Reactivity of Dioxoruthenium(VI) Porphyrins toward Amines. Synthesis and Characterization of Bis(arylamine)ruthenium(II), Bis(arylamido)- and Bis(diphenylamido)ruthenium(IV), and Oxo(*tert*-butylimido)ruthenium(VI) Porphyrins

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Abstract: Reactions of dioxoruthenium(VI) porphyrins, $[Ru^{VI}O_2(Por)]$, with *p*-chloroaniline, trimethylamine, *tert*-butylamine, *p*-nitroaniline, and diphenylamine afforded bis(amine)ruthenium(II) porphyrins, $[Ru^{II}(Por)(L)_2]$ ($L = p\text{-}ClC_6H_4NH_2$, Me_3N, Por = TTP, 4-Cl-TPP; $L = tBuNH_2$, Por = TPP, 3,4,5-MeO-TPP, TTP, 4-Cl-TPP, 3,5-Cl-TPP) and bis(amido)ruthenium(IV) porphyrins, $[Ru^{IV}(Por)(X)_2]$ ($X = p\text{-}NO_2C_6H_4NH$, Por = TTP, 4-Cl-TPP; $X = Ph_2N$, Por = 3,4,5-MeO-TPP, 3,5-Cl-TPP), respectively. Oxidative deprotonation of $[Ru^{II}(Por)(NH_2\text{-}p\text{-}C_6H_4Cl)_2]$ in chloroform by air generated bis(arylamido)ruthenium(IV) porphyrins, $[Ru^{IV}(Por)(NH\text{-}p\text{-}C_6H_4Cl)_2]$ (Por = TTP, 4-Cl-TPP). Oxidation of $[Ru^{II}(Por)(NH_2tBu)_2]$ by bromine in dichloromethane in the presence of *tert*-butylamine and traces of water produced oxo(imido)ruthenium(VI) porphyrins, $[Ru^{VI}O(Por)(NtBu)]$ (Por = TPP, 3,4,5-MeO-TPP, TTP, 4-Cl-TPP, 3,5-Cl-TPP). These new classes of ruthenium complexes were characterized by ^1H NMR, IR, and UV/visible spectroscopy, mass spectrometry, and elemental analysis. The structure of $[Ru^{IV}(TTP)(NH\text{-}p\text{-}C_6H_4Cl)_2]\cdot 2CH_2Cl_2$ was determined by X-ray crystallography. The Ru–N bond length and the Ru-N-C angle of the Ru-NHAr moiety are 1.956(7) Å and 135.8(6)°, respectively.

Keywords: amines · imides · macrocyclic ligands · ruthenium

Introduction

Secondary amine monooxygenase[1] and cytochrome P-450,[2] both containing heme prosthetic groups, play an important role in biological oxidation of amines. Secondary amine monooxygenase catalyzes the oxidative dealkylation of secondary amines to aldehydes and primary amines. Cytochrome P-450 catalyzes a number of amine oxidation processes, including deamination, *N*-dealkylation and *N*-hydroxylation.[3] The proposed catalytic cycles of both enzymes involve high-valent oxoiron ($O{=}Fe^{IV}$) porphyrin complexes as the reactive oxygen intermediates.[3] To probe the intrinsic reactivity of these intermediates toward amines, it would be of interest to investigate the interaction of synthetic oxoiron(IV) porphyrins with amines. Although synthetic examples of oxoiron(IV) porphyrins are known, isolation of such complexes as pure solids is hampered by their thermal instability.[4] Owing to the unique periodic relationship of iron and ruthenium, high-valent ruthenium porphyrins that bear Ru=O functional groups attracted our attention. A dioxoruthenium(VI) porphyrin, $[Ru^{VI}O_2(TMP)]$[5] (**1**), was first isolated by Groves and co-worker in 1984.[6] Thereafter, research in our group led to the isolation of several such complexes (**2**) with *sterically unencumbered* porphyrinato ligands.[7] Studies on the interaction of **1** and **2** with alkenes to mimic the alkene epoxidation catalyzed by cytochrome P-450 have been documented.[6, 7b]

We have investigated in some detail the reaction of **2**, formed in situ, with primary and secondary alkylamines and prepared a series of bis(alkylamine)ruthenium(II) porphyrins such as **3**.[8] Remarkably, oxidation of bis(*tert*-butylamine) adducts **3a** and **3b** by bromine in the presence of traces of water led to the isolation of oxo(*tert*-butylimido) complexes **4a** and **4b**,[9] the first examples of a mononuclear ruthenium alkylimido complex. Very recently, James and Bailey first observed the catalytic dehydrogenation by **1**, formed in situ, of primary and secondary alkylamines and isolated $[Ru^{II}(TMP)(NH_2CH_2Ph)_2]$.[10] Metalloporphyrins bearing amines as the sole axial ligands are also known for iron,[11] rhodium,[12] and osmium,[13, 14] but again all these axial ligands are alkylamines.

The reactivity of **2** towards an arylamine should be of interest. Firstly, arylamines are generally much less basic than alkylamines and significantly less basic than pyridine and

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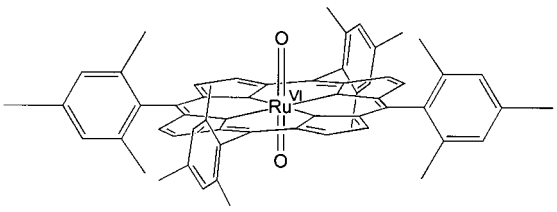

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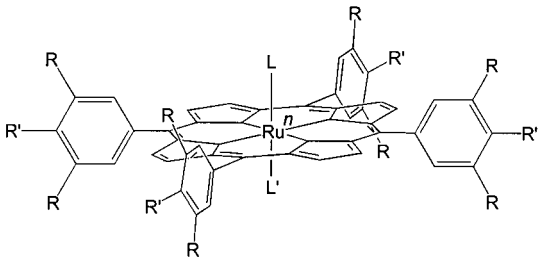


2: n = VI,[a] L = L' = O^{2-} (Ru=O)

No.	R	R'
2a	H	H
2b	OMe	OMe
2c	H	Me
2d	H	Cl
2e	Cl	H

3: n = II, L = L' = $tBuNH_2$

No.	R	R'
3a	H	H
3b	OMe	OMe
3c	H	Me
3d	H	Cl
3e	Cl	H

4: n = VI, L = $tBuN^{2-}$, L' = O^{2-} (Ru=N*t*Bu and Ru=O)

No.	R	R'
4a	H	H
4b	OMe	OMe
4c	H	Me
4d	H	Cl
4e	Cl	H

5: n = IV, L = L' = Ph_2N^-

No.	R	R'
5a	OMe	OMe
5b	Cl	H

6: n = II, L = L' = p-$ClC_6H_4NH_2$

No.	R	R'
6a	H	Me
6b	H	Cl

7: n = IV, L = L' = p-$ClC_6H_4NH^-$

No.	R	R'
7a	H	Me
7b	H	Cl

8: n = IV, L = L' = p-$NO_2C_6H_4NH^-$

No.	R	R'
8a	H	Me
8b	H	Cl

9: n = II, L = L' = Me_3N

No.	R	R'
9a	H	Me
9b	H	Cl

10: n = VI, L = L' = $tBuN^{2-}$ (Ru=N*t*Bu)

R	R'
H	Me

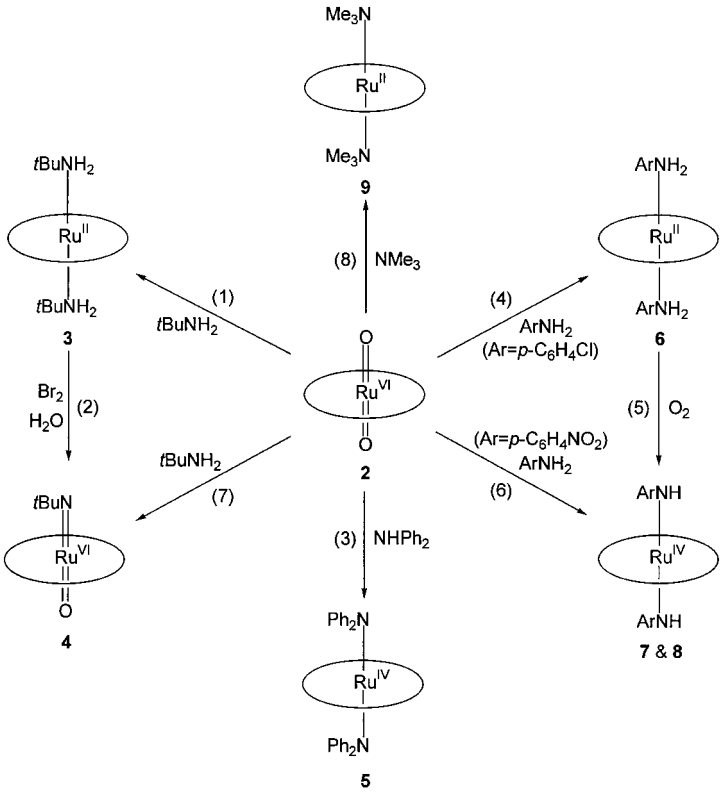
[a] n is the formal oxidation number of the respective Ru ion in the compound.

imidazole. It remains unclear whether their adducts with a metalloporphyrin are stable enough to be isolated. Secondly, we have reported that reaction of **2b** with diphenylamine produced a stable bis(diphenylamido)ruthenium(IV) complex **5a**,[15] unlike the case for alkylamines. Thus, bis(arylamine)-ruthenium(II) porphyrins, if they can be isolated, may undergo oxidative deprotonation to give the corresponding bis(arylamido) complexes. Although formation of amido complexes by deprotonation of coordinated amines is not uncommon,[16] such reactions that involve redox processes are extremely rare[17] and remain fully unknown in the case of metalloporphyrins. Thirdly, bis(arylamido)ruthenium(IV) porphyrins should be good precursors for arylimido ruthenium(VI) complexes, just like their osmium analogues.[14]

Here we present the first synthesis and characterization of bis(arylamine)ruthenium(II) porphyrins (**6**) and bis(arylamido)ruthenium(IV) porphyrins (**7** and **8**) as well as a full account of the synthesis and characterization of **4** and **5**.[18] The amido complexes **7** were definitely formed through oxidative deprotonation of the amine complexes **6**. The synthesis and characterization of bis(trimethylamine) adducts **9**, prepared from reaction of **2** with the *tertiary* amine, and the formation of **4c** and a bis(*tert*-butylimido) complex (**10**) directly from the reaction of **2c** with *tert*-butylamine are also described.

