Ruthenium Complexes with a Terminal Hydrazido Ligand. Synthesis, Spectroscopy, and X-ray Crystal Structure

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Bis(1,1-diphenylhydrazido(1−))ruthenium(IV) porphyrins, [Ru^{IV}(Por)($NHNPh_2$)$_2$] (Por = TPP, TTP, 4-Cl-TPP, 4-MeO-TPP), were prepared in ~60% yields through the reaction of dioxoruthenium(VI) porphyrins, [Ru^{VI}(Por)-O_2], with 1,1-diphenylhydrazine in ethanol. This new type of ruthenium complex has been characterized by ^{1}H NMR, IR, UV−vis, and FABMS with elemental analysis. The crystal structure of [Ru^{IV}(TTP)($NHNPh_2$)$_2$], which reveals an η^1-coordination mode for both hydrazido axial ligands, has been determined. The average Ru−$NHNPh_2$ distance and Ru−N−N angle were found to be 1.911(3) Å and 141.1(3)°, respectively. The porphyrin ring exhibits a ruffling distortion that is unprecedentedly large for ruthenium complexes with simple porphyrinato ligands (such as TTP). This is probably due to the steric effect of the axial hydrazido(1−) ligands.

Introduction

Since the first dinitrogen metal complex, [$Ru(NH_3)_5(N_2)]^{2+}$, was reported in 1965,[1] the chemistry of metal complexes bearing diazo ligands, namely, dinitrogen, diazenido, diazene, hydrazido-(2−), hydrazido(1−), and hydrazine, has grown very rapidly,[2−8] particularly because such types of complexes are closely related to the process of biological nitrogen fixation.[4,5] Because molybdenum is widely perceived as having an essential role in this process (e.g., the case of Mo-nitrogenase), the chemistry of metal complexes bearing the above diazo ligands, especially the terminal hydrazido ligands, has been dominated by molybdenum and its congener, tungsten, for many years.[2−8] The recent discovery of Fe-nitrogenase,[9] whose active sites contain no molybdenum but are expected to have structures similar to those of Mo-nitrogenase,[10] raised the issue of developing a parallel chemistry for iron and its congeners, ruthenium and osmium.

Currently, there are a good number of terminal hydrazido-(1−) metal complexes known in the literature, all of which are monohydrazido(1−) species with metal centers spanning the groups IIIB (Sm),[11] IVB (Ti, Zr),[12−18] VB (Ta),[19] VIB (Mo, W),[20−37] VIIB (Tc, Re),[38−44] and VIIIB (Ir).[45,46] Strikingly, these complexes remain fully unknown for the entire subgroup of iron, ruthenium, and osmium. On the other hand, although complexes with terminal hydrazido(2−) ligands have been reported for both

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iron[47,48] and osmium,[49,50] respectively, none of these complexes have been isolated or even observed for ruthenium.

Herein, we describe the synthesis, spectroscopic characterization, and X-ray crystal structure of ruthenium complexes $[Ru^{IV}(Por)(NHNPh_2)_2]$ (Por = porphyrinato dianion) with terminal hydrazido ligands. Prior to this work, there were a handful of ruthenium hydrazido complexes reported in the literature, all of which are organometallic species with triply bridging hydrazido groups.[51−53] In the case of metalloporphyrins, the isolated complexes bearing axial diazo ligands are still sparse, among which are the dinitrogen,[54−58] diazenido,[59,60] diazene,[61,62] hydrazido(2−),[47,48] and hydrazine[61,62] complexes. The present work provides the first examples of hydrazido(1−) metalloporphyrins.

Experimental Section

Materials. $Ru_3(CO)_{12}$ (Strem), *m*-chloroperoxybenzoic acid (Fluka, 55%), 1,1-diphenylhydrazine hydrochloride (Aldrich, 97%), potassium hydroxide (Aldrich, 85+%), pyrrole (Aldrich, 98%), and benzaldehyde (Aldrich, 99%) (and its para-substituted derivatives *p*-X-C_6H_5CHO (X = Me, Cl, and MeO) (Aldrich, 97−98%)) were used as received. All of the solvents were of the AR grade and used without purification. The free porphyrin bases $H_2(Por)$ (Por = *meso*-tetraphenylporphyrinato (TPP), *meso*-tetrakis(*p*-tolyl)porphyrinato (TTP), *meso*-tetrakis(4-chlorophenyl)porphyrinato (4-Cl-TPP), and *meso*-tetrakis(4-methoxyphenyl)porphyrinato (4-MeO-TPP) dianions) were prepared by the method found in the literature.[63] The complexes $[Ru^{VI}(Por)O_2]$ (**1**)[64,65] and their precursors $[Ru^{II}(Por)(CO)(MeOH)]$[66] were both prepared according to the standard procedures.

