Synthesis and Axial Ligand Substitution Chemistry of Ru(TTP)(NO)X. Structures of Ru(TTP)(NO)X (X = ONO, OH)

D. Scott Bohle,* Chen-Hsiung Hung, and Bryan D. Smith

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071-3838

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New complexes of the family Ru(TTP)(NO)X, where TTP = tetra-*p*-tolylporphyrinato dianion, and X = OMe, Cl, OH, SH, S-*p*-tolyl, O_2CH, ONO, ONO_2, N_3, or NCS, have been prepared by a variety of high-yield metathesis techniques from Ru(TTP)(CO)(MeOH). New complexes have been characterized by IR, NMR, and UV spectroscopies as well as by cyclic voltammetry, elemental analysis, and, in two cases, by X-ray crystallography. The two complexes which have been characterized by single-crystal X-ray diffraction, the hydroxide and nitrite complexes **6** and **10** both crystallize in the monoclinic space group $P2_1/n$ and have $Z = 6$, with two independent metalloporphyrins in the unit cell, one (ordered) lying on a general position and the other (disordered) with the ruthenium on an inversion center. Acid labilization of the methoxide results in facile substitution kinetics at room temperature and with the exception of the sulfhydryl complex, L = SH, the resulting complexes are air stable and thermally robust species. For example, the formate derivative cannot be decarboxylated thermally or photolytically to give a hydrido complex, and the azido complex does not eliminate dinitrogen under similar conditions to give a nitrido complex.

The family of group 8 metallonitrosyls contain species which are biologically and heuristically important. On one hand the nitrosyl adducts of both heme and nonheme iron enzymes have recognized biological functions ranging from signal transduction by soluble guanylyl cyclase, sGC,[1] to the regulation of gene transcription by the *soxRS*-mediated oxidative-stress response.[2] On the other hand ruthenium has a renowned high affinity for NO,[3] and of these complexes, the cationic *cis*-dinitrosyl complex $[RuCl(NO)_2(PPh_3)_2]^+$, with both bent and linear nitrosyls, is an archetype for the relationship of MNO binding geometry to the metal's electronic structure and fluxionality.[4−7] Because of the critical biological roles of the NO/heme interaction, there is a resurgence of interest in the chemistry of iron porphyrin nitrosyls[8−12] and this has in turn rekindled interest in the corresponding ruthenium analogues.

Despite the similar organometallic chemistries of iron and ruthenium metallonitrosyls, the two metals have distinctly different bonding trends for the complexes with metals in an intermediary oxidation state and/or ones with weak ligand fields. Under these conditions the iron adducts are often paramagnetic with bent Fe−N−O geometries,[9,10] while the corresponding ruthenium complexes are typically diamagnetic with linear nitrosyls.[13−18] Perhaps the best characterized paramagnetic ruthenium nitrosyl is $[Ru(bipy)_2(NO)Cl]^+$ which is obtained from the one electron reduction of $[Ru(bipy)_2(NO)Cl]^{+2}$.[19]

At the outset of these studies only a few reports concerning nitrosyl adducts of ruthenium porphyrins had appeared in the literature,[20−23] and it was curious that substantially more was known about the family of Os(OEP)(NO)X, X = OMe^-, Cl^-, NO, F^-.[22,24,25] Since 1995 a number of papers have reported aspects of the chemistries of Ru(OEP)(NO)X,[18,26] Ru(TPP)-

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(NO)X,[14,16] and Ru(TTP)(NO)X.[13,27] Herein we describe a number of new results relating to the chemistry of Ru(TTP)(NO)X, in particular: (1) a high-yield synthesis of Ru(TTP)(NO)(OMe), **2**, directly from Ru(TTP)(CO)(MeOH), **1**; (2) the derivatization of this complex to give a series of new complexes Ru(TTP)(NO)X with X = Cl^-, OH^-, ONO^-, O_2CH^-, S(*p*-tolyl)$^-$, SH^-, NCS^-, and N_3^-; (3) the structure of two these derivatives Ru(TTP)(NO)(OH), **6**, and Ru(TTP)(NO)(ONO), **10**; and (4) spectroscopic and electrochemical characterization of this series of compounds. Some of these results have been described briefly before.[13]

Experimental Section

General experimental techniques, methods, and instruments have been described in detail in prior publications.[28] Except where noted, the new derivatives are air and water stable and can be handled without precautions in solution in the open for brief periods of time. Most are very stable in the solid state. Nitric oxide used in the following experiments was either prepared fresh from the reduction of nitrite with ferrous salts[29] or by the solid state thermal reduction of nitrite with a mixture of chromic and ferric oxide.[30] Commercial nitric oxide used in the preparation of **2** was scrubbed with potassium hydroxide pellets to remove nitrogen dioxide.[31]

Methoxide(nitrosyl)(*meso*-tetra-*p*-tolylporphyrinato)ruthenium(II), Ru(TTP)(NO)(OMe), 2. This procedure is a modification of the reductive nitrosylation reaction developed for iron porphyrins.[32,33] Ru(TTP)(CO)(MeOH), prepared by the method of Rillema *et al.*[34] (275 mg, 0.331 mmol), is added to a mixture of dichloromethane (25 mL), methanol (5 mL), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 100 μL). This solution is purged with nitrogen for 45 min, and then a stream of nitric oxide is introduced by passing it slowly through the stirred mixture at atmospheric pressure for 10 min. A color change from orange-red to brick-red is noted. To ensure complete nitrosylation, addition of nitric oxide is continued for a further 10 min. The solution is then purged with dinitrogen to remove any excess nitric oxide. Concentration of the solution on a rotary evaporator effected crystallization of the product which was obtained as air stable red-purple crystals. The crystals were filtered, washed with cold methanol and vacuum-dried, to afford **2** (242 mg, 87.9%). The isolated product is essentially pure by NMR spectroscopy, but it can be readily purified even further by recrystallization from dichloromethane/methanol. ^1H NMR (22 °C, C_6D_6, ppm): 9.16 (s, 8H, H_β), 8.10 (d, $^3J_{HH}$, 6.8 Hz, 4H, H_m), 8.00 (d, $^3J_{HH}$, 7.7 Hz, 4H, H_m), 7.24 (t, $^3J_{HH}$, 6.0 Hz, H_o, $H_{o'}$, partially obscured by C_6D_5H), 2.39 (s, 12H, *p*-CH_3), ligand −1.50 (s, 3H, OCH_3). IR (KBr, cm^{-1}): ν(NO) 1802. UV−vis (CH_2Cl_2) λ_{max} nm (log ϵ): 316 (4.32), 412 (Soret) (5.11), 556 (4.15), 594 (3.84). Elemental anal. calcd (found) for $C_{49}H_{39}N_5O_2Ru$: C, 70.83 (70.24); H, 4.73 (4.99); N, 8.43 (8.38). Crystals suitable for single-crystal X-ray diffraction are obtained by vapor phase diffusion of a hexanes/dichloromethane solution.