Results and Discussion

Dioxoruthenium(VI) porphyrins **2a–e** exhibit high reactivity toward amines. Various products could be isolated from such reactions, depending on the types of amines used. We found that the reactions of the in situ formed **2a–e** with excess primary and secondary alkylamines exclusively afforded the corresponding bis(amine)ruthenium(II) porphyrins in high yields.[8, 9] In this work, we concentrated on the reactions between **2** (as the *isolated* product) and amines (especially arylamines), which in some cases generated different products from those obtained by using **2** formed in situ. Importantly, the reactivity of **2** toward amines makes them good precursors to several new classes of ruthenium porphyrins, as shown in Scheme 1. The synthesis of bis(*tert*-butylamine)ruthenium(II) porphyrins (**3a–e**) through reaction 1 in the scheme has been described elsewhere.[8, 9]



Scheme 1. Reactivity of dioxoruthenium(VI) porphyrins. Note that the reactions 1 and 7 were carried out by using isolated **2** and **2** formed in situ, respectively.

Synthesis of oxo(alkylimido)ruthenium(VI) porphyrins 4: Since the first synthesis of $[Os^{VIII}O_3(NtBu)]$ in 1956,[19] many osmium alkylimido complexes have been prepared.[20] Extensive studies in other groups showed that the common methods for preparing a mononuclear metal alkylimido complex were

not applicable to ruthenium.[21] We also observed that while air oxidation of osmium analogues of **3a–d** afforded osmium analogues of **4a–d** in good yields,[9, 14] similar treatment of **3a–d** gave intractable products.

Interestingly, reactions of **3a–e** with bromine in dichloromethane in the presence of *tert*-butylamine generated **4a–e** in high yields (reaction 2 in Scheme 1). These reactions might proceed via bis(*tert*-butylimido)ruthenium(VI) intermediates such as **10**, which rapidly hydrolyzed to give **4a–e** owing to the presence of trace amounts of water in the solvent and/or *tert*-butylamine. The presence of both free *tert*-butylamine and water during the reactions seems necessary. It is possible that free *tert*-butylamine would react with HBr, which exists in aerobic bromine solutions, to form $t\mathrm{BuNH_3^+ \cdot Br^-}$ and, thus, keep the coordinated amine in **3** from leaving the ruthenium ion as a result of protonation. The progress of the reactions should be monitored by UV/visible spectrophotometry, because addition of excess bromine would produce a dark green solution and lead to a bromination of the porphyrinato ligands.

Notably, before we reported the isolation of **4a** and **4b**,[9] no mononuclear ruthenium alkylimido complexes had been known.[22] Up to now, the species **4a–e** remain the only examples of mononuclear ruthenium(VI) alkylimido complexes and, especially, the only examples of mononuclear ruthenium compounds bearing both Ru=NR and Ru=O functional groups.[23]

Unlike $[Ru^{VI}(NSiMe_3)(CH_2SiMe_3)_4]$,[22b] which is extremely air and water sensitive, **4a–e** are all stable to moist air for months in the solid state. A significant difference exists between the auto-degradation of **2a–e** and **4a–e**. For example, in chloroform solutions exposed to the atmosphere, compounds **2a–e** were converted to μ-oxo diruthenium(IV) complexes within one day. However, in the same solvent, **4a–e** slowly lost their axial *tert*-butyl groups to generate nitrosylruthenium porphyrins.[24] It seems likely that formation of the strong Ru=N*t*Bu multiple bond significantly activates the C–N bond of the *tert*-butylimido group and thus facilitates its cleavage.

Synthesis of bis(diarylamido)ruthenium(IV) porphyrins 5: Reaction of **2b** and **2e** with diphenylamine in dichloromethane results in formation of complexes **5a** and **5b** in moderate yields (reaction 3 in Scheme 1). The synthesis of metal dialkyl- or diarylamido complexes from reaction of metal oxo complexes with corresponding secondary amines is rarely seen in the literature.[16, 25] We found that the reaction between **2** and diphenylamine was considerably affected by the substituents on the phenyl groups of *meso*-tetraarylporphyrinato ligands.

Extension of reaction 3 to other porphyrinato ligands used in this work generated a mixture of products that were difficult to separate. The mechanism of reaction 3 is unclear; one of the possibilities is that **2b** and **2e** were first converted to bis(diphenylamine)ruthenium(II) porphyrins, which immediately underwent oxidative deprotonation to give **5a** and **5b**.[26] Both complexes **5a** and **5b** are air-stable solids. They are stable for at least one week in chloroform solutions exposed to the atmosphere.

Synthesis of bis(arylamine)ruthenium(II) porphyrins 6: In the literature, arylamines are rarely seen as the sole axial ligands in metalloporphyrins.[27] There are only a few reports on the interaction of metalloporphyrins with arylamines. Besides the reaction between **2b** and diphenylamine mentioned above that affords the bis(amido) complex **5a**,[15] reactions of $[Os^{II}(Por)(N_2)(THF)]$[14] and $[P^{V}(TTP)Cl_2]^+$[28] with arylamines also result in formation of amido porphyrin complexes. In addition, treatment of $[Ru^{IV}(Por)Cl_2]$ with arylamines generates imidoruthenium(IV) porphyrins.[29] To our knowledge, no metalloporphyrins bearing arylamine axial ligands have been isolated. Our present work has demonstrated that reactions of **2c** and **2d** with excess *p*-chloroaniline in dichloromethane or ethanol at room temperature readily afford **6a** and **6b**, respectively, in close to quantitative yields (reaction 4 in Scheme 1). Since reaction 4 could be conveniently carried out in air, the ligation of *p*-chloroaniline to the ruthenium(II) ion seems fairly robust. Evidently, reaction 4 resulted in a reduction of the metal center from ruthenium(VI) to ruthenium(II) and, accordingly, *p*-chloroaniline was oxidized by **2c** and **2d** to bis(*p*-chlorophenyl)diazene.[30] A question might arise whether **2c** and **2d** were first reduced to an oxoruthenium(IV) porphyrin intermediate. Inasmuch as **2c** and **2d** can be almost completely converted into **6a** and **6b**, respectively, by *p*-chloroaniline, such an intermediate, if really involved, must also be reactive towards the arylamine.

Synthesis of bis(arylamido)ruthenium(IV) porphyrins 7 and 8

*Oxidative deprotonation of **6***: Complexes **7a** and **7b** were prepared in high yields by autooxidation of **6a** and **6b**, respectively, in chloroform solutions exposed to the atmosphere (reaction 5 in Scheme 1). This is the first case in which an amido metalloporphyrin is generated unambiguously through oxidative deprotonation of the corresponding amine complex. Even in non-porphyrin systems, the *oxidative* deprotonation of amine complexes to form amido complexes is extremely rare. We have found only one such example.[17] In that case the process is rather complicated, not only affording the amido products in low to moderate yields, but also changing the metal ion from four- to six-coordinate. Interestingly, the formation of **7a** and **7b** from **6a** and **6b** is almost quantitative and causes very little change in the coordination environment of ruthenium.

*Direct reaction of **2** with p-nitroaniline*: Under the same conditions as for reaction 4, but by employing *p*-nitro- instead of *p*-chloroaniline, complexes **8a** and **8b** were isolated in high yields (reaction 6 in Scheme 1). No analogues of **6a** and **6b** were obtained in these cases. Note that *p*-nitroaniline is much more acidic than *p*-chloroaniline, so its adducts with ruthenium(II) porphyrins might be very unstable, as in the case of diphenylamine described above.

Reaction of isolated 2 with alkylamines: Since there have been no reports on the reactions between *isolated* **1** or **2** and alkylamines, we examined such reactions for all the major types of alkylamines, including *n*-octylamine, isopropylamine, *tert*-butylamine, diethylamine, and trimethylamine by UV/

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visible spectrophotometry. In the cases of *n*-octylamine, isopropylamine, and diethylamine, their reactions with the **2a–e**, both isolated and formed in situ, are similar. However, the reaction of *tert*-butylamine with isolated **2a–e** was very surprising (reaction 7 in Scheme 1). There was no appreciable reaction within the first five minutes. After about two hours, complexes **4a–e** and **3a–e** were formed, with the former being the major products. In contrast, treatment of *tert*-butylamine with **2a–e** formed in situ afforded complexes **3a–e** in high yields (reaction 1) within five minutes. None of the complexes **4a–e** were detected in this case.

Interestingly, both the isolated **2** and the **2** formed in situ are reactive towards tertiary amines such as trimethylamine. In both dichloromethane and in chloroform, **2c** and **2d**, formed in situ, reacted with excess trimethylamine to form **9a** and **9b**, respectively, within one hour. No other metalloporphyrin species were detected after the reaction was complete. When the isolated **2c** and **2d** were suspended in an aqueous trimethylamine solution (40 wt%) and stirred overnight, they were quantitatively converted into **9a** and **9b** (reaction 8 in Scheme 1).

To our surprise, reaction of **2c** with excess *tert*-butylamine in refluxing hexane followed by removal of the solvent afforded a mixture of **4c** and **10** as a dark purple solid. When the solid was dissolved in deuterochloroform exposed to the atmosphere, **10** rapidly hydrolyzed to **4c**, as revealed by time-dependent ^{1}H NMR measurements, which showed that the signal intensities of **10** decreased, whereas those of **4c** increased rapidly. For example, the molar ratio of **4c**:**10** increased from about 10:1 at time = 5 min to 30:1 at time = 15 min. Due to the extreme moisture sensitivity, the isolation of pure **10** proved difficult.

Table 1. ^{1}H NMR spectral data (δ) of complexes **4–10** in $CDCl_3$.[a] The spectral data of the osmium analogues of **4** and **10** (from ref. [14]) are also shown for comparison.