Table 1. Structure Determination Summary

chemical formula	$C_{72}H_{58}N_8Ru$
fw	1136.37
space grp	$P2_1/n$ (No. 14)
a, Å	14.536(2)
b, Å	22.359(3)
c, Å	18.125(3)
β, deg	93.70(2)
V, Å^3	5878(2)
Z	4
$F(000)$	2360
T, °C	28
λ, Å	0.71073
ρ_{calcd}, g cm^{-3}	1.284
μ, cm^{-1}	3.07
R^a	0.046
$R_w{}^b$	0.062

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

Synthesis of Bis(hydrazido)ruthenium(IV) Porphyrins $[Ru^{IV}(Por)(NHNPh_2)_2]$ (2) (Por = TPP, 2a; TTP, 2b; 4-Cl-TPP, 2c; 4-MeO-TPP, 2d). To a mixture of 1,1-diphenylhydrazine hydrochloride (228 mg, 1 mmol) and potassium hydroxide (90 mg, 1.4 mmol) in ethanol (10 mL) was added $[Ru^{VI}(Por)O_2]$ (**1**) (0.05 mmol). The mixture was stirred for ∼3 h and then filtered. The collected precipitate was washed with ethanol and then extracted with dichloromethane (10 mL). The addition of *n*-heptane (5 mL) to the extract was followed by the reduction of the solvent amount on a rotary evaporator. This caused the precipitation of the desired product as purple crystals. Yield: ∼60%.

$[Ru^{IV}(TPP)(NHNPh_2)_2]$ (2a). Anal. Calcd for $C_{68}H_{50}N_8Ru$: C, 75.63; H, 4.63; N, 10.38. Found: C, 75.65; H, 4.83; N, 10.22. ^{1}H NMR (300 MHz, $CDCl_3$): δ H_β 8.31 (s, 8H), H_o 7.94 (m, 8H), H_m, H_p 7.62 (m, 12H); NHN*Ph*$_2$, H'_p 6.74 (t, 4H), H'_m 6.41 (t, 8H), H'_o 3.98 (d, 8H) (the NH proton resonances were not located). IR (KBr pellet, cm^{-1}): "oxidation state marker" band 1008. UV−vis (1.73 × 10^{-5} M, $CHCl_3$, nm): λ_{max} (log ϵ) 423 (5.15), 550 (4.13) sh, 598 (3.89) sh. FABMS ($CHCl_3$): m/z 1079 ($[M - H]^+$), 897 ($[M - NHNPh_2]^+$), 728 ($[M - NHNPh_2 - HNPh_2]^+$), 714 ($[M - 2NHNPh_2]^+$).

$[Ru^{IV}(TTP)(NHNPh_2)_2]$ (2b). Anal. Calcd for $C_{72}H_{58}N_8Ru$: C, 76.12; H, 5.11; N, 9.87. Found: C, 75.73; H, 5.31; N, 9.71. ^{1}H NMR (300 MHz, $CDCl_3$): δ H_β 8.33 (s, 8H), H_o 7.82 (d, 8H), H_m 7.42 (d, 8H), *p*-Me 2.63 (12H, s); NHN*Ph*$_2$, H'_p 6.71 (t, 4H), H'_m 6.38 (t, 8H), H'_o 3.95 (d, 8H) (the NH proton resonances were not located). IR (KBr pellet, cm^{-1}): "oxidation state marker" band 1008. UV−vis (1.41 × 10^{-5} M, $CHCl_3$, nm): λ_{max} (log ϵ) 425 (5.19), 551 (4.15) sh, 598 (3.92) sh. FABMS ($CHCl_3$): m/z 1136 (M^+), 953 ($[M - NHNPh_2]^+$), 784 ($[M - NHNPh_2 - HNPh_2]^+$), 770 ($[M - 2NHNPh_2]^+$).

$[Ru^{IV}(4\text{-}Cl\text{-}TPP)(NHNPh_2)_2]$ (2c). Anal. Calcd for $C_{68}H_{46}N_8Cl_4Ru$: C, 67.05; H, 3.78; N, 9.20. Found: C, 66.75; H, 3.89; N, 9.13. ^{1}H NMR (300 MHz, $CDCl_3$): δ H_β 8.29 (s, 8H), H_o 7.84 (d, 8H), H_m 7.61 (d, 8H); NHN*Ph*$_2$, H'_p 6.74 (t, 4H), H'_m 6.40 (t, 8H), H'_o 3.95 (d, 8H) (the NH proton resonances were not located). IR (KBr pellet, cm^{-1}): ν_{NH} 3256; "oxidation state marker" band 1008. UV−vis (1.30 × 10^{-5} M, $CHCl_3$, nm): λ_{max} (log ϵ) 425 (5.14), 550 (4.13) sh, 598 (3.85) sh. FABMS ($CHCl_3$): m/z 1218 (M^+), 1036 ($[M - NHNPh_2]^+$), 866 ($[M - NHNPh_2 - HNPh_2]^+$), 852 ($[M - 2NHNPh_2]^+$).