Chloride(nitrosyl)(*meso*-tetra-*p*-tolylporphyrinato)ruthenium(II), Ru(TTP)(NO)(Cl), 3. A round-bottom flask is charged with **2** (224.1 mg, 2.697 × 10^{-1} mmol) and methylene chloride (50 mL) and fitted with a septum. This solution is deoxygenated with a slow purge of nitrogen (20 min) at which time the purge gas is switched to HCl. A slow stream of HCl is continued for 10 min, and the reaction vessel is then swept with nitrogen to remove excess HCl. Hexanes (10 mL) are added, and the solution is concentrated on a rotary evaporator until dark purple-black microcrystals form. The crystals are collected by filtration, washed with hexanes, and dried in vacuo to yield **3** (216.3 mg, 96.0%). ^1H NMR (22 °C, C_6D_6, ppm): 9.16 (s, 8H, H_β), 8.11 (d, $^3J_{HH}$, 7.1 Hz, 4H, H_m), 7.91 (d, $^3J_{HH}$, 7.7 Hz, 4H, $H_{m'}$), (H_o and $H_{o'}$ obscured by C_6D_5H), 2.39 (s, 12H, *p*-CH_3). IR (KBr, cm^{-1}): ν(NO) 1845, 1830. UV−vis (CH_2Cl_2) λ_{max} nm (log ϵ): 322 (4.34), 414 (Soret) (5.28), 534 sh, 562 (3.94), 610 sh. Elemental anal. calcd (found) for $C_{48}H_{36}N_5OClRu$: C, 69.01 (69.00); H, 4.34 (4.48); N, 8.38 (8.34).

Formato(nitrosyl)(*meso*-tetra-*p*-tolylporphyrinato)ruthenium(II), Ru(TTP)(NO)(O_2CH), 4. To a dichloromethane (25 mL) solution of **2** (101.4 mg, 1.22 × 10^{-1} mmol) is added excess aqueous formic acid (88%, 2.1 mL, 50 mmol), and this mixture is stirred for 5 min. The crude reaction mixture is evaporated to dryness in vacuo and recrystallized from dichloromethane/hexanes. The resulting dark purple crystals were filtered, rinsed with hexanes followed by pentane, and vacuum-dried to yield **4** (68.7 mg, 66.6%). ^1H NMR (22 °C, C_6D_6, ppm): 9.17 (s, 8H, H_β), 8.09 (dd, $^3J_{HH}$, 7.6 Hz, $^4J_{HH}$, 1.9 Hz, 4H, H_m), 7.91 (dd, $^3J_{HH}$, 7.6 Hz, $^4J_{HH}$, 1.9 Hz, 4H, H_m), 7.25 (t, $^3J_{HH}$, 6.0 Hz, H_o, $H_{o'}$, partially obscured by C_6D_5H), 2.40 (s, 12H, *p*-CH_3), ligand 2.87 (s, 1H, OOC*H*). IR (KBr, cm^{-1}): ν(NO) 1837, ν_s(COO) 1661, ν_a(COO) 1228. IR (Nujol mull, cm^{-1}): ν(NO) 1839, ν_s(COO) 1662, ν_a(COO) 1228. UV−vis (CH_2Cl_2) λ_{max} nm (log ϵ): 326 (4.35), 410 (Soret) (5.31), 560 (4.13), 592 sh. Elemental anal. calcd (found) for $C_{49}H_{37}N_5O_3Ru\cdot0.5CH_2Cl_2$: C, 67.00 (67.27); H, 4.32 (4.39); N, 7.89 (8.07).

[Aquo(nitrosyl)(*meso*-tetra-*p*-tolylporphyrinato)ruthenium(II)][hexafluorophosphate], [Ru(TTP)(NO)(H_2O)][PF_6], 5. A 50 mL vessel is charged with a methylene chloride (20 mL) solution of **2** (200 mg, 2.41 × 10^{-1} mmol). To this is added aqueous HPF_6 (60 wt %, 5 drops), and the reaction mixture is stirred for 5 min. The solvent is removed in vacuo, and the remaining solid residue is placed under vacuum at 2 × 10^{-5} Torr for 24 h to remove any residual H_2O. The black-purple residue is recrystallized by taking it up into dichloromethane, diluting the solution with an equal quantity of hexane, and concentrating it on a rotoevaporator. The resulting crystallites are isolated by filtration, followed by a wash with hexanes followed by pentane, and dried in vacuo. The reaction produced **5** (189.3 mg, 82%). ^1H NMR (22 °C, C_6D_6, ppm): 9.22 (s, 8H, H_β), 8.12 (d, $^3J_{HH}$, 7.5 Hz, 4H, H_m), 8.07 (d, $^3J_{HH}$, 7.3 Hz, 4H, $H_{m?}$), 7.27 (t, $^3J_{HH}$, 8.1 Hz, H_o, $H_{o'}$, partially obscured by C_6D_5H), 2.40 (s, 12H, *p*-CH_3). The water ligand was not detected. IR (KBr, cm^{-1}): ν(NO) 1859, ρ_r(H_2O) 848, ρ_w(H_2O) 524. UV−vis (CH_2Cl_2) λ_{max} nm (log ϵ): 318 (4.36), 410 (Soret) (5.22), 562 (4.09). Elemental anal. calcd (found) for $C_{48}H_{38}N_5O_2PF_6Ru$: C, 59.87 (60.00); H, 3.98 (4.36); N, 7.27 (6.94).

Hydroxo(nitrosyl)(*meso*-tetra-*p*-tolylporphyrinato)ruthenium(II), Ru(TTP)(NO)(OH), 6. To a concentrated acetonitrile solution of **5** (52.1 mg, 5.41 × 10^{-2} mmol) is added tetra-*n*-butylammonium hydroxide (40 wt. %, 200 μL). The product, **6**, spontaneously crystallizes as brilliant red crystallites which are isolated via filtration and dried in vacuo. The reaction yielded **6** (37.3 mg, 84%). ^1H NMR (22 °C, C_6D_6, ppm): 9.16 (s, 8H, H_β), 8.11 (d, $^3J_{HH}$, 7.5 Hz, 4H, H_m), 7.94 (d, $^3J_{HH}$, 7.4 Hz, 4H, H_m), 7.24 (t, $^3J_{HH}$, 8.4 Hz, 8H, H_o, $H_{o'}$), 2.40 (s, 12H, *p*-CH_3); ligand not observed. IR (KBr, cm^{-1}): ν(NO) 1813; ν(OH) 3597; δ(RuOH) 877; ν(RuO) 570. UV−vis (CH_2Cl_2) λ_{max} nm (log ϵ): 316 (4.25), 412 (Soret) (5.05), 556 (4.18), 594 (3.86). Elemental anal. calcd (found) for $C_{48}H_{37}N_5O_2Ru$: C, 70.48 (70.39); H, 4.56 (4.62); N, 8.57 (8.52). Crystals suitable for single-crystal X-ray diffraction were obtained by vapor phase diffusion of a benzene/methanol solution. The deep brown prism selected had the dimensions 0.62 × 0.45 × 0.28 mm^3.