	H (s, 8H)	H_o (m, 4H)	H'_o (m, 4H)	H_m,H'_m,H_p (m, 12H)		tBuN^{2-} (s, 9H)	
4a	8.91	8.44	8.12	7.78		−2.55	
4a-Os	8.93	8.43	8.11	7.78		−2.60	
		H_o (d, 4H)	H'_o (d, 4H)	*m*-OMe (s, 12H)	*m*′-OMe (s, 12H)	*p*-OMe (s, 12H)	tBuN^{2-} (s, 9H)
4b	9.03	7.64	7.42	4.01	3.98	4.20	−2.47
4b-Os	9.05	7.65	7.41	4.01	3.98	4.20	−2.53
		H_o (dd, 4H)	H'_o (dd, 4H)	H_m, H'_m (qd, 8H)	H_p (t, 4H)	*p* − Me (s, 12H)	tBuN^{2-} (s, 9H)
4c	8.91	8.32	7.99	7.57	[b]	2.72	−2.58
4c-Os	8.94	8.32	7.98	7.57	[b]	2.72	−2.63
4d	8.91	8.35	8.05	7.78	[b]	[b]	−2.57
4d-Os	8.93	8.35	8.04	7.78	[b]	[b]	−2.63
4e	8.96	8.31	8.03	[b]	7.87	[b]	−2.54
		H_o (d, 8H)	H_m (d, 8H)	*p*-Me (s, 12H)		Axial ligands	
5b	8.29	7.68	[b]	[c]	6.33 (tm, 4H, H'_p), 5.94 (tm, 8H, H'_m), 2.61 (d, 8H, H'_o)		
6a	8.10	7.86	7.48	2.65	6.05 (d, 4H, H'_m), 2.95 (d, 4H, H'_o), −4.30 (br, 4H, NH_2)		
7a[d]	8.41	7.88	7.49	2.67	5.84 (d, 4H, H'_m), 2.85 (d, 4H, H'_o)		
7b[d]	8.40	7.91	7.68	[b]	5.84 (d, 4H, H'_m), 2.82 (d, 4H, H'_o)		
8a[d]	8.43	7.87	7.51	2.67	6.79 (d, 4H, H'_m), 2.95 (d, 4H, H'_o)		
8b[d]	8.44	7.92	7.71	[b]	6.77 (d, 4H, H'_m), 2.92 (d, 4H, H'_o)		
9a	8.12	7.91	7.44	2.64	−2.49 (s, 18H, Me_3N)		
9b	8.09	7.95	7.63	[b]	−2.49 (s, 18H, Me_3N)		
10	8.73	8.08	7.53	2.70	−2.46 (s, 18H, tBuN^{2-})		
10-Os	8.73	8.08	7.53	2.70	−2.50 (s, 18H, tBuN^{2-})		

[a] The spectral data of **5a** appear in ref. [15]. The spectrum of **6b** was not obtained due to insufficient solubility of the complex in proper deuterated solvents. [b] Not applicable. [c] H_p δ = 7.75 (t, 4H). [d] The NH proton resonances were not located.

Characterization of complexes 4–10

^{1}H NMR spectrsocopy: All the complexes **4–10** show well-resolved ^{1}H NMR spectra with the signals of the porphyrinato ligands appearing at normal fields; this suggests that they are all diamagnetic. Owing to the porphyrin ring current effect, the proton resonances of axial ligands generally experience a significant up-field shift. In each case, the integration ratio of signals is consistent with the formula of the complex. The spectral data are summarized in Table 1.

A common feature of the spectra of **4a–e** lies in the splitting of the *ortho* and *meta*, if any, proton resonances of the porphyrinato ligands; this is consistent with the asymmetrical coordination at the axial sites. The spectrum of **4d** is shown in Figure 1 as an example. All signals in the figure can be reasonably assigned, except for the distinction of H_o and H'_o or H_m and H'_m resonances, according to integration ratio and by comparison with the spectra of **2d**,[7b] **4a–c**, and **4e**. We suggest that the H_o rather than H'_o chemical shifts of **4d** should be similar to those of H_o signals of

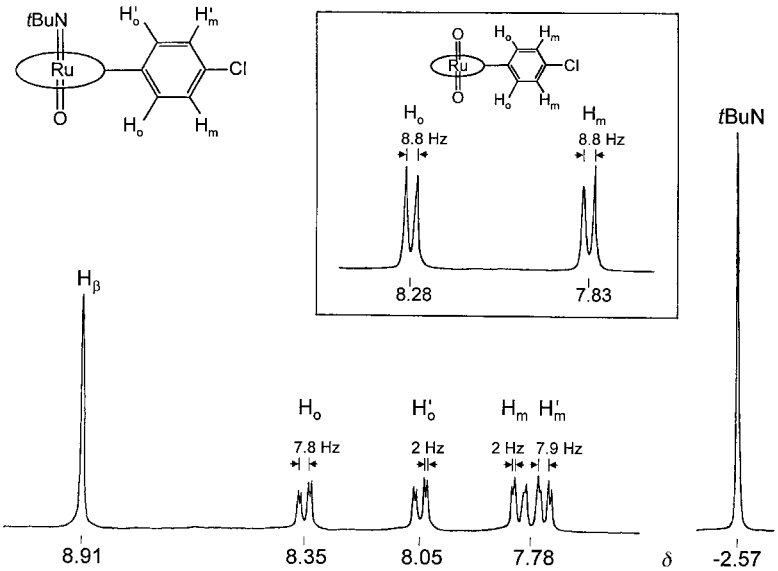

Figure 1. ^{1}H NMR spectrum (300 MHz) of **4d** in $CDCl_3$. The inset shows the proton resonances of the phenyl groups of the porphyrin ring of **2d** under the same conditions. Coupling constants are indicated.

2d. While both the *ortho* and *meta* proton resonances of the porphyrinato ligand in **2d** appear as doublets (Figure 1, inset), each of those resonances for **4d** is split into two doublets of doublets. A similar phenomenon has also been observed for **4c** and the osmium analogues of **4c** and **4d**. Since the crystal structure of $[Os^{VI}O(TTP)(NtBu)]$ ("**4c**-Os") has an essentially linear Os=N*t*Bu geometry,[14] and the complexes **4c** and **4d** are expected to be isostructural with their osmium analogues, the observation of two doublets of doublets rather than two doublets could reasonably be attributed to a coupling between H_o and H'_o or H_m and H'_m protons.

For a given porphyrinato ligand, replacing an oxo with a *tert*-butylimido group lowers the H_β chemical shift by about 0.17 ppm; this suggests that the latter is a better π-donor. On the other hand, complexes **3a–e** show the *t*Bu signals at about $\delta = -1.9$.[8, 9] Conversion of **3a–e** to **4a–e** significantly shifts these signals upfield to about $\delta = -2.5$. This might arise from a shortening of the axial Ru–N bond lengths,[31] which would render the *t*Bu groups more strongly affected by the porphyrin ring current. As expected, for each porphyrinato ligand, the spectrum of any of **4a–d** or **10** is virtually identical with that of its osmium analogue (Table 1).

Complexes **5–10** exclusively exhibit only one set of *ortho* and *meta*, if any, proton resonances of the porphyrinato ligands, as expected for the symmetrical coordination at the axial sites. A typical spectrum of **7b** is shown in Figure 2. All the signals arising from H_o, H_m, H'_o, and H'_m appear as sharp doublets. Since the *ortho* or *meta* protons on both sides of the phenyl group of *p*-$ClC_6H_4NH^-$ are equivalent, there must be a rapid rotation of the phenyl ring about the C–N bond of the arylamido ligand. This is in contrast with the case of $[(PhNH)Ru^{II}H(PMe_3)_4]$,[32] in which such a rotation is prohibited.

The solutions of **6a** and **6b** in chloroform are very air-sensitive (vide infra). Addition of free *p*-chloroaniline to the solution appreciably stabilized **6a** so that its ^1H NMR spectrum could be obtained. Free *p*-chloroaniline exhibits the *meta*, *ortho*, and NH_2 signals at $\delta = 7.08$, 6.57, and 3.63, respectively. On binding to the ruthenium(II) ion, all these signals shift to high fields and appear at $\delta = 6.05$, 2.95, and -4.30, respectively. After addition of D_2O, the NH_2 signals of both the free and bound arylamine almost completely disappear. However, the other signals of **6a** were essentially unaffected. A comparison of the *ortho* and *meta* proton resonances of the axial *p*-chlorophenyl groups of **6a** with those of **7a** reveals that the resonances of **6a** ($\delta = 2.95$ and 6.05, respectively) appear at appreciably lower fields than those of **7a** ($\delta = 2.85$ and 5.84, respectively); this suggests that the axial groups in **6a** are less strongly affected by the porphyrin ring current and are further from the porphyrin ring. This is also in agreement with longer Ru–N(axial) bond lengths expected for **6a**.

It is well known that, for *diamagnetic* metalloporphyrins, H_β chemical shifts usually increase with the oxidation state of the metal ions.[33, 34] This is well reflected in Table 1. Further, the H_β chemical shifts of the ruthenium(VI) (**4a–e** and **10**), ruthenium(IV) (**5a**, **5b**, **7a**, **7b**, **8a**, and **8b**), and ruthenium(II) (**6a**, **9a**, and **9b**) complexes are found to be in the range of $\delta =$ 8.73–9.03, 8.29–8.44, and 8.09–8.12, respectively, and are similar to those reported for the dioxoruthenium(VI),[7] bis(alkyl)ruthenium(IV),[35] and bis(alkylamine)ruthenium(II)[8b, 9] porphyrins, respectively.

IR spectroscopy: Both complexes **6a** and **6b** exhibit two sharp, albeit weak NH_2-stretching bands at about 3315 and 3263 cm^{-1}. In contrast, the spectra of **7a**, **7b**, **8a**, and **8b** each show *only one* NH-stretching band (also sharp but weak) at about 3265 cm^{-1}, a frequency slightly higher than that observed for their osmium analogues (ca. 3255 cm^{-1}),[14] but substantially lower than that of $[(PhNH)Ru^{II}H(PMe_3)_4]$ (3370 cm^{-1}).[32] As expected, there are no N–H-stretching bands in the spectra of **4a–e**, **5a**, **5b**, **9a**, and **9b**.