$[Ru^{IV}(4\text{-}MeO\text{-}TPP)(NHNPh_2)_2]$ (2d). Anal. Calcd for $C_{68}H_{50}N_8O_4Ru\cdot 0.5C_7H_{16}$: C, 71.90; H, 4.89; N, 9.38. Found: C, 71.62; H, 4.77; N, 9.23. ^{1}H NMR (300 MHz, $CDCl_3$): δ H_β 8.34 (s, 8H), H_o 7.85 (d, 8H), H_m 7.16 (d, 8H), *p*-MeO 4.05 (12H, s); NHN*Ph*$_2$, H'_p 6.72 (t, 4H), H'_m 6.39 (t, 8H), H'_o 3.95 (d, 8H) (the NH proton resonances were not located). IR (KBr pellet, cm^{-1}): "oxidation state marker" band 1008. UV−vis (1.54 × 10^{-5} M, $CHCl_3$, nm): λ_{max} (log ϵ) 426 (5.17), 550 (4.10) sh, 599 (3.87) sh.

X-ray Structural Determinations. Single crystals of **2b** (Table 1) were grown by slow evaporation of a solution of **2b** in dichloromethane/*n*-heptane (1:5 v/v). A purple crystal of dimensions 0.30 × 0.20 × 0.10 mm in a glass capillary was used for data collection at 28 °C on

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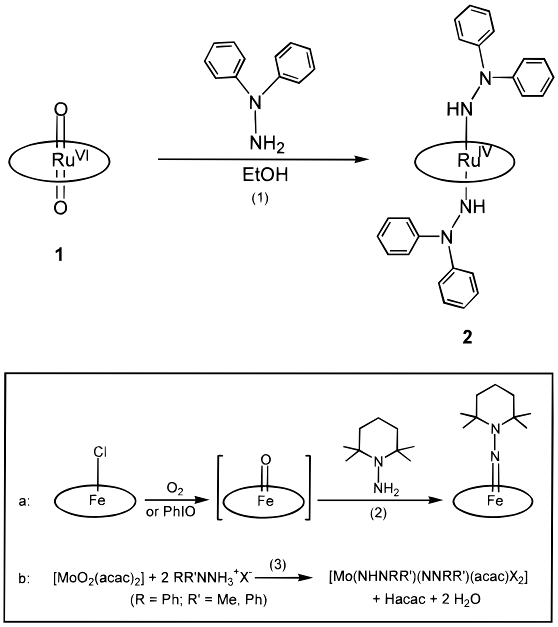
an MAR diffractometer with a 300 mm image-plate detector using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection was made with 3° oscillation (64 images) at 120 mm distance and 600 s exposure. The images were interpreted and the intensities integrated using the DENZO program.[67] The space group was uniquely determined on the basis of systematic absences, and the structure was solved using Patterson methods, expanded using Fourier methods (PATTY[68]), and refined by full-matrix least-squares methods using the software package TeXsan[69] on a Silicon Graphics Indy computer. A crystallographic asymmetric unit consists of one molecule. C29 and C30 were disordered with occupation numbers 0.6, and C29′ and C30′ had occupation numbers of 0.4. In the least-squares refinement, 79 non-hydrogen atoms were refined anisotropically, whereas the disordered C atoms were refined isotropically. The 54 H atoms, located at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms, were not refined. Neither the H atoms attached to the disordered C atoms nor the H atoms bonded to N5 and N7 were included. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.37 and 0.50 e Å^{-3}, respectively.

Other Physical Measurements. ^{1}H NMR spectra were recorded on a Bruker DPX 300 spectrometer (300 MHz). The chemical shifts (δ, ppm) are reported relative to tetramethylsilane (TMS). IR spectra were measured on a Bio-Rad FT-IR spectrometer. UV−vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Fast atom bombardment mass spectra (FABMS) were measured on a Finnigan MAT 95 mass spectrometer by using 3-nitrobenzyl alcohol as the matrix. Elemental analyses were performed by the Institute of Chemistry of the Chinese Academy of Sciences.

Results and Discussion

Synthesis. The treatment of dioxoruthenium(VI) porphyrins, [Ru^{VI}(Por)O$_2$] (**1**),[64,65] with excess 1,1-diphenylhydrazine, prepared in situ by mixing the commercially available 1,1-diphenylhydrazine hydrochloride with potassium hydroxide in ethanol, readily gave crude [Ru^{IV}(Por)(NHNPh$_2$)$_2$] (**2**) as a dark purple precipitate (Scheme 1, reaction 1). Analytically pure **2** was obtained as purple crystals through recrystallization of the crude products from dichloromethane/*n*-heptane in ∼60% isolated yields. The preparation of metal hydrazido complexes from reactions of metal oxo complexes with hydrazines or their hydrohalide salts is not unprecedented. Two typical examples are shown in Scheme 1 for comparison. One affords the hydrazido(2−) complexes (reaction 2), whereas the other affords the complexes bearing both hydrazido(2−) and hydrazido(1−) ligands (reaction 3). Interestingly, reaction 1 formed the complexes containing only hydrazido(1−) ligands, thus representing a new type of reaction between metal oxo complexes and hydrazines.