Sulfhydro(nitrosyl)(*meso*-tetra-*p*-tolylporphyrinato)ruthenium(II), Ru(TTP)(NO)(SH), 7. A toluene (25 mL) solution of **2** (135.5 mg, 1.631 × 10^{-1} mmol) is prepared in a Schlenk flask under an inert atmosphere of nitrogen. Gaseous H_2S is flushed through the solution, and an immediate color change from red to brick-red is observed. The solvent and excess H_2S are removed in vacuo after 10 min, and the air-sensitive product recrystallized from dichloromethane/hexane to give deep brick-red crystals of **7** in nearly quantitative yield. ^1H NMR (22 °C, $CDCl_3$, ppm): 8.99 (s, 8H, H_β), 8.16 (d, $^3J_{HH}$, 7.3 Hz, 8H, H_m, $H_{m?}$), 7.60 (d, $^3J_{HH}$, 6.7 Hz, 8H, H_o, $H_{o'}$), 2.74 (s, 12H, *p*-CH_3); ligand −6.20 (s, 1H, S*H*). IR (KBr, cm^{-1}): ν(NO) 1796, ν(SH) not observed.

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UV−vis (CH_2Cl_2) λ_{max} nm (log ϵ): 318 sh; 346 (4.44), 418 (Soret) (5.27), 576 (3.89), 612 sh. Elemental anal. calcd (found) for $C_{48}H_{37}N_5O_2Ru$: C, 70.48 (70.39); H, 4.56 (4.62); N, 8.57 (8.52).

Nitrosyl(*p*-thiocresolate)(*meso*-tetra-*p*-tolylporphyrinato)ruthenium(II), Ru(TTP)(NO)(SC_7H_7), 8. A benzene (10 mL) solution of **2** (12.7 mg, 1.53 × 10^{-2} mmol) is treated with an excess of *p*-thiocresol (21.2 mg, 1.71 × 10^{-1} mmol) for 15 min at room temperature. The reaction progress can be monitored by withdrawing aliquots of the reaction mixture and following the Soret shift from 412 to 420 nm in the UV−vis spectrum. Upon completion the solvent is removed *in vacuo*, and the vessel is connected to a diffusion-assisted vacuum line and maintained at 10^{-5} Torr for 24 h to ensure removal of all residual mercaptan. Recrystallization from dichloromethane/hexane affords dark red-purple crystals which are filtered, rinsed with hot hexanes, and vacuum-dried. This process yields **8** (10.2 mg, 72.3%). ^{1}H NMR (22 °C, C_6D_6, ppm): 9.14 (s, 8H, H_β), 8.09 (d, $^3J_{HH}$, 7.3 Hz, 4H, H_m), 8.05 (d, $^3J_{HH}$, 7.3 Hz, 4H, $H_{m'}$), 7.30 (d, $^3J_{HH}$, 7.3 Hz, 4H, H_o), 7.25 (d, $^3J_{HH}$, 7.3 Hz, 4H, H_o), 2.41 (s, 12H, *p*-CH_3); S-*p*-tolyl ligand 3.65 (d, $^3J_{HH}$, 8.5 Hz, 2H, H_o), 5.92 (d, $^3J_{HH}$, 8.5 Hz, 2H, H_p), 1.88 (s, 3H, *p*-CH_3). IR (KBr, cm^{-1}): ν(NO) 1784 s. UV−vis (C_6H_6) λ_{max} nm (log ϵ): 334 (4.41), 420 (Soret) (5.08), 510 (4.13). Elemental anal. calcd (found) for $C_{55}H_{43}N_5OSRu$: C, 71.56 (71.31); H, 4.70 (4.52); N, 7.59 (7.05).

Imidazolide(nitrosyl)(*meso*-tetra-*p*-tolylporphyrinato)ruthenium(II), Ru(TTP)(NO)(Im), 9. A small-volume sublimation apparatus is loaded with **2** (76.9 mg, 9.25 × 10^{-2} mmol), a 5-fold excess of imidazole (6.8 mg, 4.6 × 10^{-1} mmol), and a small stir bar. Oxygen is removed from the reaction chamber by repeated evacuation and backfilling with nitrogen. Under an atmosphere of nitrogen the reaction mixture is then heated to 90 °C, just above the melting point of imidazole, and maintained at this temperature with stirring for 2 h. The mixture is cooled and then evacuated, and gentle heat applied to sublime the excess unreacted HIm. Trace HIm is completely removed by placing the crude product mixture on a high-vacuum line and maintaining the pressure at 10^{-5} Torr for 24 h. Purple microcrystals are obtained after recrystallization from dichloromethane/hexanes. The product is filtered, washed with hexanes, and dried in vacuo to give **9** (53.2 mg, 66.3%). ^{1}H NMR (22 °C, C_6D_6, ppm): 9.13 (s, 8H, H_β), 8.07 (d, $^3J_{HH}$, 7.2 Hz, 4H, H_m), 7.87 (d, $^3J_{HH}$, 7.1 Hz, 4H, $H_{m'}$), (H_o and $H_{o'}$ are obscured by C_6D_5H), 2.41 (s, 12H, *p*-CH_3); imidazolide ligand 4.93 (s, 1H), 2.55 (s, 1H), 0.54 (s, 1H). IR (KBr, cm^{-1}): ν(NO) 1846 s. UV−vis (C_6H_6) λ_{max} nm (log ϵ): 298 (4.50), 412 (Soret) (5.20), 508 (4.25).

