*/*z* 1917.1 that is attributable to the protonated parent ion $[M{+}\mathrm{H}]^+$. This peak is totally absent in the mass spectrum of complex **6a** under the same conditions. Note that, while a number of other dinuclear ruthenium(IV) porphyrins which contain the $\{[\mathrm{Ru(Por)}]_2\mathrm{O}\}^{2+}$ cores have been reported,[52] none of them have an *N*-donating axial ligand.

Conclusions

First of all, the present work demonstrates that simple imine and methyleneamido groups can form stable complexes with a metalloporphyrin. Bis(imine)ruthenium(II) porphyrins, $[\mathrm{Ru^{II}(Por)(N(Et){=}CHMe)_2}]$ (**5a** and **5b**), were prepared by the treatment of dioxoruthenium(VI) porphyrin with triethylamine, which provides an unusual approach to metal imine complexes. Reaction of dioxoruthenium(VI) porphyrins with benzophenone imine affords bis(methyleneamido) ruthenium(IV) complexes $[\mathrm{Ru^{IV}(Por)(N{=}CPh_2)_2}]$ (**6a** and **6b**). The formulation of both the new classes of metalloporphyrins is confirmed by X-ray structure determinations. The spectral features of **5a** and **5b** and the key bond lengths and angles of **5a** are remarkably similar to those of their bis(pyridine) analogues, so that these species most strongly resemble a metalloporphyrin which binds only the "head" of the pyridine. In contrast to the linear/bent and bent/bent configurations proposed for bis(nitrosyl)metalloporphyrins, the structure of **6b** features two linear methyleneamido groups in a *trans* configuration, and an unprecedented hetero[4]cumulene backbone. Both spectroscopic and structural measurements indicate that complexes **6a** and **6b** resemble bis(arylamido)ruthenium(IV) porphyrins. However, there should be a certain amount of Ru → N=CPh$_2$ backbonding in the methyleneamido complexes.

Experimental Section

General: NH=CPh$_2$ (97%, Aldrich), Et$_2$NH (98%, Merck), *m*-chloroperoxybenzoic acid (*m*-CPBA; 55%, Merck) were used as received. Et$_3$N (>99%, Merck) was purified to remove any traces of primary and secondary amines by the standard method.[53] All solvents were of AR grade. The complexes **7a**, **7b**,[54] and $[\mathrm{Ru^{II}(Por)(CO)(MeOH)}]$ (Por = TTP, 3,4,5-MeO-TPP)[55] were prepared according to the published procedures. Ultraviolet and visible (UV/Vis) spectra were recorded on a HP8452A Diode Array spectrophotometer. ^{1}H NMR spectra were measured on a Bruker DPX300 spectrometer. Unless otherwise stated, the solvent (CDCl$_3$) contained tetramethylsilane (TMS) as an internal standard. Chemical shifts (ppm) are reported relative to TMS. Infrared spectra (KBr pellets) were obtained with a Nicolet 20SXC FT-IR spectrometer. Mass spectra were measured on a Finnigan MAT95 mass spectrometer (FAB) and a Finnigan LCQ quadrupole ion trap mass spectrometer (electrospray). Elemental analyses were performed by the Institute of Chemistry, the Chinese Academy of Sciences.

Bis(imine)ruthenium(II) porphyrins (5): A mixture of freshly prepared **7a** or **7b** (50 mg) and Et$_3$N (10 mL) was stirred for 0.5 h to give a homogenous brown solution. The solution was evaporated to dryness and the residual solid was recrystallized from dichloromethane/*n*-hexane to afford **5a** or **5b** as a dark purple crystalline solid.