Scheme 1. Preparation of bis(1,1-diphenylhydrazido(1−))-ruthenium(IV) porphyrins.[a]



[a] For comparison, the preparations of (a) hydrazido(2-)iron porphyrins (refs 47,48) and (b) hydrazidomolybdenum complexes [Mo(NHNRR′)(NNRR′)(acac)X$_2$] (ref 35) are also shown.

We found that under the same conditions, except for the use of 1,1-diphenylhydrazine hydrochloride instead of the corresponding hydrazine, reaction 1 afforded an almost homogeneous solution, the workup of which gave no **2**. On the other hand, by employing a hydrazine derivative bearing α-hydrogens, such as 1,1-dimethylhydrazine, the corresponding bis(hydrazido)-ruthenium(IV) porphyrins could not be obtained in a similar manner. This is analogous to the case of reaction 2, which has also been found to be applicable only to the indicated α-hydrogen-free hydrazine.[47,48] The mechanism for the formation of **2** is not yet clear. There is a possibility that the **1** complexes were first reduced to ruthenium(II) or ruthenium(III) porphyrins bearing hydrazine axial ligands, which underwent oxidative deprotonation in air to give **2**. Indeed, when reaction 1 was performed under nitrogen, the precipitates formed (different from **2**) were found to be very air-sensitive. Attempts to characterize these intermediates were unsuccessful, but more importantly, exposure of the solutions of the intermediates in aerobic chloroform readily resulted in the formation of **2** as the only detectable ruthenium porphyrin products. It can be envisaged that the **2** complexes are potential precursors for the preparation of intriguing ruthenium complexes with a terminal hydrazido-(2−) ligand via oxidative deprotonation.

^{1}H NMR. The ^{1}H NMR spectra of **2** complexes in CDCl$_3$ all show well-resolved signals at the fields typical for a diamagnetic-ruthenium porphyrin of a pseudo-D_{4h} symmetry. Figure 1 shows the spectrum of **2c** as an example. The H$_\beta$ chemical shifts of 8.29−8.34 ppm observed for **2** fall in the range of 8.21−8.37 ppm previously reported for the diamagnetic bis(alkyl)ruthenium(IV) porphyrins [Ru^{IV}(Por)R$_2$][70] and bis-(diphenylamido)ruthenium(IV) porphyrin [Ru^{IV}(3,4,5-MeO-TPP)(NPh$_2$)$_2$] (3,4,5-MeO-TPP = *meso*-tetrakis(3,4,5-trimethoxyphenyl)porphyrinato dianion).[71] The integration ratios of all of the signals are consistent with the bis(hydrazido) axial ligations of **2**. Because of the porphyrin ring current effect, the phenyl proton resonances of the hydrazido axial ligands are markedly upfield shifted. However, such upfield shifts are substantially smaller than those of the diphenylamido axial ligands of [Ru^{IV}(3,4,5-MeO-TPP)(NPh$_2$)$_2$], indicating that all of the hydrazido phenyl groups of **2** are considerably farther from the porphyrin ring than the amido phenyl groups of [Ru^{IV}-(3,4,5-MeO-TPP)(NPh$_2$)$_2$]. This suggests that both the hydrazido

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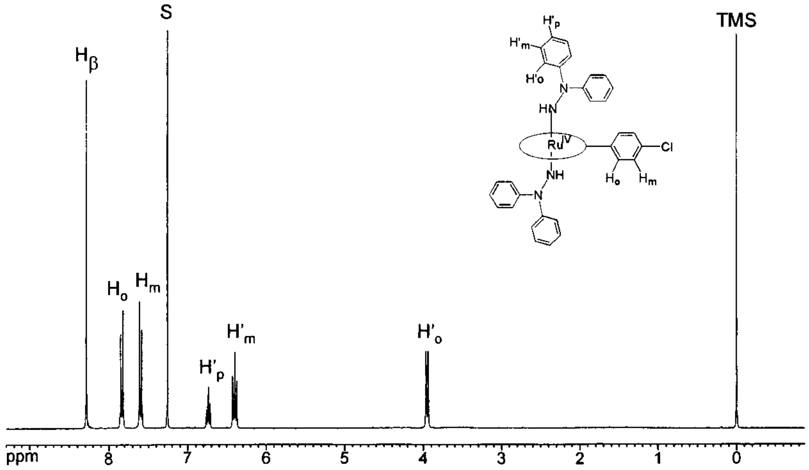

Figure 1. ^{1}H NMR spectrum (300 MHz) of [Ru^{IV}(4-Cl-TPP)(NHNPh$_2$)$_2$] (**2c**) in CDCl$_3$. Signal assignments are indicated.

ligands of **2** assume an η^1 rather than η^2 coordination mode, which minimizes the repulsion between the hydrazido phenyl groups and the porphyrin ring. The rapid rotations of (i) the hydrazido groups about the axial Ru−N bonds and (ii) the NPh$_2$ moieties in the hydrazido groups about the N−N bonds should allow **2** to maintain a pseudo-D_{4h} symmetry, consistent with the observed simple spectra. In contrast, an η^2 coordination mode of the hydrazido group would generate an *eight-coordinate* ruthenium center fully unprecedented in ruthenium porphyrin chemistry. It would also considerably lower the symmetry of **2**, leading to the formation of several geometric isomers (the most symmetric isomer has a symmetry of C_{2v}) and thus rendering the spectra of **2** much more complicated.