Nitrito(nitrosyl)(*meso*-tetra-*p*-tolylporphyrinato)ruthenium(II), Ru(TTP)(NO)(ONO), 10. Method a. A round-bottom flask is charged with **3** (25.1 mg, 3.00 × 10^{-2} mmol) dissolved in a 1:1 mixture of benzene and acetonitrile (20 mL), and one and a half equiv of silver nitrite (6.9 mg, 4.5 × 10^{-2} mmol) is then added with stirring. A silver chloride precipitate forms immediately, but the reaction is stirred an additional 20 min before the silver chloride is removed by passing the mixture through diatomaceous earth and washing the residue with dichloromethane. All solvents were removed in vacuo, and the residue was taken up in dichloromethane and then purified by flash chromatography on a silica gel column. The product elutes with dichloromethane as the single mobile red-purple product from immobile impurities. Recrystallization of this fraction from dichloromethane/hexane, filtration, and vacuum-drying affords **10** (15.2 mg, 60%). ^{1}H NMR (22 °C, C_6D_6, ppm): 9.15 (s, 8H, H_β), 8.10 (dd, $^3J_{HH}$, 7.7 Hz, $^4J_{HH}$, 1.8 Hz, 4H, H_m), 7.81 (dd, $^3J_{HH}$, 7.7 Hz, $^4J_{HH}$, 1.8 Hz, 4H, $H_{m'}$), 7.26 (d, $^3J_{HH}$, 7.3 Hz, 4H, H_o), 7.20 (d, $^3J_{HH}$, 7.3 Hz, 4H, $H_{o'}$), 2.38 (s, 12H, *p*-CH_3). ^{15}N NMR (22 °C, C_6D_6, 40.4 MHz, ppm): 236.6 (s, Ru−O^{15}*N*O), −26.2 (s, Ru−^{15}*N*O). IR (KBr, cm^{-1}): ν(NO) 1835 s, $\nu_s(NO_2)$ 1511 m, $\nu_a(NO_2)$ 927 m, $\delta(NO_2)$ 844 w, $\nu(^{15}NO)$ 1807 s, $\nu_s(^{15}NO_2)$ 1480 m, $\nu_a(^{15}NO_2)$ 904 m, $\delta(^{15}NO_2)$ 846 w. UV−vis (CH_2Cl_2) λ_{max} nm (log ϵ): 332 (4.25), 412 (Soret) (5.25), 558 (3.93), 600 (3.77). Elemental anal. calcd (found) for $C_{48}H_{36}N_6O_3Ru$: C, 68.15 (67.71); H, 4.29 (4.52); N, 9.93 (9.22). Crystals suitable for X-ray diffraction were grown by slow evaporation from a 1:5 dichloromethanehexanes solution. The purple-black block selected had the dimensions 1.2 × 0.6 × 0.4 mm^3.

Method b. This compound can also be obtained by treating a toluene or benzene solution of $[Ru(TTP)]_2$,[35] with excess nitric oxide under strictly anaerobic conditions. For this transformation an efficient inert atmosphere box was used during the reaction. The extremely air-sensitive $[Ru(TTP)]_2$ (40.0 mg, 2.60 × 10^{-2} mmol) is dissolved in toluene (50 mL) under nitrogen, and a stream of nitric oxide, prepared from thermal decomposition of nitrite/chromate mixtures,[29] is bubbled through the stirred solution. An instant color change from black-red to red is noted, and the solvent is removed in vacuo. At this point the spectroscopic characteristics of the product are identical to that prepared by method a, and so the product can then purified in the open as described in method a to yield **10** (38.3 mg, 87.1%).

Nitrato(nitrosyl)(*meso*-tetra-*p*-tolylyporphyrinato)ruthenium(II), Ru(TTP)(NO)(ONO_2), 11. This preparation follows the same procedure as the method for compound **10** except that silver nitrate is used. In this case chromatographic purification is not required and after filtration through diatomaceous earth, the product is recrystallized from dichloromethane/hexane to give **11** (14.9 mg, 76%). ^{1}H NMR (22 °C, C_6D_6, ppm): 9.19 (s, 8H, H_β), 8.09 (d, $^3J_{HH}$, 7.3 Hz, 4H, H_m), 7.95 (d, $^3J_{HH}$, 7.3 Hz, 4H, $H_{m'}$), 7.24 (t, $^3J_{HH}$, H_o, $H_{o'}$, partially obscured by C_6D_5H), 2.39 (s, 12H, *p*-CH_3). IR (KBr, cm^{-1}): ν(NO) 1860 s, ν(NO) 1212 m, $\nu_a(NO_2)$ 1273 s, $\nu_s(NO_2)$ 964 m. UV−vis (CH_2Cl_2) λ_{max} nm (log ϵ): 324 (4.26), 412 (Soret) (5.28), 564 (3.87), 605 sh. Elemental anal. calcd (found) for $C_{48}H_{36}N_6O_4Ru$: C, 66.89 (66.24); H, 4.21 (4.52); N, 9.75 (9.52).

Azido(nitrosyl)(*meso*-tetra-*p*-tolylporphyrinato)ruthenium(II), Ru(TTP)(NO)(N_3), 12. A 50 mL flask is charged with a dichloromethane (20 mL) solution of **3** (19.5 mg, 2.33 × 10^{-2} mmol). To this is added trimethylsilyl azide (Me_3SiN_3) (∼0.2 mL), and the reaction mixture is stirred for 10 min. The solvent is removed under reduced pressure, and the solid residue is placed under vacuum at 2 × 10^{-5} Torr for 24 h to remove any unreacted Me_3SiN_3 as well as any Me_3SiCl formed during the reaction. All recovered products are taken up in dichloromethane and then recrystallized with hexanes to give black-purple crystals which were isolated via filtration and rinsing with hexanes followed by pentane to yield **12** (15.8 mg, 80.2%). ^{1}H NMR (22 °C, CD_2Cl_2, ppm): 9.03 (s, 8H, H_β), 8.14 (dd, $^3J_{HH}$, 8.2 Hz, $^4J_{HH}$, 1.3 Hz, 8H, H_m, $H_{m?}$), 7.60 (d, $^3J_{HH}$, 7.9 Hz, 8H, H_o, $H_{o'}$), 2.71 (s, 12H, *p*-CH_3). IR (KBr, cm^{-1}): ν(NO) 1821, ν_a(NNN) 2048, ν_s(NNN) 1291. UV−vis (CH_2Cl_2) λ_{max} nm (log ϵ): 332 (4.27), 414 (Soret) (5.26), 568 (3.84), 604 sh.

Isothiocyanato(nitrosyl)(*meso*-tetra-*p*-tolylporphyrinato)ruthenium(II), Ru(TTP)(NO)(NCS), 13. A 100 mL flask is fitted with a Vigreaux condenser in the inert atmosphere box and loaded with toluene (30 mL), **3** (62.1 mg, 7.43 × 10^{-2} mmol) and trimethylsilylisothiocyanate (Me_3SiNCS) (1 mL, 7.09 mmol). The reaction mixture is heated to reflux for 20 min with stirring. Cooling the solution to room temperature and removing the solvent in vacuo resulted in a solid residue which is recrystallized from dichloromethane/hexane to give black-red crystals which are collected by filtration and rinsed with pentane to yield **13** (62.6 mg, 98.1%). ^{1}H NMR (22 °C, CD_2Cl_2, ppm): 9.09 (s, 8H, H_β), 8.16 (d, $^3J_{HH}$, 8.1 Hz, 8H, H_m, $H_{m?}$), 7.63 (dd, $^3J_{HH}$, 8.2 Hz, $^4J_{HH}$, 0.6 Hz, 4H, H_o, $H_{o?}$), 2.73 (s, 12H, *p*-CH_3). IR (KBr, cm^{-1}): ν(NO), 1847, ν(CN) 2026 cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} nm (log ϵ): 322 (4.37), 414 (Soret) (5.31), 570 (3.81), 610 sh. Elemental anal. calcd (found) for $C_{49}H_{36}N_6OSRu$: C, 68.59 (69.37); H, 4.23 (4.44); N, 9.79 (9.55).