***(meso*-Tetrakis(*p*-tolyl)porphyrinato)bis(*N*-ethylideneethanamine)ruthenium(II) (5a)**: Yield: 81%; UV/Vis (9.6×10^{-6} M, CHCl$_3$): $\lambda_{\max}$ ($\lg\varepsilon$) = 260 (4.41), 293 (4.52), 329 (4.27, sh), 412 (5.26), 507 (4.29), 532 nm (3.60, sh); IR: $\tilde{\nu}$ = 999 cm^{-1} ("oxidation state marker" band); FAB MS (CHCl$_3$): *m*/*z*: 912 $[M]^+$, 841 $[M-\mathrm{L}]^+$, 770 $[M-2\mathrm{L}]^+$ (L = N(Et)=CHMe); $\mathrm{C_{56}H_{54}N_6Ru}$ (912.15): calcd: C 73.74, H 5.97, N 9.21; found: C 73.83, H 5.94, N 9.25.

***(meso*-Tetrakis(*p*-chlorophenyl)porphyrinato)bis(*N*-ethylideneethanamine)ruthenium(II) (5b)**: Yield: 85%; UV/Vis (8.23×10^{-6} M, CHCl$_3$): $\lambda_{\max}$ ($\lg\varepsilon$) = 263 (4.33), 293 (4.43), 330 (4.20, sh), 412 (5.21), 507 (4.20), 532 nm (3.56, sh); IR: $\tilde{\nu}$ = 1000 cm^{-1} ("oxidation state marker" band); FAB MS (CHCl$_3$): *m*/*z*: 994 $[M]^+$, 923 $[M-\mathrm{L}]^+$, 852 $[M-2\mathrm{L}]^+$ (L = N(Et)=CHMe); $\mathrm{C_{52}H_{42}N_6Cl_4Ru}$ (993.83): calcd: C 62.85, H 4.26, N 8.46; found: C 62.52, H 3.97, N 8.49.

Bis(methyleneamido)ruthenium(IV) porphyrins (6): A solution of $[\mathrm{Ru^{II}(Por)(CO)(MeOH)}]$ (60 mg, Por = TTP or 3,4,5-MeO-TPP) in dichloromethane (15 mL) was treated with *m*-CPBA (90 mg) for about 2 min to generate complexes **7b** or **7c** in situ. NH=CPh$_2$ (25 drops) was then added to the mixture. The progress of the reaction was monitored by UV/Vis spectrophotometry. After the β band of **7b** or **7c** at ≈520 nm completely disappeared, the mixture was filtered and the filtrate was concentrated to 5 mL. Addition of ethanol (5 mL) followed by rotary evaporation caused **6a** or **6b** to precipitate as a dark purple, crystalline solid. The solid was collected by filtration, washed with ethanol, and dried.

***(meso*-Tetrakis(*p*-tolyl)porphyrinato)bis(diphenylmethyleneamido)ruthenium(IV) (6a)**: Yield: 66%; UV/Vis (3.54×10^{-6} M, CHCl$_3$): $\lambda_{\max}$ ($\lg\varepsilon$) = 421 (5.48), 526 (4.44), 557 nm (4.15, sh); IR: $\tilde{\nu}$ = 1011 cm^{-1} ("oxidation state marker" band); FAB MS (CHCl$_3$): *m*/*z*: 1130 $[M]^+$, 950 $[M-\mathrm{L}]^+$, 770 $[M-2\mathrm{L}]^+$ (L = N=CPh$_2$); $\mathrm{C_{74}H_{56}N_6Ru\cdot H_2O}$ (1148.39): calcd: C 77.40, H 5.09, N 7.32; found: C 77.41, H 4.99, N 6.96.

***(meso*-Tetrakis(3,4,5-trimethoxyphenyl)porphyrinato)bis(diphenylmethyleneamido)ruthenium(IV) (6b)**: Yield: 65%; UV/Vis (2.79×10^{-6} M, CHCl$_3$): $\lambda_{\max}$ ($\lg\varepsilon$) = 422 (5.53), 526 (4.49), 557 nm (4.14, sh); IR: $\tilde{\nu}$ = 1012 cm^{-1} ("oxidation state marker" band); FAB MS (CHCl$_3$): *m*/*z*: 1435 $[M]^+$, 1254 $[M-\mathrm{L}]^+$, 1074 $[M-2\mathrm{L}]^+$ (L = N=CPh$_2$); $\mathrm{C_{82}H_{72}N_6O_{12}Ru}$ (1434.59): calcd: C 68.65, H 5.06, N 5.86; found: C 68.28, H 4.82, N 5.75.