IR. The IR spectrum of **2c** shows the N−H stretching vibrations of the coordinated NHNPh$_2$ groups as a sharp, albeit weak, band at 3256 cm^{-1}, which shifts to 2417 cm^{-1} when the proton is replaced by deuterium. The observed ν_{N-H}/ν_{N-D} ratio (1.35) is almost identical to the calculated value (~1.37). The ν_{N-H} frequency of **2c** is very similar to that (3258 cm^{-1}) observed for the same η^1-hydrazido(1−) ligand in [Mo^{VI}(NHNPh$_2$)(NNPh$_2$)(acac)Cl$_2$].[35] Note that the ν_{N-H} bands were not located for complexes **2a**,**b**,**d**. Perhaps such vibrations are too weak to be observed in these cases. The "oxidation state marker" bands[71] of **2** all appear at 1008 cm^{-1}, a frequency slightly lower than that found for [Ru^{IV}(3,4,5-MeO-TPP)(NPh$_2$)$_2$] (1012 cm^{-1})[71] but significantly higher than that reported for bis(amine)ruthenium(II) complexes bearing *meso*-tetraarylporphyrinato ligands (~1000 cm^{-1}).[72]

UV−vis. The UV−vis spectra of **2** complexes in chloroform are very unusual. A typical spectrum of **2c** is shown in Figure 2. Although the known diamagnetic carbonyl-,[66] dioxo-,[64,65] oxo(imido)-,[72] bis(amine)-,[71,72] bis(diphenylamido)-,[71] and bis(tosylimido)-ruthenium[73] complexes bearing *meso*-tetraarylporphyrinato ligands all show a prominent β band, such a band is barely discernible for **2**. In fact, the spectra of **2** exclusively feature a prominent tail to the red of the Soret band. On the tail are superimposed two faint bands at ~550 and 598 nm, which could be ascribed to the β and α bands, respectively. As compared with the spectrum of [Ru^{IV}(3,4,5-MeO-TPP)(NPh$_2$)$_2$] (Figure 2, inset), both bands are substantially red-shifted.

FABMS. The positive-ion FABMS of **2a**−**c** were measured, all of which exhibited a set of three prominent cluster peaks attributable to the parent ion (M$^+$ or [M − H]$^+$) and the fragments [Ru(Por)(NHNPh$_2$)]$^+$ and [Ru(Por)N]$^+$, due to the sequential loss of an NHNPh$_2$ group and diphenylamine. However, the fragment [Ru(Por)]$^+$, resulting from a complete loss of the NHNPh$_2$ axial groups of the parent ion, is rather weak. Interestingly, in all cases, the most intense cluster peak is the one due to the fragment [Ru(Por)N]$^+$, implying a remarkable stability of the nitrido species and a facile cleavage of an Ru−N(hydrazido) bond and the NH−NPh$_2$ bond of the remaining hydrazido(1−) axial ligand in **2** complexes under the mass spectrometry conditions.

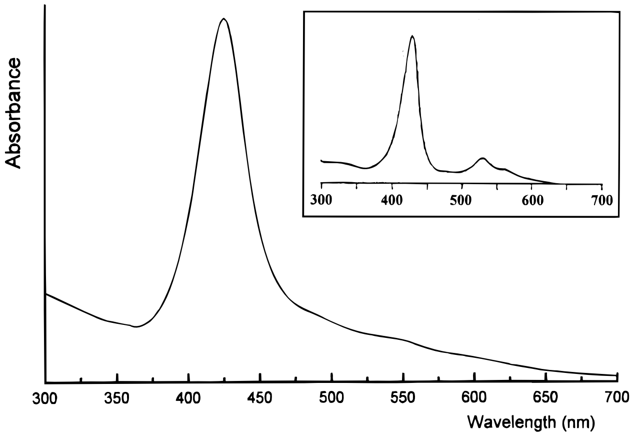

Figure 2. UV−vis spectrum of [Ru^{IV}(4-Cl-TPP)(NHNPh$_2$)$_2$] (**2c**) in chloroform. For comparison, the spectrum of [Ru^{IV}(3,4,5-MeO-TPP)(NPh$_2$)$_2$] (ref 71) in the same solvent is shown in the inset.