Single-Crystal X-ray Structure Determinations. Single-crystal X-ray data were collected on a Siemens P3 diffractometer equipped with a molybdenum tube [$\lambda(K\alpha) = 0.710\,73$ Å] and a highly oriented graphite crystal monochromator. Crystal quality was monitored throughout the data collection by measuring the intensities of three standard reflections after every 100 reflections were collected. The structures were solved by a combination of Patterson synthesis and direct methods and subsequently refined by full-matrix least-squares techniques, using the Siemens SHELXTL IRIS[36] system of programs.

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Table 1. Crystallographic Data and Refinement Parameters

	6	**10**
empirical formula	$C_{48}H_{37}N_5O_2Ru$	$C_{48}H_{36}N_6O_3Ru$
mass (g mol^{-1})	816.9	845.9
color; habit	brown; block	black-purple; prism
crystal size (mm)	0.62 × 0.45 × 0.28	1.2 × 0.6 × 0.4
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	11.322(2)	11.469(2)
b (Å)	26.781(5)	27.465(5)
c (Å)	19.355(4)	19.363(4)
β (deg)	92.98(3)	93.10(3)
volume (Å^3)	5860.7(23)	6090(2)
Z	6	6
density$_{calcd}$ (Mg m^{-3})	1.389	1.384
μ (mm^{-1})	0.448	0.436
2θ range (deg)	4.08 to 45.00	4.0 to 50.0
index ranges h	$0 \leq h \leq 12$	$0 \leq h \leq 13$
k	$-28 \leq k \leq 0$	$0 \leq k \leq 32$
l	$-20 \leq l \leq 20$	$-23 \leq l \leq 22$
no. of obsd reflcns	4987 ($F > 6.0\sigma(F)$)	7186 ($F > 4.0\sigma(F)$)
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0008F^2$	$w^{-1} = \sigma^2(F) + 0.0078F^2$
final R (obsd)	$R = 0.053$, $R_w = 0.120$	$R = 0.064$, $R_w = 0.108$
goodness-of-fit	1.03	1.07
data-to-parameter ratio	10.05:1	9.0:1
largest diff peak (e Å^{-3})	0.65	0.81
largest diff hole (e Å^{-3})	−0.37	−0.99

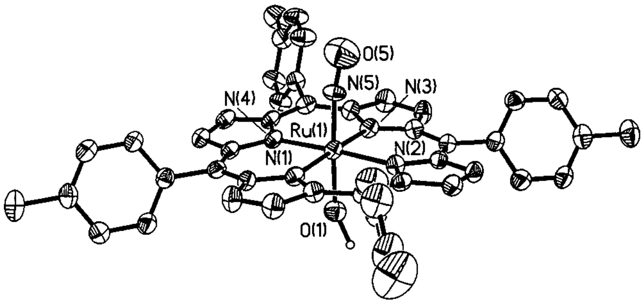

Figure 1.

Table 1 contains crystallographic parameters relating to the data collection and refinement.

Both **6** and **10** crystallized in the centrosymmetric monoclinic space group $P2_1/n$, $Z = 6$ with two independent molecules per unit cell. Molecule A has a ruthenium located at a general position, while the ruthenium atom of molecule B is at an inversion center. This inversion center generates half of a molecule B from symmetry. Coordinates for the disordered axial ligands of molecule B were calculated from the bond lengths and bond angles found in the ordered molecule A and were fixed during the final refinement. The ORTEP representation of **6,** Figure 1, depicts a nitrosyl that is bound to ruthenium in a nearly linear fashion with a Ru(1)−N(5)−O(5) bond angle of 167.4(6)°. Table 2 presents important bond lengths and angles. Bond distances and angles for the nitrosyl ligands are typical for Ru(II) complexes, but the oxygen atom of the nitrosyl group has a larger degree of thermal motion and as a consequence bond lengths and angles involving the nitrosyl ligand have higher standard deviations. Overall, both systems display a slight S_4-ruffling distortion, with the ruthenium displaced 0.0536 and 0.13 Å, in **6** and **10**, respectively, from the porphyrin plane as defined by the 24 core porphyrin ring atoms. In both cases the metal is displaced toward the nitrosyl ligand. While this distortion is commonly observed among first row transition metal porphyrin compounds, it has not been documented as frequently for ruthenium porphyrin complexes. While the causal forces which induce porphyrin ring distortion are still a matter of debate, a recent report by Munro and Scheidt *et al.*[37] demonstrates that nonbonding steric repulsion between axial ligands and porphyrin *meso*-position aryl groups dominates the S_4-ruffling of the porphyrin ring in six-coordinate low-spin iron complexes. This distortion is also commonly observed in the structures of five-coordinate metalloporphyrins possessing a strong π-accepting ligand in the axial position.[8] Porphyrin ring distortion in ruthenium compounds is probably not well recognized due to the general scarcity of structural data available for ruthenium porphyrin complexes, and their largely low-spin diamagnetic behavior. Owing to the small size of the axial ligands in this instance, the steric repulsion between axial ligands and porphyrin tolyl groups is small to negligible, and therefore electronic effects probably best rationalize the observed S_4-ruffling. Similar distortions in a pair of ruthenium octaethylporphyrin nitrosyl complexes have recently been described.[26]

Results and Discussion

The synthetic pathways for all new compounds are organized in Scheme 1. Since all compounds are ultimately prepared from Ru(TTP)(NO)(OMe), **2**, it represents a useful synthon akin to Ru(TTP(CO)L, the initial metallation product from $TTPH_2$ and $Ru_3(CO)_{12}$. Perhaps equally useful is Ru(TTP)(NO)Cl, **3**, which can be prepared in high yield from **2**, or alternatively directly from **1** with the use of nitrosyl chloride.[15] It is difficult to decarbonylate **1** with the two most useful methods being exhaustive UV-photolysis in the presence of excess ligand, often as solvent, to give Ru(por)L_2,[22,38−40] or by oxidation with peracids or halogens to give ruthenium(IV) complexes.[41,42]

In the preparation of **2** it is remarkable that NO readily substitutes for the carbon monoxide in **1** at room temperature. This reaction is complicated in that the final complex has an $\{RuNO\}^6$ structure, which most likely stems from one electron oxidation of a $\{RuNO\}^7$ intermediate. Thus electron transfer from the putative Ru(TTP)(NO)L intermediate gives a $[Ru(TTP)(NO)L]^+$ species which is then trapped with methoxide