The "oxidation-state marker" bands[36] of ruthenium(VI) (**4a–e**), ruthenium(IV) (**5a**, **5b**, **7a**, **7b**, **8a**, and **8b**), and ruthenium(II) (**6a**, **6b**, **9a**, and **9b**) complexes appear at about 1016, 1010, and 1000 cm^{-1}, respectively, and are again similar to those of other reported ruthenium porphyrins of the same oxidation states.[6c, 7, 8b, 9, 15] For the oxo(imido) complexes **4a**, **4d**, and **4e**, a band of moderate intensity at 1232,[9] 1222 and 1219 cm^{-1}, respectively, might correspond to the Ru=N*t*Bu group. Such bands are totally absent in the spectra of carbonyl-, dioxo-, and bis(*tert*-butylamine)ruthenium complexes with the corresponding porphyrinato ligands. The Ru=O stretching bands of **4a**, **4b**, and **4d** are located at about 803 cm^{-1}, a frequency significantly lower than that of their dioxo analogues (ca. 820 cm^{-1}).[6, 7] This could be explained by a push–pull effect.[31] The phenomenon of considerably lowering the remaining M∼O stretching fre-

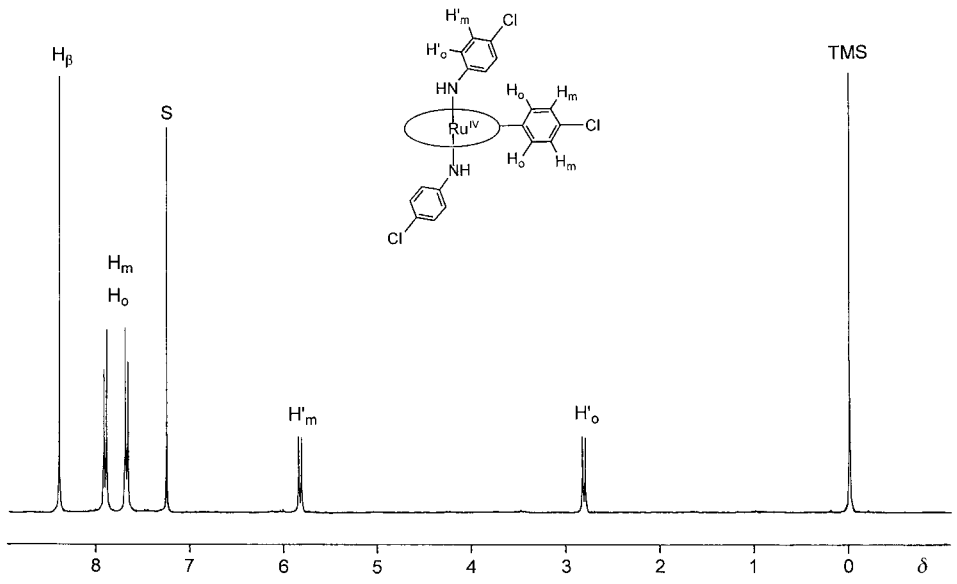

Figure 2. ^1H NMR spectrum (300 MHz) of **7b** in $CDCl_3$.

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quencies, by replacing an oxo group with an alkylimido group, has also been observed for $[Os^{VIII}O_n(NtBu)_{4-n}]$[37] and $[Os^{VI}O_n(Por)(NtBu)_{2-n}]$[14] systems.

UV/visible spectroscopy: While dioxoruthenium(VI) (**2**)[7] and osmium(VI)[38] porphyrins show very different UV/visible spectra, the spectra of oxo(imido)-ruthenium(VI) porphyrins **4** are similar to those of their osmium analogues ("**4**-Os") in some spectral regions. For example, both **4a**–**d** and **4a**–**d**-Os[14] exhibit the β and α bands at about 560 and 600 nm, respectively. However, relative to **4a**–**d**-Os, the Soret bands of **4a**–**d** are blue-shifted by as much as about 20 nm. A typical spectrum of **4b** is shown in Figure 3. For comparison, the spectrum of its dioxo analogue **2b** is given in the inset. Evidently, replacing an oxo group of the dioxo complex with a *tert*-butylimido group only causes a slight change on the Soret band, but red shifts both the β and α bands by more than 40 nm.

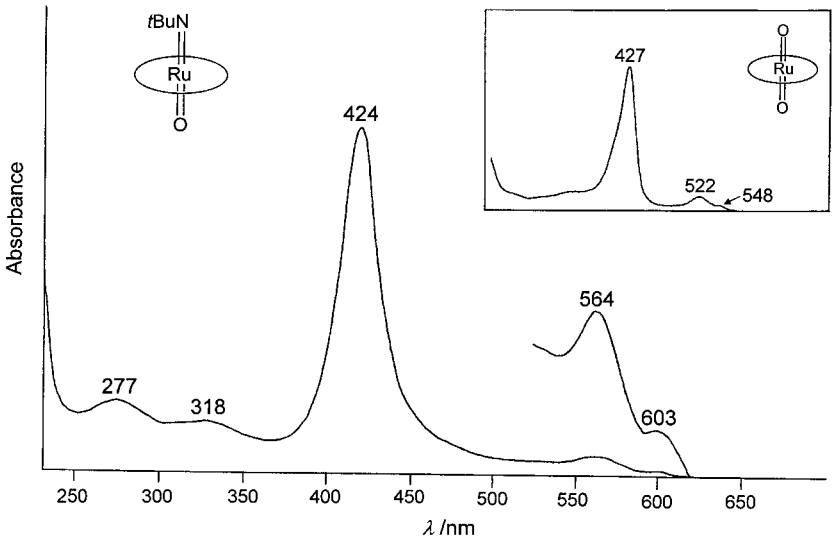

Figure 3. UV/Vis spectrum of **4b** in $CHCl_3$. The inset shows the spectrum of **2b** in the same solvent.

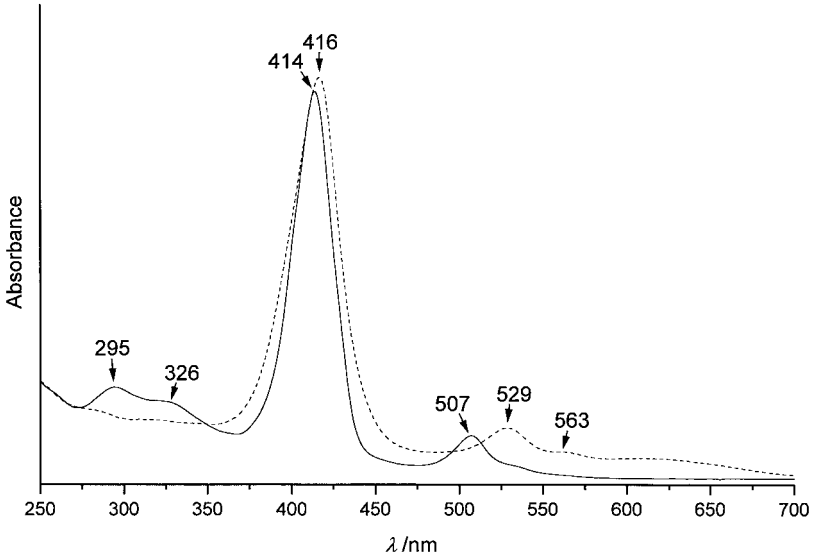

Figure 4. UV/Vis spectra of **6a** (——) and **7a** (– – –) in $CHCl_3$.

Bis(amido)ruthenium(IV) complexes **5a**, **5b**, **7a**, **7b**, **8a**, and **8b** generally exhibit β and α bands at around 527 and 562 nm, respectively. However, relative to the diphenylamido complex **5a** and **5b**, the arylamido complexes **7a**, **7b**, **8a**, and **8b** have slightly blue-shifted Soret bands. A representative spectrum of **7a** is shown in Figure 4 (dashed line). Like bis(arylamido)osmium(IV) porphyrins,[14] complexes **7a**, **7b**, **8a**, and **8b** exclusively show a long tail on the red side of the band. The spectra of bis(amine)ruthenium(II) adducts **6a**, **6b**, **9a**, and **9b** all exhibit bands at about 295, 330, 410 (Soret), 505 (β), and 530 (α) nm, very similar to those of the reported bis(alkylamine)ruthenium(II) porphyrins.[8, 9] The spectrum of **6a** is also shown in Figure 4 (solid line). Evidently, conversion of the bis(amine) complex **6a** to the bis(amido) complex **7a** red shifts its β and α bands by about 20 nm.

The oxidative deprotonation processes of **6** to form **7** could be conveniently monitored by UV/visible spectrophotometry. Figure 5 depicts the time-dependent UV/visible spectra of **6a** in aerobic chloroform. The overall process shows no *clean* isosbestic points; this suggests that the conversion of **6a** to **7a** is not smooth and must involve an unknown intermediate(s). Under the UV/visible conditions, it took only three minutes for **6a** to be completely oxidized to **7a**.

X-ray structure determination of $\boldsymbol{7a \cdot 2\,CH_2Cl_2}$: The molecular structure of **7a** was determined by a single-crystal X-ray diffraction study. Figure 6 shows the ORTEP drawing and atom-numbering scheme. Crystallographic data for the structure determination, and selected bond lengths and angles are listed in Tables 2 and 3 respectively. To the best of our knowledge, complex **7a** is the first structurally characterized arylamido metalloporphyrin.