X-ray crystal structure determination of 5a and 6b: Crystals of **5a** were grown by cooling a solution of **5a** in dichloromethane/triethylamine/*n*-hexane (1:1:10 v/v) under nitrogen at −15 °C for ≈2 d. Slow evaporation of a solution of **6b** in dichloromethane/*n*-hexane (1:5 v/v) at room temperature for ≈3 d afforded single crystals of **6b**.

Complex 5a: A dark red crystal of dimensions 0.30 × 0.10 × 0.07 mm, placed inside a glass capillary, was used for data collection at 28 °C on a MAR diffractometer with a 300 mm image plate detector. Data collection was made with 3° oscillation (60 images) at 120 mm distance and 400 s exposure. The images were interpreted and intensities integrated with the program DENZO.[56] The space group was determined based on systematic absences and a statistical analysis of the intensity distribution. The structure was solved by Patterson methods, and expanded by Fourier methods (PATTY[57]).

Complex 6b: A purple crystal of dimensions $0.30 \times 0.15 \times 0.10$, placed inside a glass capillary, was used for data collection at 28°C on a Rigaku AFC7R diffractometer with $\omega - 2\theta$ scans with ω-scan angle $(0.79 + 0.35 \tan \theta)^{\circ}$ at a scan speed of $8.0\,\mathrm{deg\,min^{-1}}$ (up to six scans for reflection with $I < 15\sigma(I)$). Intensity data (three standard reflections measured after every 300 reflections showed no decay) were corrected for Lorentz and polarization effects, and empirical absorption corrections based on the ψ scan of five strong reflections (minimum and maximum transmission factors 0.950 and 1.000). The space group was determined based on a statistical analysis of the intensity distribution and the successful refinement of the structure solved by direct methods (SIR 92[58]) and expanded by the Fourier method.

For both complexes **5a** and **6b**, the structure was refined by full-matrix least-squares with the software package TeXsan[59] on a Silicon Graphics Indy computer. A crystallographic asymmetric unit consists of only half of one complex molecule with the Ru atom at the origin (in the case of **6b** the asymmetric unit also contains one solvent molecule). In the least-squares refinement, all non-H atoms were refined anisotropically, and the H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140058 (complex **6b**) and CCDC-140059 (complex **5a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[35] a) Both cytochrome P-450 and synthetic metalloporphyrins are known to catalyze *N*-dealkylation of tertiary amines. Metal-oxo species are proposed as the key intermediates in these processes. However, to our knowledge, there are no reports on the *N*-dealkylation by isolated oxo metalloporphyrins, see: J. R. Lindsay Smith, D. N. Mortimer, *J. Chem. Soc. Perkin Trans II* **1986**, 1743; b) M. M. T. Khan, D. Chatterjee, S. Kumar, R. R. Merchant, K. N. Bhatt, *J. Mol. Catalysis* **1991**, *67*, 317.

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[38] The free N(Et)=CHMe ligand exhibits the ethylidene CH proton resonances at δ = 7.63 (C. Stevens, N. D. Kimpe, *J. Org. Chem.* **1993**, *58*, 132). Formation of **5a** shifted such resonances upfield by 6.18 ppm, a value very similar to the upfield shift of 6.14 ppm observed for the *ortho* proton resonances of pyridine after formation of **9** (see Table 1).

[39] The chemical shifts of H_β protons for diamagnetic metalloporphyrins usually increase with the oxidation state of the metal ions: a) See ref. [13f]; b) H. Scheer, J. J. Katz in *Porphyrins and Metalloporphyrins* (Ed.: K. M. Smith), Elsevier, Amsterdam, **1975**, p. 460.

[40] Note that ruthenium(II) *meso*-tetraarylporphyrins with a strong Ru → L axial backbonding (for example, L = CO and NO) exhibit unusually large H_β chemical shifts (δ = 8.6–8.9).

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