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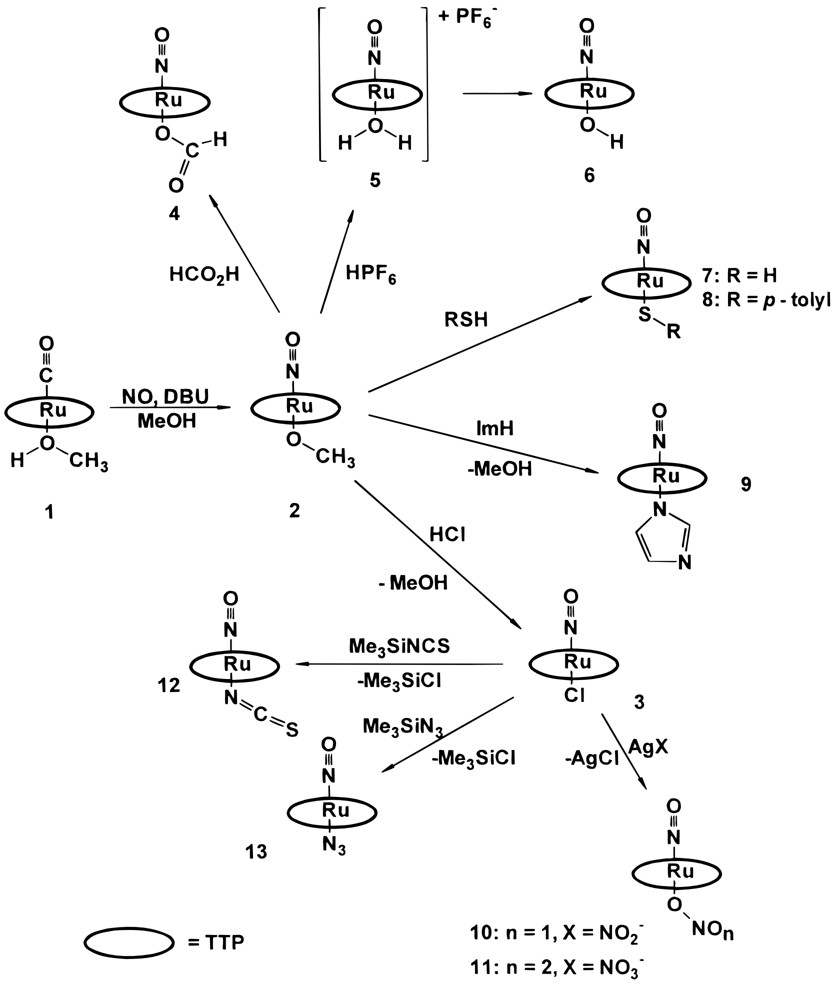
Table 2. Metrical Parameters for the Ru(TTP)(NO)X, X = OH, 6, and X = ONO, **10**[a]

6			**10**	
		For the Nitrosyl Ligand		
Ru(1)−N(5)	1.751(5)	Ru−NO (Å)	Ru(1)−N(1)	1.752(6)
N(5)−O(5)	1.142(8)	RuN−O (Å)	N(1)−O(1)	1.152(9)
Ru(1)−N(5)-O(5)	167.4(6)	Ru−N−O (deg)	Ru(1)−N(1)-O(1)	173.3(6)
		For the Axial X Ligand		
Ru(1)−O(1)	1.943(5)	Ru−O (Å)	Ru(1)−O(3)	1.998(6)
		RuO−N (Å)	O(3)−N(2)	1.148(18)
		RuON−O (Å)	N(2)−O(2)[b]	1.126(25)
		Ru−O−NO (deg)	Ru(1)−O(3)-N(2)[b]	124.0(11)
		RuO−N−O (deg)	O(3)−N(2)-O(2)[b]	110.9(20)
N(5)−Ru(1)-O(1)	177.0(2)	ON−Ru−OE (deg)	N(1)−Ru(1)-O(3)	176.4(3)
		For the Porphyrin		
Ru(1)−$N_{pyrrole}$	2.055(5)	mean Ru−$N_{pyrrole}$ (Å)	Ru(1)−$N_{pyrrole}$	2.053(6)

[a] Values listed for the ordered molecule, **A**, which lies on a general position in the unit cell. [b] Values for the major nitrite orientation given only.

Scheme 1



to give **2**. Without the addition of base or alcohol to the reaction mixture the product contains variable quantities of diamagnetic complexes Ru(TTP)(NO)X with X = $^{-}$OH and $^{-}$ONO being the predominant species by ^{1}H NMR spectroscopy. The formation of nitrite suggests a possible metal catalyzed disproportionation of NO to give NO_2 and N_2O, and an elegant recent study has demonstrated that nitrous oxide is produced in the reaction of Ru(OEP)(CO)(ROH) with nitric oxide.[14] Similar products have been characterized in the alcohol free reaction of Ru(TPP)(CO) with NO.[16] The position of the ν(NO) stretch in the IR suggests that the nitric oxide adopts a linear conformation in this complex,[43] and this has been confirmed by X-ray crystallography.[13]

In analogy to the reactivity of Ru(porphyrin)(CO)(MeOH), which undergoes rapid ligand substitution of methanol by a wide range of neutral two electron donor ligands,[44] the methoxide ligand in **2** is rapidly substituted by HX {HX = HCl, HO_2CH,

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HPF_6, H_2S, HS(*p*-tolyl), HIm} to give derivatives **3**−**5** and **7**−**9**, respectively (Scheme 1). In general, axial ligand substitution under basic conditions is very slow and even strongly nucleophilic ligands, for example, ones which might pass through an associative transition state involving a bent nitrosyl, exhibit slow rates of reaction. The tentative conclusion from this observation and the acid promoted substitution noted above is that ligand substitution pathways for Ru(TTP)(NO)X are predominately dissociative. This conclusion must of course be considered tentative until more definitive kinetic studies on these and related systems have been performed.

The formate derivative **4**, prepared by treating **2** with formic acid, is a remarkably stable dark purple crystalline product which could not be successfully decarboxylated to give a putative Ru(TTP)(NO)H, eq 1. Solution thermolysis of a toluene-d_8

$$\underset{\mathbf{4}}{\mathrm{Ru(TTP)(NO)\{OC(O)H\}}} \not\xrightarrow[-\,\mathrm{CO_2}]{\Delta \text{ or } h\nu} \mathrm{Ru(TTP)(NO)H} \qquad (1)$$

solution of **4** at 100 °C for 42 h resulted in no observable decomposition between 1, 3, or 6 h; however, complete decomposition had occurred by 42 h. Another attempt employed the use of vacuum pyrolysis at 10^{-4} Torr on a lyophilized solid sample of **4** at 140 °C; again, by the time any reactivity was noted, there was concurrent decomposition. Irradiating with a glass-filtered medium pressure mercury lamp to affect decarboxylation photolytically also resulted in decomposition. It is of course possible that Ru(TTP)(NO)H may be a transient intermediate in these decomposition reactions, but the known large high-field shifts of the hydride resonance in the proton NMR for Ru(porphyrin)(H) species[45,46] means that these types of species are relatively easily detected if they are present in any appreciable quantity. A key feature of metal mediated formate decarboxylation is the availability of a vacant coordination site to promote the β-migration reaction.[47,48] The IR results for **4** are clearly consistent with *monohapto* coordination of the formate, or coordinative saturation of the metal, and once again the observed reactivity suggests that an associative seven-coordinate intermediate, which would most likely require a linear to bent nitrosyl interconversion, is not energetically accessible. Treating **3** with lithium triethylborohydride in THF failed to generate hydride-containing species as determined by ^{1}H NMR.