The structure of **7a** has a C_2 rotation axis through the atoms C28, C27, C24, C11, Ru1, C1, C12, C15, and C16. The ruthenium(IV) ion is located in the center of the porphyrinato ring and has a distorted octahedral environment coordinated to six nitrogen atoms. The Ru–N(arylamido) bond lengths are both 1.956(7) Å, and are similar to that of the Ru–NHAr bond (1.94(2) Å) in $[(\eta^6\text{-}C_6Me_6)Ru^{II}Cl(NHAr)]$,[23d] slightly shorter than that of the Ru–N(tosylamido) bond (2.025(11) Å) in $[Ru^{IV}(TPP)(NHTs)(Pz)]$,[39] and significantly shorter than that of the Ru–NHPh bond (2.160(6) Å) in $[(PhNH)Ru^{II}H(PMe_3)_4]$.[32] The Ru1-N3-C29 and Ru1-N3*-C29* angles are 135.8(6)° and are similar to the

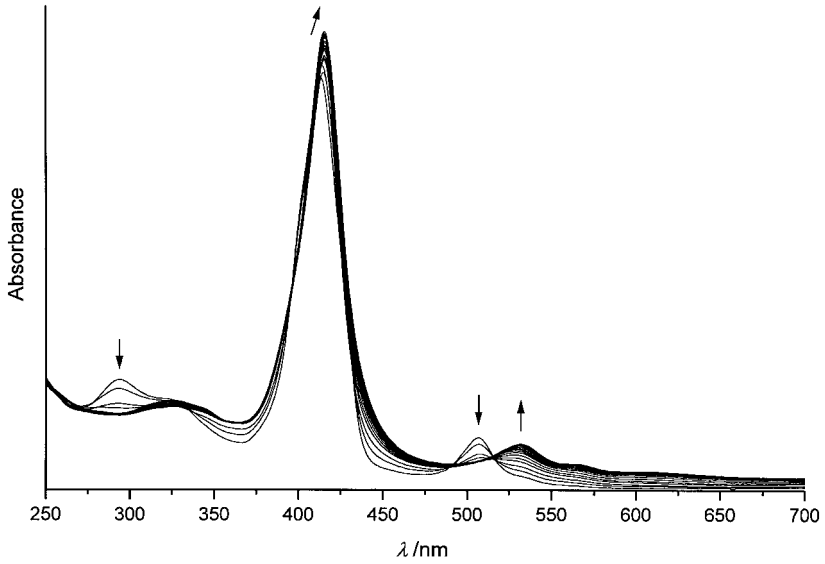

Figure 5. Time-dependent UV/Vis spectra of **6a** in $CHCl_3$. The spectra were recorded at 10 second intervals within a total of 200 seconds.

corresponding angles observed for other amido complexes.[32, 39]

The *p*-chlorophenylamido axial ligands are both planar. Both of their least-squares planes form a dihedral angle of about 60° with that of the porphyrin ring. The N3-Ru1-N3* angle of 167.5(4)° is similar to the axial N-Os-N angle of 165.1(2)° in the bis(arylimido) complex $[Os^{VI}(TTP)(N\text{-}p\text{-}C_6H_4NO_2)_2]$.[40] However, the torsion angle of C29-N3-N3*-C29* in **7a** is about 136°, and is very different from the corresponding angle of about 3° in $[Os^{VI}(TTP)(N\text{-}p\text{-}C_6H_4NO_2)_2]$.[40] According to our previous rationalization for the diamagnetism of **5a**,[15] an idealized structure of **7a** should have an N3-Ru1-N3* angle of 180° and a C29-N3-N3*-C29* torsion angle of either 180° or 0°. Evidently, the observed structure of **7a** is substantially distorted from this idealized geometry. Such a distortion might be a result of a solid state effect or packing forces.[40] While the structure of **7a** has low symmetry in the solid state, its solution ^{1}H NMR spectrum corresponds to structure of quasi-D_{4h} symmetry.

Mass spectrometry: Despite extensive efforts, diffraction-quality single crystals of the complexes **4**–**6** and **9** have not been obtained. In order to provide further support to the formulation of these types of complexes, we measured the electrospray mass spectra of **4d** and **5b** and the FAB mass spectra of **6a**, **6b**, **9a**, and **9b**. In all cases, the peaks due to the parent ions $[M]^+$ of these complexes with correct isotope patterns were observed. The positive ion FAB mass spectra of

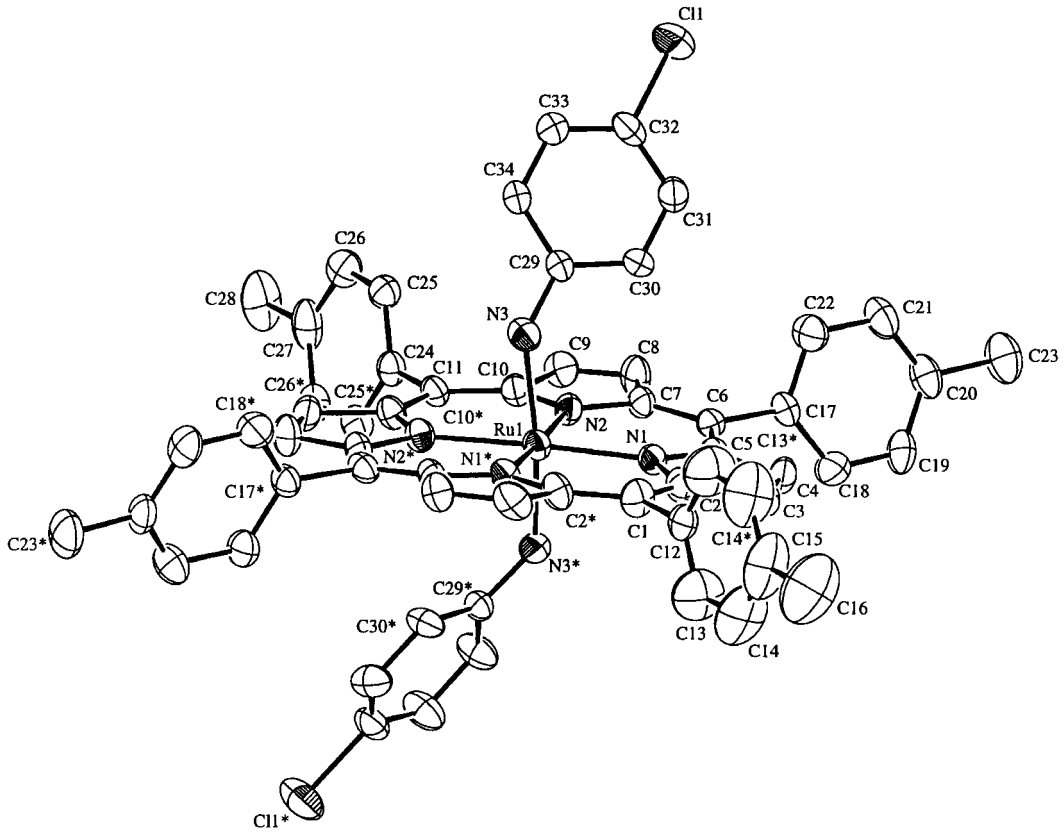

Figure 6. ORTEP drawing and atom-numbering scheme for **7a**. H atoms are omitted. Thermal ellipsoids are drawn at the 40% probability level. Starred atoms have coordinates at $-x$, y, $0.5-z$.

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Table 2. Structure determination summary for **7a**·2 CH_2Cl_2

empirical formula	$C_{60}H_{46}N_6Cl_2Ru_2CH_2Cl_2$
formula weight	1192.91
crystal system	monoclinic
space group	$C2/c$ (No. 15)
a [Å]	22.583(3)
b [Å]	22.536(3)
c [Å]	11.369(2)
β [°]	110.43(2)
V [Å^3]	5662(1)
Z	4
$F(000)$	2440
T [K]	301
ϱ_{calcd} [g cm^{-3}]	1.399
μ [mm^{-1}]	0.423
data collected	$h, k, \pm l$
reflections collected	24971
independent reflections	4565
observed reflections [$I > 3\sigma(I)$]	2790
parameters	346
R[a]	0.076
R_w[b]	0.106
goodness-of-fit	2.19
$(\Delta/\rho)_{max}$	0.05

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

Table 3. Selected bond lengths [Å] and angles [°] for **7a**·2 CH_2Cl_2

Ru1–N1	2.051(6)	Ru1–N1*	2.051(6)
Ru1–N2	2.057(7)	Ru1–N2*	2.057(7)
Ru1–N3	1.956(7)	Ru1–N3*	1.956(7)
N3–C29	1.39(1)	N3*–C29*	1.39(1)
N3-Ru-1N3*	167.5(4)		
Ru1-N3-C29	135.8(6)	Ru1-N3*-C29*	135.8(6)
N1-Ru1-N1*	91.4(4)	N1-Ru1-N2	88.7(2)
N2-Ru1-N2*	91.4(4)	N1-Ru1-N2*	88.7(2)
N3-Ru1-N1	99.2(3)	N3-Ru1-N1*	89.5(3)
N3*-Ru1-N1*	99.2(3)	N3*-Ru1-N1	89.5(3)
N3-Ru1-N2	87.7(3)	N3-Ru1-N2*	83.6(3)
N3*-Ru1-N2*	87.7(3)	N3*-Ru1-N2	83.6(3)

bis(amine)ruthenium(II) adducts **6a**, **6b**, **9a**, and **9b** generally show a set of three cluster peaks corresponding to $[M]^+$ and the fragments $[M-L]^+$ and $[M-2L]^+$ due to sequential loss of the coordinated amine axial ligands (L). The positive-ion electrospray mass spectrum of **5b** shows two prominent peaks attributable to $[M]^+$ and $[M-NPh_2]^+$, with the former being considerably more intense. Interestingly, the positive-ion electrospray mass spectrum of **4d** exhibits very little fragmentation. The parent ion $[M]^+$ was located at *m/z* 939.0. A much weaker cluster peak at *m/z* 922.9 might come from the loss of the oxo group from $[M]^+$. It is worth noting that no peak attributable to the loss of the *tert*-butylimido group was observed. It seems that the Ru=N*t*Bu group is more robust than the Ru=O group under the electrospray-MS conditions.

Conclusion

The isolated dioxoruthenium(VI) porphyrins are highly reactive toward primary, secondary, and even tertiary amines and serve as good precursors for the preparation of several interesting types of ruthenium complexes including bis(arylamine) and bis(*tert*-butylamine)ruthenium(II), bis(arylamido)- and bis(diphenylamido)ruthenium(IV), and oxo(*tert*-butylimido)ruthenium(VI) porphyrins. The simple isolation of [Ru^{II}(Por)(NH_2-*p*-$C_6H_4Cl)_2$] (Por = TTP; 4-Cl-TPP) first demonstrated that an arylamine can form fairly stable adducts with a metalloporphyrin despite being more weakly basic than an alkylamine. The formation of [Ru^{IV}(Por)(NH-*p*-$C_6H_4Cl)_2$] (Por = TTP; 4-Cl-TPP) from autooxidation of [Ru^{II}(Por)(NH_2-*p*-$C_6H_4Cl)_2$] in chloroform exposed to the atmosphere, provided the first cases in which an amido metalloporphyrin is formed unambiguously through oxidative deprotonation of the corresponding amine adducts. Oxo(*tert*-butylimido)ruthenium(VI) porphyrins [Ru^{VI}O(Por)(N*t*-Bu)] (Por = TPP; 3,4,5-MeO-TPP; TTP; 4-Cl-TPP; 3,5-Cl-TPP), the only examples of mononuclear ruthenium compounds bearing both Ru=NR and Ru=O functional groups, could be generally prepared through oxidation of the corresponding bis(*tert*-butylamine) adducts by bromine in dichloromethane in the presence of *tert*-butylamine and traces of water.