X-ray Crystal Structure of [Ru^{IV}(TTP)(NHNPh$_2$)$_2$] (2b). Figure 3 shows the ORTEP drawing of **2b** together with the atom-numbering scheme. The N−H hydrogen atoms of the axial hydrazido groups were not located. The Ru−NHNPh$_2$ distances (average 1.911(3) Å) and Ru−N−N angles (average 141.1(3)°) are similar to the Mo−NHNPh$_2$ distance (1.948(5) Å) and Mo−N−N angle (140.5(4)°) in [Mo^{VI}(NHNPh$_2$)(NNPh$_2$)(acac)Cl$_2$],[35] respectively. With regard to the hydrazido(1−) ligands in **2b** (see Table 2), the N5, N6, C49, and C55 atoms are basically coplanar, along with the N7, N8, C61, and C67 atoms; the N−N bonds (average 1.280(4) Å) are appreciably shorter than the corresponding bond in [Mo^{VI}(NHNPh$_2$)(NNPh$_2$)(acac)Cl$_2$] (1.359(6) Å)[35] but fall in the range of 1.236(19) to 1.47(2) Å, found for such bonds in the reported hydrazido(1−) complexes.[11−46]

The orientations of the hydrazido(1−) axial ligands in **2b** with respect to the porphyrin macrocycle are depicted in Figure 4. Evidently, the NPh$_2$ moieties of the hydrazido groups both

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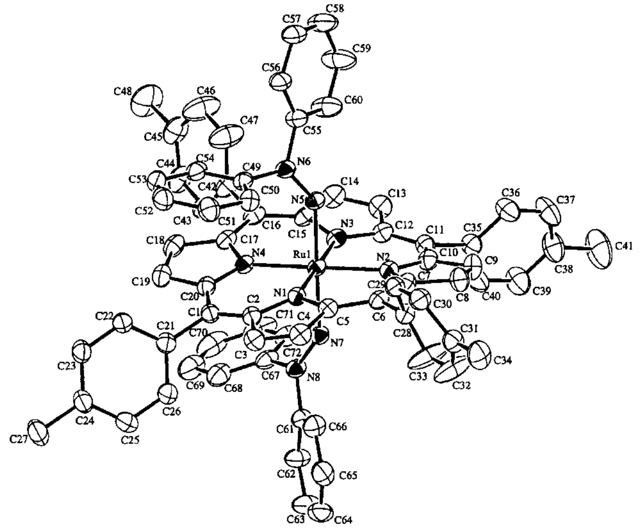

Figure 3. ORTEP drawing of [$Ru^{IV}(TTP)(NHNPh_2)_2$] (**2b**) with atomic numbering scheme (25% probability ellipsoids). Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [$Ru^{IV}(TTP)(NHNPh_2)_2$] (**2b**)

	bond distance (Å)		
Ru1−N1	2.060(3)	Ru1−N2	2.053(3)
Ru1−N3	2.056(3)	Ru1−N4	2.049(3)
Ru1−N5	1.907(3)	Ru1−N7	1.915(3)
N5−N6	1.277(4)	N7−N8	1.283(4)
N6−C49	1.454(5)	N6−C55	1.449(5)
N8−C61	1.452(5)	N8−C67	1.449(5)
	bond angle (deg)		
		N5−Ru1−N7	178.6(1)
Ru1−N5−N6	140.5(3)	Ru1−N7−N8	141.7(3)
N5−N6−C49	124.2(3)	N5−N6−C55	116.6(4)
N7−N8−C61	117.1(3)	N7−N8−C67	124.1(3)
N1−Ru1−N2	90.5(1)	N1−Ru1−N4	89.6(1)
N2−Ru1−N3	89.9(1)	N3−Ru1−N4	90.0(1)
N5−Ru1−N1	97.4(1)	N5−Ru1−N2	89.9(1)
N5−Ru1−N3	82.7(1)	N5−Ru1−N4	90.1(1)
N7−Ru1−N1	81.8(1)	N7−Ru1−N2	88.9(1)
N7−Ru1−N3	98.2(1)	N7−Ru1−N4	91.1(1)

tilt toward the N4 side (Figure 4b), with N6−N5−Ru1−N4 and N8−N7−Ru1−N4 torsion angles of ~31° and 14°, respectively.

To our surprise, the porphyrin ring of **2b** *in the solid state* is significantly distorted from a planar geometry, assuming a typical *ruffled* conformation[74] (Figure 5a,b) with an average absolute displacement of as large as 0.33 Å for the C_m (mesocarbon) atoms. Comparable or even larger ruffling distortions of porphyrin rings have been observed for complexes of transition metals such as iron, cobalt, and nickel, which can almost exclusively be considered to be a result of *achieving shorter M−N(Por) bonds*[74,75] or *reducing the repulsion between the substituents on the porphyrin rings*.[76,77] However, such a large ruffling distortion of the porphyrin ring, as observed in this work, has never been reported for *ruthenium* complexes with *simple* porphyrinato ligands, namely TPP,[78−85] TTP,[86−89] TMP (*meso*-tetrakis(2,4,6-trimethylphenyl)porphyrinato dianion),[90−92] and OEP (octaethylporphyrinato dianion).[85,93−98] Almost all of these porphyrin rings are basically *planar* (the absolute displacements of their component atoms