A Ru(TTP)(NO)X complex where X is a weakly coordinating anion was sought as another approach to preparing axially substituted complexes. To this end, a methylene chloride solution of **2** was treated with aqueous hexafluorophosphoric acid. The expected product, Ru(TTP)(NO)(PF_6), was not realized; instead, [Ru(TTP)(NO)(OH_2)]PF_6, **5**, was generated. Efforts to remove the ligated water, including placement under high vacuum at 2×10^{-5} Torr at 110 °C for 24 h, proved futile. Ligation of the water was confirmed by IR with rocking and wagging modes observed at 848 and 524 cm,$^{-1}$ respectively.[49] Although the water protons were not observed in the ^{1}H NMR, the elemental analysis was consistent with the formulation [Ru(TTP)(NO)(H_2O)][PF_6]. A similar complex, with similar spectroscopic characteristics, forms from the addition of nitrosonium tetrafluoroborate to Ru(TPP)(CO).[16,17] In these latter results the ν(NO) modes are at 1853 and 1872 cm^{-1} for the OEP and TPP analogues, respectively, which agree with a ν(NO) stretching frequency of 1859 cm^{-1} observed for complex **5**. When **5** was treated with bases such as pyridine, the water is rapidly deprotonated rather than substituted and the neutral hydroxide complex Ru(TTP)(NO)(OH), **6**, forms in quantitative yield. The most efficacious method to prepare **6** is by treating a concentrated acetonitrile solution of **5** with a slight excess of aqueous tetra-*n*-butylammonium hydroxide. The presence of a hydroxide ligand was confirmed by IR, elemental analysis, and X-ray crystallography, see below.

In a similar vein, when a toluene solution of **2** is exposed to hydrogen sulfide gas, there is an immediate reaction to produce Ru(TTP)(NO)(SH), **7**, quantitatively. Because of their multiple redox and ligation possibilities only a few well-defined mononuclear compounds containing a terminal HS ligand have been reported.[50,51] Although the ν(SH) band was broad and weak in the IR spectrum of **7**, the −SH proton was observed in the ^{1}H NMR spectrum at −6.20 ppm. This shift is consistent with both the presence of a coordinated hydrosulfide ligand, in that these ligands often have large high-field chemical shifts, as well as an additional contribution to the upfield shift due to the porphyrin ring current. In solution the hydrosulfide complex **7** is extremely oxygen sensitive and rapidly gives a complex mixture of products, including the hydroxide complex **6**, upon exposure to air. Similar IR spectroscopic and reactivity patterns were found for the five-coordinate low-spin iron porphyrin complex Fe(TPPOMe)(SH).[50]

Treatment of a benzene solution of **2** with an excess of *p*-thiocresol rapidly affords **8** in 72% yield. The mercaptide complex is a second row model for the active metal site in nitric oxide adducts of the heme-proteins cytochrome P-450 and nitric oxide synthase.[52,53] Although Fe(porphyrin)(NO)(X) analogues to those described herein have been reported for high-field ligands such as methyl and phenyl,[54,55] the corresponding mercaptides have not been documented. This may be due, in part, to the intrinsic instability of the mercaptide adducts of the ferric porphyrins, which tend to undergo facile autoxidation and reductive elimination of disulfide.[56,57] In contrast, **8** is thermally stable to prolonged thermolysis at 180 °C and ligand displacement at reflux in neat pyridine. Finally, the pronounced thermal stability is in contrast with the corresponding high-valent mercaptides such as Os(IV)(TTP)$(SR)_2$ {R = 2,3,5,6-tetrafluorophenyl, 4-methylphenyl, 2-methylphenyl, 2,6-dimethylphenyl}, which readily eliminate disulfide under these conditions.[58] A recent series of elegant studies have described the

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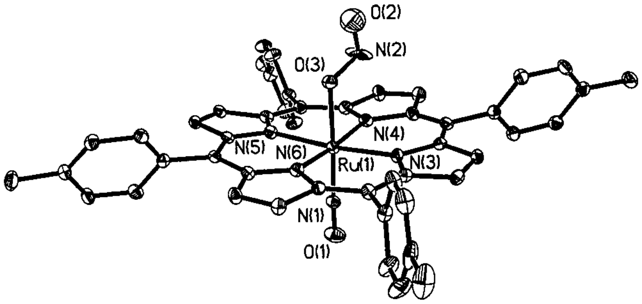

Figure 2.

chemistry of Ru(por)(NO)(SR) which are readily prepared by addition of RSNO to Ru(por)(CO).[17,18,26,59]

The chloride derivative **3** is readily prepared in high purity on large scales by treating **2** with anhydrous hydrochloric acid. Not only does this facile access make **3** an ideal synthon, but it is also remarkably air and thermally stable (decomposition point 480 °C by DSC), and undergoes a range of metathesis reactions to give Ru(TTP)(NO)X (X = NO_2^-, NO_3^-, N_3^-, and NCS^- to form compounds **9**−**13**. Treatment of a benzene/acetonitrile solution of **3** at reflux with excess $AgNO_2$ in the presence of ambient oxygen produces **10** in 60% yield. This compound is formulated as containing an oxygen-bound (nitrito) ligand on the basis of its spectroscopic and structural data. In the IR spectrum of **10** there is a large difference, 584 cm^{-1}, between the $\nu_s(NO_2)$ mode and the $\nu_a(NO_2)$ modes, indicative of a η^1-ONO nitrito configuration.[60] The ^{15}N NMR spectrum exhibits two resonances at 236.6 and −26.2 ppm which are assigned to a downfield-shifted nitrite with a bent ligand geometry and a linear nitrosyl, respectively.[61] Single-crystal X-ray diffraction confirms that the M−O−N=O unit adopts a trans configuration, Figure 2. The nitrosyl−nitrito complex **10** also results from a disproportionation reaction which occurs when the metal−metal bonded dimeric complex $[Ru(TTP)]_2$ is treated with nitric oxide at room temperature under rigorously oxygen-free conditions, eq 2. The formation of N_2O has not been demonstrated in the course of this research, however it has been demonstrated to be present in the nitrosylation of Ru(TPP)(CO)L.[14]

$$[\mathrm{Ru(TTP)}]_2 \xrightarrow{\mathrm{NO_{(excess)}}} \underset{\mathbf{10}}{2\mathrm{Ru(TTP)(NO)(ONO)}} + 2\mathrm{N_2O} \qquad (2)$$