Experimental Section

General: $Ru_3(CO)_{12}$ (99%, Aldrich), *m*-chloroperoxybenzoic acid (*m*-CPBA; 55%, Merck), NH_2tBu (99.5+%, Aldrich), *n*-octylamine (99%, Aldich), isopropylamine (99%, Fluka), dimethylamine (40 wt% solution in water, Aldrich), $NHPh_2$ (99%, BDH), NMe_3 (40 wt% solution in water, Fluka), and 4-nitroaniline (99+%, Aldrich) were all used as received. 4-Chloroaniline (98%, Aldrich) was recrystallized from chloroform before use. All the solvents were of AR grade. The free porphyrin bases, H_2(Por) (Por = TPP; 3,4,5-MeO-TPP; TTP; 4-Cl-TPP; 3,5-Cl-TPP),[5] were prepared by literature methods.[41] The complexes **2a**–**e**[7] and their precursors [Ru^{II}(Por)(CO)(MeOH)][42] were all synthesized according to standard procedures. The spectral data of **4a** and **4b**[9] and the characterization of **5a**[15] have been reported in previous communications. Ultraviolet and visible (UV/Vis) spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker DPX300 spectrometer. In all cases, the solvent ($CDCl_3$) contained tetramethylsilane (TMS) as an internal standard. Chemical shifts (ppm) were reported relative to TMS. Infrared spectra were obtained with a Nicolet 20 SXC FT-IR spectrometer. FAB mass spectra were measured on a Finnigan MAT 95 mass spectrometer with 3-nitrobenzyl alcohol as a matrix. Electrospray mass spectra were measured on a Finnigan LCQ quadrupole ion trap mass spectrometer. Samples were dissolved in dichloromethane. The spray and capillary voltages were 3.0 eV and 46.0 eV, respectively. GC–MS measurements were carried out on a HP G1800C GCD Series II spectrometer. Elemental analyses were performed by Butterworth (UK) and Institute of Chemistry, the Chinese Academy of Sciences.

Oxo(*tert*-butylimido)ruthenium(VI) porphyrins 4: Compound **3** (50 mg) was dissolved in dichloromethane (15 mL) in the presence of *tert*-butylamine (0.2 mL). A dilute solution of bromine (60 mM) in dichloromethane was added dropwise, and the progress of the reaction was monitored by UV/Vis spectrophotometry. Addition of bromine continued until the β band of **3** at about 506 nm disappeared completely. At this stage, the reaction mixture contained a small amount of white precipitate and was greenish-red. After filtration, the filtrate was concentrated to ca. 5 mL and then transferred to an alumina column. The leading band (brown) was eluted with a dilute solution of *tert*-butylamine in dichloromethane (1:200 v/v). *n*-Heptane (10 mL) was added to the eluate. Reducing the solvent volume on a rotary evaporator to ca. 5 mL led to precipitation of the product as a dark purple solid, which was collected by filtration, washed with hexane, and dried.

Oxo(*tert*-butylimido)(*meso*-tetraphenylporphyrinato)ruthenium(VI) (4a): Yield: 95%; $C_{48}H_{37}N_5ORu$ (800.93): calcd C 71.98, H 4.66, N 8.74; found C 71.64, H 4.81, N 8.49.

Oxo(*tert*-butylimido)(*meso*-tetrakis{3,4,5-trimethoxyphenyl}porphyrinato)-ruthenium-(VI) (4b): Yield: 90%; $C_{60}H_{61}N_5O_{13}Ru$ (1161.25): calcd C 62.06, H 5.29, N 6.03; found C 61.74, H 5.30, N 5.71.

Oxo(*tert*-butylimido)(*meso*-tetrakis{*p*-tolyl}porphyrinato)ruthenium(VI) (4c): Yield: 85%; UV/Vis (1.47×10^{-5} M, $CHCl_3$): λ_{max} ($\log\varepsilon$) = 272 (4.38), 317 (4.22), 422 (5.18), 565 (3.86), 605 nm (3.53); IR (Nujol): $\tilde{\nu}$ = 1016 cm^{-1} ("oxidation state marker" band); both the Ru=O and Ru=N*t*Bu stretching bands were obscured by those of the porphyrinato ligand; $C_{52}H_{45}N_5ORu$ (857.03): calcd C 72.88, H 5.29, N 8.17; found C 72.39, H 5.42, N 8.30.

Oxo(*tert*-butylimido)(*meso*-tetrakis{*p*-chlorophenyl}porphyrinato)ruthenium(VI) (4d): Yield: 90%; UV/Vis (1.36×10^{-5} M, $CHCl_3$): λ_{max} ($\log\varepsilon$) = 279 (4.49), 329 (4.20), 420 (5.21), 561 (3.88), 601 nm (3.52); IR (Nujol): $\tilde{\nu}$ = 1222 (Ru=N*t*Bu), 804 (Ru=O), 1013 cm^{-1} ("oxidation state marker" band); Electrospray MS (CH_2Cl_2): *m*/*z*: 939.0 $[M]^+$, 922.9 $[M-O]^+$; $C_{48}H_{33}N_5OCl_4Ru$ (938.70): calcd C 61.42, H 3.54, N 7.46; found C 61.17, H 3.70, N 7.61.

Oxo(*tert*-butylimido)(*meso*-tetrakis{3,5-dichlorophenyl}porphyrinato)ruthenium(VI) (4e): Yield: 88%; UV/Vis (1.20×10^{-5} M, $CHCl_3$): λ_{max} ($\log\varepsilon$) = 279 (4.37), 334 (4.31), 418 (5.17), 559 (3.93), 597 nm (3.58); IR (Nujol): $\tilde{\nu}$ = 1219 (Ru=N*t*Bu), 1016 cm^{-1} ("oxidation state marker" band). The Ru=O stretching band waas obscured by an intense band at ca. 800 cm^{-1} of the porphyrinato ligand; $C_{48}H_{29}N_5OCl_8Ru$ (1076.48): calcd C 53.56, H 2.71, N 6.51; found C 53.21, H 2.90, N 6.29.

Bis(diphenylamido)ruthenium(IV) porphyrins (5): Freshly prepared **2** (0.5 equiv) was added to a solution of diphenylamine (28 mg) in dichloromethane (20 mL). The mixture was stirred at room temperature for 15 h. The resulting red solution was concentrated to ca. 2 mL and subjected to chromatography over alumina with chloroform as the eluent. The leading brown band was collected and evaporated to dryness. Recrystallization of the residual solid from dichloromethane/heptane yielded dark purple crystals.

(*meso*-Tetrakis{3,5-dichlorophenyl}porphyrinato)bis(diphenylamido)ruthenium(IV) (5b): Yield: 62%; UV/Vis (6.71×10^{-6} M, $CHCl_3$): λ_{max} ($\log\varepsilon$) = 279 (4.38), 330 (4.20), 424 (5.20), 525 (4.34), 555 nm (4.18); IR (Nujol): 1013 cm^{-1} ("oxidation state marker" band); Electrospray MS (CH_2Cl_2): *m*/*z*: 1325.9 $[M]^+$, 1157.7 $[M-NPh_2]^+$; $C_{68}H_{40}N_6Cl_8Ru$ (1325.80): calcd C 61.60, H 3.04, N 6.34; found C 61.28, H 2.80, N 6.27.

Bis(arylamine)ruthenium(II) porphyrins (6)

Method a: Freshly prepared **2** (50 mg) was added to a solution of *p*-chloroaniline (500 mg) in ethanol (10 mL). The mixture was stirred overnight to give a brown suspension. The solid was collected by filtration, washed with ethanol and dried.

Method b: Freshly prepared **2** (50 mg) was added to a solution of *p*-chloroaniline (500 mg) in dichloromethane (10 mL). The solid dissolved immediately and the mixture turned dark green; it then changed into a brown solution within 15 min. After removal of the solvent, the residual was washed with ethanol and dried.

Methods a and b afforded the following products as yellowish-brown solids in almost the same yields.

(*meso*-Tetrakis{*p*-tolyl}porphyrinato)bis(*p*-chloroaniline)ruthenium(II) (6a): Yield: 89%; UV/Vis ($CHCl_3$): λ_{max} = 295, 326 (sh), 414 (Soret), 507, 533 nm (sh); IR (KBr pellet): $\tilde{\nu}$ = 3309 (NH), 3259 (NH), 1000 cm^{-1} ("oxidation state marker" band); FAB MS ($CHCl_3$): *m*/*z*: 1025 $[M]^+$, 897 $[M-NH_2Ar]^+$, 770 $[M-2NH_2Ar]^+$; $C_{60}H_{48}N_6Cl_2Ru$ (1025.06): calcd C 70.30, H 4.72, N 8.20; found C 70.01, H 4.70, N 8.18.

(*meso*-Tetrakis{*p*-chlorophenyl}porphyrinato)bis(*p*-chloroaniline)ruthenium(II) (6b): Yield: 91%; UV/Vis ($CHCl_3$): λ_{max} = 293, 329 (sh), 414 (Soret), 507, 530 nm (sh); IR (KBr pellet): $\tilde{\nu}$ = 3322 (NH), 3268 (NH), 1000 cm^{-1} ("oxidation state marker" band); FAB MS ($CHCl_3$): *m*/*z*: 1107 $[M]^+$, 979 $[M-NH_2Ar]^+$, 852 $[M-2NH_2Ar]^+$; $C_{56}H_{36}N_6Cl_6Ru$ (1106.73): calcd C 60.78, H 3.28, N 7.59; found C 60.37, H 3.55, N 7.70.

Bis(arylamido)ruthenium(IV) porphyrins 7: A mixture of **6** (40 mg) and chloroform (20 mL) exposed to the atmosphere was stirred for 0.5 h for **6a** and 1.5 h for **6b**, and gave rise to a homogeneous dark green solution. The solvent was then removed on a rotary evaporator, and the residual solid was recrystallized from dichloromethane/*n*-hexane to give the desired product as dark purple crystals.