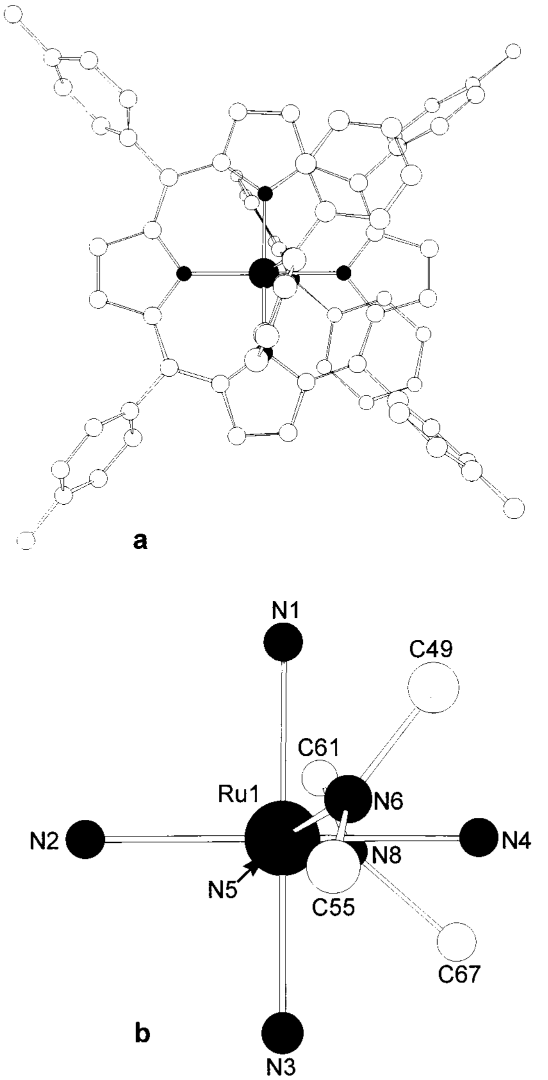

Figure 4. (a) Ball and stick drawing of [$Ru^{IV}(TTP)(NHNPh_2)_2$] (**2b**) viewed along the N5−Ru1−N7 axis showing the orientation of the hydrazido(1−) axial ligands with respect to the porphyrin macrocycle. (b) The core structure in (a).

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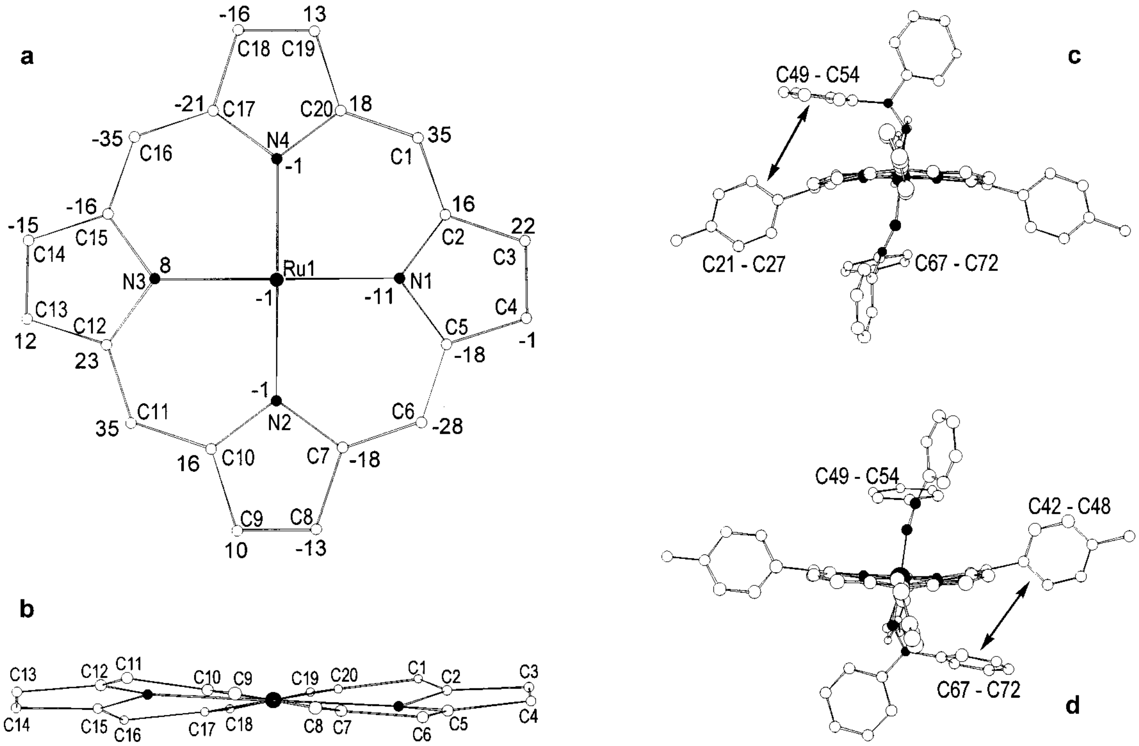

Figure 5. Ball and stick drawing of [Ru^{IV}(TTP)(NHNPh$_2$)$_2$] (**2b**) showing the significant ruffling distortion of the porphyrin ring. (a) The displacement in units of 0.01 Å of each of the component atoms together with ruthenium from the least-squares plane. (b) A view of the porphyrin ring along N2−Ru1−N4 axis. (c) and (d) Two side-views of **2b** showing the interactions between the hydrazido phenyl group and the porphyrinato tolyl group.

from the mean plane are less than 0.15 Å)[74] because all of the macrocycles have a cavity that matches ruthenium ions very well and exhibit no significant interactions between the substituents on the porphyrin rings. Therefore, the origin of the ruffled conformation in **2b** deserves attention.

Inasmuch as the mean Ru−N(Por) distance of 2.055(3) Å in **2b** falls in the range (2.048(4)−2.058(5) Å) of the corresponding distances found for other ruthenium−TTP complexes with basically planar porphyrin rings,[86−89] which indicates the absence of any significant shortening of such distances during the formation of **2b**, we attribute the above-mentioned large ruffling distortion in **2b** to the *steric effect of the axial ligands*. As is obvious from Figure 5c,d, in the crystal structure of **2b**, each hydrazido ligand has one phenyl group, that is, the phenyl group of C49 to C54 or C67 to C72, roughly parallel and rather close to the porphyrin ring. Apparently, by assuming the ruffled conformation, the porphyrinato ligand can considerably reduce its interaction with these phenyl groups in that the tolyl groups C21 to C27 and C42 to C48 both substantially tilt away from the phenyl groups C49 to C54 and C67 to C72, respectively. Note that both of the phenyl groups are right above or below the mesocarbons to which these tolyl groups are bonded (Figure 4a). Very recently, the nonplanarity of the porphyrin ring of TPP in complexes [M^{II}(TPP)(NMeIm)(CO)] (M = Fe, Ru, Os; NMeIm = 1-methylimidazole) was also ascribed to the influence of axial ligands, which, however, exclusively results in a *saddle* distortion.[99] The extent of the porphyrin ring distortion in [Ru^{II}(TPP)(NMeIm)(CO)] is appreciably smaller than in **2b**.

Summary

(1) Bis(1,1-diphenylhydrazido(1−))ruthenium(IV) porphyrins, [Ru^{IV}(Por)(NHNPh$_2$)$_2$] (Por = TPP, TTP, 4-Cl-TPP, 4-MeO-TPP), were prepared as analytically pure purple crystals in ∼60% yields by treating the corresponding dioxoruthenium(VI) porphyrins, [Ru^{VI}(Por)O$_2$], with 1,1-diphenylhydrazine in ethanol followed by a recrystallization from dichloromethane/*n*-heptane.

(2) Complexes [Ru^{IV}(Por)(NHNPh$_2$)$_2$] are diamagnetic, exhibiting an ^{1}H NMR spectrum of pseudo-D_{4h} symmetry in deuteriochloroform solutions at room temperature with H$_\beta$ chemical shifts in a narrow range of 8.29−8.34 ppm, very similar to those of previously reported diamagnetic bis(alkyl)- and bis(diphenylamido)-ruthenium(IV) porphyrins. However, their UV−vis spectra in chloroform are very unusual, featuring a prominent long tail to the red of the Soret band with the β bands barely discernible. The positive-ion FABMS of [Ru^{IV}(Por)(NHNPh$_2$)$_2$] shows the peaks attributable to their parent ions, but the most intense peaks always correspond to the fragments ascribable to [Ru(Por)N]$^+$, formed probably by the loss of an NHNPh$_2$ group and the cleavage of the HN−NPh$_2$ bond of the remaining hydrazido ligand under the mass spectrometry conditions.

(3) The crystal structure of [Ru^{IV}(TTP)(NHNPh$_2$)$_2$] has been determined. Both the hydrazido(1−) axial ligands assume an

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η^1 coordination mode. Both the average Ru−NHNPh$_2$ distance of 1.911(3) Å and the Ru−N−N angle of 141.1(3)° are similar to the previously reported Mo−NHNPh$_2$ distance and Mo−N−N angle, respectively, in [Mo^{VI}(NHNPh$_2$)(NNPh$_2$)(acac)Cl$_2$] (ref 35). Surprisingly, the porphyrin ring assumes a ruffled conformation, with the average absolute displacement of C$_m$ from the least-squares plane as large as 0.33 Å. Such a large ruffling distortion of the porphyrin ring has never been observed for ruthenium complexes bearing simple porphyrinato ligands and can be ascribed to the steric effect of the axial hydrazido(1−) ligands.

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Supporting Information Available: FABMS for the complex [Ru^{IV}(4-Cl-TTP)(NHNPh$_2$)$_2$] (**2c**). An X-ray crystallographic file in cif format for [Ru^{IV}(TTP)(NHNPh$_2$)$_2$] (**2b**). This material is available free of charge via the Internet at http://pubs.acs.org.

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