(*meso*-Tetrakis{*p*-tolyl}porphyrinato)bis(*p*-chlorophenylamido)ruthenium(IV) (7a): Yield: 90%; UV/Vis (8.99×10^{-6} M, $CHCl_3$): λ_{max} ($\log\varepsilon$) = 416 (5.12), 529 (4.26), 563 nm (4.02, sh); IR (KBr pellet): $\tilde{\nu}$ 3267 (NH), 1009 cm^{-1} ("oxidation state marker" band). $C_{60}H_{46}N_6Cl_2Ru\cdot2CH_2Cl_2$ (1192.91): calcd C 62.43, H 4.22, N 7.04; found C 62.42, H 4.28, N 6.93.

(*meso*-Tetrakis{*p*-chlorophenyl}porphyrinato)bis(*p*-chlorophenylamido)ruthenium(IV) (7b): Yield: 93%; UV/Vis (8.69×10^{-6} M, $CHCl_3$): λ_{max} ($\log\varepsilon$) = 417 (5.15), 527 (4.28), 561 nm (4.01, sh); IR (KBr pellet): $\tilde{\nu}$ = 3264 (NH), 1009 cm^{-1} ("oxidation state marker" band); $C_{56}H_{34}N_6Cl_6Ru$ (1104.71): calcd C 60.89, H 3.10, N 7.61; found C 60.50, H 3.43, N 7.55.

Bis(arylamido)ruthenium(IV) porphyrins 8: Freshly prepared **2** (30 mg) was added To a solution of *p*-nitroaniline (500 mg) in ethanol (10 mL). The mixture was stirred overnight to give a dark purple suspension. The solid was collected by filtration, washed with ethanol and dried. The desired products were isolated as dark purple solids.

(*meso*-Tetrakis{*p*-tolyl}porphyrinato)bis(*p*-nitrophenylamido)ruthenium(IV) (8a): Yield: 85%; UV/Vis (8.11×10^{-6} M, $CHCl_3$): λ_{max} ($\log\varepsilon$) = 412 (5.11), 527 (4.17), 561 nm (3.88, sh); IR (KBr pellet): $\tilde{\nu}$ 3266 (NH), 1011 cm^{-1} ("oxidation state marker" band); $C_{60}H_{46}N_8O_4Ru$ (1044.14): calcd C 69.02, H 4.44, N 10.73; found C 69.00, H 4.42, N 10.41.

(*meso*-Tetrakis{*p*-chlorophenyl}porphyrinato)bis(*p*-nitrophenylamido)-ruthenium(IV) (8b): Yield: 88%; UV/Vis (7.68×10^{-6} M, $CHCl_3$): λ_{max} ($\log\varepsilon$) = 413 (5.12), 528 (4.19), 562 nm (3.89, sh); IR (KBr pellet): $\tilde{\nu}$ 3265 (NH), 1011 cm^{-1} ("oxidation state marker" band); $C_{56}H_{34}N_8Cl_4O_4Ru\cdot4H_2O$ (1197.88): calcd C 56.15, H 3.53, N 9.35; found C 55.83, H 3.04, N 9.26.

Bis(trimethylamine)ruthenium(II) porphyrins (9): Freshly prepared **2** (30 mg) was suspended in a solution of trimethylamine in water (40 wt%, 15 mL). The mixture was stirred overnight. The solid was then collected by filtration, washed with ethanol, and dried. The following products were obtained as yellowish-brown solids in essentially quantitative yield.

(*meso*-Tetrakis{*p*-tolyl}porphyrinato)bis(trimethylamine)ruthenium(II) (9a): UV/Vis (8.30×10^{-6} M, $CHCl_3$): λ_{max} ($\log\varepsilon$) = 265 (4.47), 296 (4.57), 330 (4.36), 407 (5.25), 504 (4.31), 530 nm (3.68, sh); IR (KBr pellet): $\tilde{\nu}$ = 998 cm^{-1} ("oxidation state marker" band); FAB MS ($CHCl_3$): *m*/*z*: 888 $[M]^+$, 829 $[M-NMe_3]^+$, 770 $[M-2NMe_3]^+$; $C_{54}H_{54}N_6Ru\cdot H_2O$ (906.15): calcd C 71.58, H 6.23, N 9.27; found C 71.82, H 6.03, N 9.50.

(*meso*-Tetrakis{*p*-chlorophenyl}porphyrinato)bis(trimethylamine)ruthenium(II) (9b): UV/Vis (9.81×10^{-6} M, $CHCl_3$): λ_{max} ($\log\varepsilon$) = 267 (4.47), 300 (4.59), 331 (4.41), 407 (5.26), 504 (4.33), 530 nm (3.67, sh); IR (KBr pellet): $\tilde{\nu}$ = 998 cm^{-1} ("oxidation state marker" band); FAB MS ($CHCl_3$): *m*/*z*: 970 $[M]^+$, 911 $[M-NMe_3]^+$, 852 $[M-2NMe_3]^+$; $C_{50}H_{42}N_6Cl_4Ru\cdot0.5H_2O$ (978.81): calcd C 61.36, H 4.43, N 8.59; found C 61.34, H 4.21, N 8.32.

Reactions of 2 with alkylamines: Freshly prepared **2** (5 mg) was added to a solution of alkylamine (0.5 mL) in dichloromethane or chloroform (2 mL). Shaking the mixture for a few seconds gave rise to a homogenous solution. The progress of the reaction was monitored by UV/Vis spectrophotometry, which gave the following results: i) For *n*-octylamine, isopropylamine, and diethylamine, complexes $[Ru^{II}(Por)(L)_2]$ (L = *n*-octylamine, isopropylamine, and diethylamine, respectively),[8] were formed within 1 min. No other ruthenium porphyrins were detected. ii) For trimethylamine, the reaction was considerably slower. Some unknown species was detected within the first 5 min. After ca. 1 h, however, the only detectable metalloporphyrin products were complexes **9a** and **9b**. iii) For *tert*-butylamine, there was no appreciable reaction within the first 5 min. After the reaction had proceeded for about 2 h, a mixture of complexes **3** and **4** was obtained.

Reaction of 2 with *tert*-butylamine in hexane: A suspension of **2c** (20 mg) in hexane (20 mL) containing *tert*-butylamine (1 mL) was refluxed for 1 h, leading to formation of a greenish-red solution. Upon cooling to ambient temperature, the solution was filtered to remove any insoluble material and then evaporated to dryness, affording a dark purple solid (12 mg), which was characterized to be a mixture of **4c** and **10** by ^{1}H NMR spectroscopy.

X-ray crystal structure determination of 7a·2CH$_2$Cl$_2$: Crystals of **7a**·$2CH_2Cl_2$ were grown by cooling a solution of **7a** in dichloromethane/*n*-hexane (1:2 v/v) at −15 °C. A purple crystal of dimensions 0.35 × 0.15 × 0.10 mm in a glass capillary was used for data collection at 28 °C on a MAR diffractometer with a 300 mm image plate detector with graphite monochromatized $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Data collection was performed with 3° oscillation (60 images) at 120 mm distance and 720 s exposure. The images were interpreted and intensities integrated by using

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the program *DENZO*.[43] Intensity data were in the range of $2\theta_{max} = 50.9°$; h: 0 to 28; k: 0 to 26; l: 12 to 12. The space group was uniquely determined based on a statistical analysis of intensity distribution. The structure was solved by Patterson methods and expanded by Fourier methods (*PATTY*[44]), and refined by full-matrix least-squares using the software package *TeXsan*[45] on a Silicon Graphics Indy computer. A crystallographic asymmetric unit consists of half of one formula unit. In the least-squares refinement, all 35 non-H atoms were refined anisotropically. 27 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.96 and 1.10 e Å^{-3}, respectively. 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-132911. 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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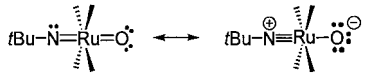
[1] a) R. R. Eady, P. J. Large, *Biochem. J.* **1969**, *111*, 37; b) J. A. Alberta, J. H. Dawson, *J. Biol. Chem.* **1987**, *262*, 11857.
[2] a) F. P. Guengerich, T. L. Macdonald, *Acc. Chem. Res.* **1984**, *17*, 9; b) R. E. White, M. J. Coon, *Annu. Rev. Biochem.* **1980**, *49*, 315.
[3] M. Sono, M. P. Roach, E. D. Coulter, J. H. Dawson, *Chem. Rev.* **1996**, *96*, 2841.
[4] a) D. H. Chin, A. L. Balch, G. N. La Mar, *J. Am. Chem. Soc.* **1980**, *102*, 1446; b) J. T. Groves, R. C. Haushalter, M. Nakamura, T. E. Nemo, B. J. Evans, *J. Am. Chem. Soc.* **1981**, *103*, 2884.
[5] Abbreviations of porphyrinato ligands: $(TMP)^{2-}$ = *meso*-tetrakis(2,4,6-trimethylphenyl)porphyrinato; $(TPP)^{2-}$ = *meso*-tetraphenylporphyrinato; $(3,4,5\text{-MeO-TPP})^{2-}$ = *meso*-tetrakis(3,4,5-trimethoxyphenyl)porphyrinato; $(TTP)^{2-}$ = *meso*-tetrakis(*p*-tolyl)porphyrinato; $(4\text{-Cl-TPP})^{2-}$ = *meso*-tetrakis(*p*-chlorophenyl)porphyrinato; $(3,5\text{-Cl-TPP})^{2-}$ = *meso*-tetrakis(3,5-dichlorophenyl)porphyrinato.
[6] a) J. T. Groves, R. Quinn, *Inorg. Chem.* **1984**, *23*, 3844; b) J. T. Groves, R. Quinn, *J. Am. Chem. Soc.* **1985**, *107*, 5790; c) J. T. Groves, K.-H. Ahn, *Inorg. Chem.* **1987**, *26*, 3831.
[7] a) W. H. Leung, C. M. Che, *J. Am. Chem. Soc.* **1989**, *111*, 8812; b) C. Ho, W. H. Leung, C. M. Che, *J. Chem. Soc. Dalton Trans.* **1991**, 2933.
[8] a) J. S. Huang, PhD Dissertation, Nankai University, **1992**; b) Z. Y. Li, C. M. Che, *Wuji Huaxue Xuebao* **1997**, *13*, 135, this paper was published without the consent of CMC.
[9] J. S. Huang, C. M. Che, C. K. Poon, *J. Chem. Soc. Chem. Commun.* **1992**, 161.
[10] A. J. Bailey, B. R. James, *Chem. Commun.* **1996**, 2343.
[11] a) C. J. Epstein, D. K. Straub, C. Maricondi, *Inorg. Chem.* **1967**, *16*, 1720; b) L. J. Radonovich, A. Bloom, J. L. Hoard, *J. Am. Chem. Soc.* **1972**, *94*, 2073; c) J. C. Fanning, *Coord. Chem. Rev.* **1991**, *110*, 235.
[12] L. K. Hanson, M. Gouterman, J. C. Hanson, *J. Am. Chem. Soc.* **1973**, *95*, 4822.
[13] a) J. W. Buchler, W. Kokisch, P. D. Smith, *Struct. Bonding (Berlin)* **1978**, *34*, 79; b) J. W. Buchler, C. Dreher, F. M. Künzel, *Struct. Bonding (Berlin)* **1995**, *84*, 1.
[14] Z. Y. Li, J. S. Huang, M. C. W. Chan, K. K. Cheung, C. M. Che, *Inorg. Chem.* **1997**, *36*, 3064.
[15] J. S. Huang, C. M. Che, Z. Y. Li, C. K. Poon, *Inorg. Chem.* **1992**, *31*, 1313.
[16] M. D. Fryzuk, C. D. Montgomery, *Coord. Chem. Rev.* **1989**, *95*, 1.
[17] G. J. Organ, M. K. Cooper, K. Henrick, M. McPartlin, *J. Chem. Soc. Dalton Trans.* **1984**, 2377.
[18] a) see ref. [8a]; b) We noted very recently that some spectral data of **4c** and **4d** had appeared in: Z. Y. Li, C. M. Che, *Chin. J. Chem.* **1997**, *15*, 1, this paper was published without the consent of CMC.
[19] A. F. Clifford, C. S. Kobayashi, *Abstracts of Papers*, 130th National Meeting of the American Chemical Society, Atlantic City, NJ, **1956**, Abstract 50R.
[20] a) W. A. Nugent, B. L. Haymore, *Coord. Chem. Rev.* **1980**, *31*, 123; b) W. A. Nugent, J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley-Interscience, New York, **1988**; c) E. W. Harlan, R. H. Holm, *J. Am. Chem. Soc.* **1990**, *112*, 186.
[21] a) W. H. Leung, G. Wilkinson, B. Hussain-Bates, M. B. Hurstouse, *J. Chem. Soc. Dalton Trans.* **1991**, 2791; b) T. P. Kee, L. Y. Park, J. Robbins, R. R. Schrock, *J. Chem. Soc. Chem. Commun.* **1991**, 121.
[22] Only two mononuclear ruthenium organoimido complexes had been reported: a) For the low-valent complex $[Ru(NC_3HF_6)(PPh_3)_2(CO)_2]$, stabilized by a strongly electron-withdrawing group (C_3HF_6), see: M. J. McGlinchey, F. G. A. Stone, *J. Chem. Soc. Chem. Commun.* **1970**, 1265; b) For the high-valent complex $[Ru^{VI}(NSiMe_3)(CH_2SiMe_3)_4]$, which is extremely air and moisture sensitive, see: P. A. Shapley, H. S. Kim, S. R. Wilson, *Organometallics* **1988**, *7*, 928.
[23] For other isolated mononuclear ruthenium alkylimido complexes, see: a) C. Redshaw, W. Clegg, G. Wilkinson, *J. Chem. Soc. Dalton Trans.* **1992**, 2059; b) A. A. Danopoulos, G. Wilkinson, B. Hussain-Bates, M. B. Hursthouse, *Polyhedron*, **1992**, *11*, 2961; c) A. K. Burrell, A. J. Steedman, *J. Chem. Soc. Chem. Commun.* **1995**, 2109; d) A. K. Burrell, A. J. Steedman, *Organometallics*, **1997**, *16*, 1203.
[24] After solutions of **4a–e** in $CDCl_3$ were kept for about 1 day, the *tert*-butyl signals of the imido groups in their ^{1}H NMR spectra completely disappeared, and the spectra became very similar to the nitrosylruthenium(II) porphyrins reported in the literature: a) D. S. Bohle, C.-H. Hung, B. D. Smith, *Inorg. Chem.* **1998**, *37*, 5798; b) K. M. Miranda, X. Bu, I. Lorkovic, P. C. Ford, *Inorg. Chem.* **1997**, *36*, 4838, and references cited therein. Importantly, upon removal of the solvent under vacuum, the residual solids all exhibited an intense band in their IR spectra within the region of 1870–1810 cm^{-1}, characteristic of ruthenium porphyrins with terminal Ru–NO groups.
[25] Quite a few dialkyl- or diarylamido ruthenium complexes have been reported, but all these species contain only *lower valent* ruthenium centers, such as Ru^{II} and Ru^{III}, for example: a) D. C. Bradley, M. H. Chisholm, *Acc. Chem. Res.* **1976**, *9*, 273; b) H. E. Bryndza, W. Tam, *Chem. Rev.* **1988**, *88*, 1163; c) B. Cetinkaya, M. F. Lappert, S. Torroni, *J. Chem. Soc. Chem. Commun.* **1979**, 841; d) H. E. Bryndza, L. K. Fong, R. C. Paciello, W. Tam, J. E. Bercaw, *J. Am. Chem. Soc.* **1987**, *109*, 1444; e) M. I. Kahn, U. C. Agarwala, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1285; f) A. R. Chakravarty, F. A. Cotton, D. A. Tocher, *Inorg. Chem.* **1984**, *23*, 4030; g) M. D. Fryzuk, C. D. Montgomery, S. J. Rettig, *Organometallics* **1991**, *10*, 467.
[26] One reviewer pointed out that reaction 3 must be far more complicated. The reducing agent for $Ru^{VI}-Ru^{IV}$ most probably is Ph_2NH, which is known to give blue dyes when oxidized in strongly acidic media. The products formed from Ph_2N radicals may explain the lower yields.
[27] D. R. Paulson, S. B. Bhakta, R. Y. Hyun, M. Yuen, C. E. Beaird, S. C. Lee, I. Kim, J. Ybarra, Jr., *Inorg. Chim. Acta* **1988**, *151*, 149.
[28] T. Barbour, W. J. Belcher, P. J. Brothers, C. E. F. Rickard, D. C. Ware, *Inorg. Chem.* **1992**, *31*, 746.
[29] W. H. Leung, T. S. M. Hun, H. W. Hou, K. Y. Wong, *J. Chem. Soc. Dalton Trans.* **1997**, 237.
[30] Identified by ^{1}H NMR spectroscopy and GC-MS measurments. The spectral data of the organic product are identical with those of an authentic sample of bis(*p*-chlorophenyl)diazene prepared by the literature method: O. H. Wheeler, D. Gonzalez, *Tetrahedron*, **1964**, *20*, 189.
[31] Since *tert*-butylimido ligand is a stronger donor than the oxo ligand, the Ru=N*t*Bu and Ru=O bonds in complexes **4** would have more triple and single bond character, respectively, due to a "push–pull" effect, as expressed by a corresponding resonance formula, see Scheme 2. We thank one reviewer for bringing the push–pull effect to our attention.
[32] J. F. Hartwig, R. A. Anderson, R. G. Bergman, *Organometallics* **1991**, *10*, 1875.
[33] A. Antipas, J. W. Buchler, M. Gouterman, P. D. Smith, *J. Am. Chem. Soc.* **1980**, *102*, 198.



Scheme 2. "Push–pull" effect on ruthenium complexes that contain Ru=N*t*Bu and Ru=O bonds.

[34] H. Scheer, J. J. Katz, in *Porphyrins and Metalloporphyrins*, (Ed.: K. M. Smith), Elsevier, Amsterdam, **1975**, chapter 10, pp. 460–462.

[35] J. P. Collman, P. J. Brothers, L. McElwee-White, E. Rose, *J. Am. Chem. Soc.* **1985**, *107*, 6110.

[36] The IR spectra of ruthenium complexes with *meso*-tetraarylporphyrinato ligands usually show an intense band at ca. 1000 cm^{-1}, the wavenumber of which appreciably increases with the oxidation state of ruthenium. See ref. [6c] for more detail.

[37] A. O. Chong, K. Oshima, K. B. Sharpless, *J. Am. Chem. Soc.* **1977**, *90*. 3420.

[38] a) C. M. Che, W. C. Chung, T. F. Lai, *Inorg. Chem.* **1988**, *27*, 2801; b) S. Mosseri, P. Neta, P. Hambright, D. Y. Sabry, A. Harriman, *J. Chem. Soc. Dalton Trans.* **1988**, 2705.

[39] S. M. Au, W. H. Fung, M. C. Cheng, C. M. Che, S. M. Peng, *Chem. Commun.* **1997**, 1655.

[40] J. A. Smieja, K. M. Omberg, G. L. Breneman, *Inorg. Chem.* **1994**, *33*, 614.

[41] A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, *J. Org. Chem.* **1967**, *32*, 476.

[42] a) M. Tsutsui, D. Ostfeld, L. M. Hoffman, *J. Am. Chem. Soc.* **1971**, *93*, 1820; b) D. P. Rillema, J. K. Nagle, L. F. Barringer, Jr., T. J. Meyer, *J. Am. Chem. Soc.* **1981**, *103*, 56.

[43] *DENZO*: in *The HKL Manual—A description of programs DENZO, XDISPLAYF, and SCALEPACK* written by D. Gewirth with the cooperation of the program authors Z. Otwinowski, W. Minor, Yale University, New Haven (USA), **1995**.

[44] *PATTY*: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, *The DIRDIF Program System*, *Technical Report of the Crystallography Laboratory*, University of Nijmegen (The Netherlands), **1992**.

[45] *TeXsan*: *Crystal Structure Analysis Package*, Molecular Structure Corporation, The Woodlands, Texas (USA), **1985** and **1992**.

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