A bisnitrosyl complex, which was the anticipated product, is ruled out by the presence of two well-separated $\nu(NO_2)$ stretches in the IR and the lack of a downfield peak in the ^{15}N NMR between 350 and 850 ppm, which would correlate to a bent nitrosyl ligand. Similar conclusions have been reached by other groups working with related complexes Ru(Por)(NO)(ONO) {Por = TPP, OEP}.[14,16] Although a variety of complexes promote nitric oxide disproportionation,[62] proposed mechanisms usually invoke a metal-mediated coupling of two cis nitrosyl ligands.[63] The cis coordination of two nitrosyl ligands is, however, very unlikely for ruthenium metalloporphyrin complexes and the mechanism for the transformation illustrated in eq 2 may involve a direct attack of nitric oxide on a bent nitrosyl ligand in an intermediate such as $[Ru(TTP)(NO)_2]^*$.[64] Similar chemistry and products have been found for the nitrosylation of a ruthenium(salen) system,[65] and a related mechanism has been proposed for the reaction between Fe(TTP)(NO) and nitric oxide. In this later case the product, formulated as an N-bound nitro complex, was stable only in solution in the presence of excess nitric oxide and was not isolable.[66]

The nitrosyl nitrito complex, **10**, crystallized in the monoclinic space group $P2_1/n$ with $Z = 6$, and with two independent molecules per unit cell. Molecule **A** is located at a general position making all of its atoms unique, while molecule **B** has its ruthenium located on an inversion center, thereby leading to axial ligand disorder within the ONO−Ru−NO fragment and thus preventing a meaningful discussion of its axial bond lengths for molecule **B**. In the final refinement the disordered axial ligand fragment in **B** was modeled on that in **A** with only the thermal parameters for the axial atoms being refined. In the discussion which follows the metric parameters all refer to those refined for molecule **A**. An ORTEP representation of the molecular structure of **A**, Figure 2, illustrates that the nitrite has a trans O-bound geometry which is trans to a slightly bent "linear" nitrosyl (Figure 2). The Ru is 0.13 Å out of the plane, defined by the porphyrin ring, toward the nitrosyl ligand. The nitrito entity is bent in the direction of a methine carbon bearing a *p*-tolyl ring, which is a typical conformation found for other axial ligands in group 8 metalloporphyrins.[67] A dinitrosyl species was ruled out during refinement, and the nitrite ligand was slightly disordered, with N2 being partitioned 0.71/0.29, over two orthogonal positions. For both nitrite orientations the oxygen atoms O(2) and O(3) share common locations. Figure S4 in the Supporting Information shows this disorder. Important bond lengths and angles of molecule **A** are summarized in Table 2. The nitrosyl ligand is bound in a nearly linear fashion as indicated by a Ru(1)−N(1)−O(1) bond angle of 173.3(6)° and bond lengths of Ru(1)−N(1) and N(1)−O(1) being 1.752(6) and 1.152(9) Å, respectively. The mean Ru(1)−N(pyrrole) bond distance is 2.053(6) Å. The Ru(1)−O(3) distance is 1.998(6) Å, and the O(3)−N(2)−O(2) bond angle is 110.9(20)°, consistent with an O-bound nitrito.[68] The core porphyrin ring exhibits a slight S_4-ruffling type distortion, Figure 3.

Me_3SiX reagents, which are useful for double displacement transformations, readily react with **3** to give volatile Me_3SiCl as a side-product and Ru(TTP)(NO)(X). For example, when a dichloromethane solution of **3** is combined with Me_3SiN_3, the resulting reaction rapidly affords **12** in 80% yield, eq 3.

$$\mathrm{Ru(TTP)(NO)Cl} \xrightarrow{\mathrm{Me_3SiX}} \mathrm{Ru(TTP)(NO)X} + \mathrm{Me_3SiCl} \qquad (3)$$

$$\mathbf{12},\ \mathrm{X} = \mathrm{N_3}^-$$

$$\mathbf{13},\ \mathrm{X} = \mathrm{SCN}^-$$

Although repeated elemental analysis of **12** indicated loss of N_2 during the combustion analysis, the spectroscopic evidence gives compelling evidence that the product of this reaction has a coordinated azide. For example, only one β-pyrrolic peak is observed in the ^1H NMR spectrum, so there is just a single

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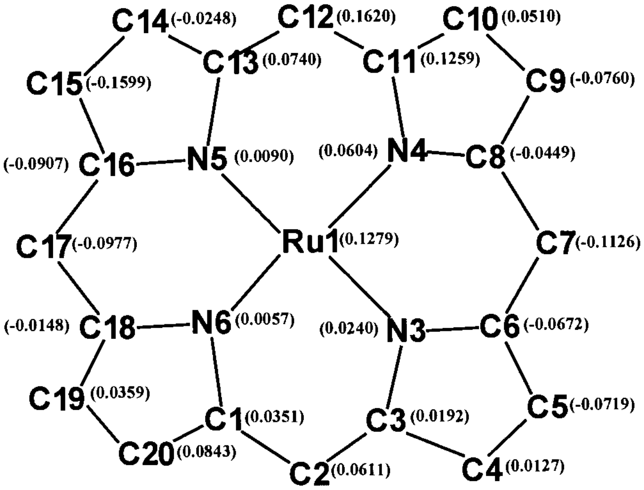

Figure 3.

diamagnetic metalloporphyrin present, and the IR spectrum exhibits two absorptions consistent with ν_a(NNN) and ν_{as}(NNN) modes at 2048 and 1291 cm,$^{-1}$ respectively.[49] Azide ligands are known to photolytically and/or thermally release dinitrogen to leave a coordinated nitride behind.[69] Both photolytic (irradiation with a medium-pressure mercury lamp for 20 min) and thermal (350 °C at 3×10^{-6} Torr for 16 h) attempts were made to produce a nitride complex but these conditions resulted in the simultaneous release of the NO ligand and the production of an inseparable mixture (by thin-layer chromatography) of ^{1}H NMR silent compounds.

Excess trimethylsilylisothiocyanate reacts with **3** under moderate thermal conditions to quantitatively give Ru(TTP)(NO)(NCS), **13**. Despite the thiophilic nature of ruthenium, the isothiocyanate complex, with a Ru−NCS bond, was formed rather than the intuitively more stable thiocyanate, Ru−SCN, configuration. This assignment is based on the IR spectrum which exhibits a ν(CN) mode at 2026 cm^{-1}. If the ligand were bound through the sulfur atom, then the ν(CN) stretching frequency is expected to at higher energy $\geq$2100 cm^{-1}.[70] There are two features of this system which favor the ligation of NCS$^-$ through the harder nitrogen atom instead of the softer sulfur atom by the normally soft ruthenium metal center. First, NO is so effective at removing electron density from the metal center that in this environment ruthenium is more accurately described as a hard metal center. Second, the ligation geometry may be kinetically controlled by elimination reactions from the intermediates generated from the complex and Me_3SiNCS.

The spectroscopic characterization of this family of Ru(TTP)(NO)X compounds allows for some insight into the electronic interaction between the axial ligand and the [Ru(TTP)(NO)]$^+$ fragment. Although there are many review articles written about nitrosyl complexes,[71−76] and these all address the hazards of overinterpreting the ν(NO) stretching energies, it is interesting to note that in dichloromethane solution at room temperature this new family of compounds has decreasing ν(NO) bands in the following order: NO_3^-, H_2O(cation) > NCS$^-$, Im$^-$, Cl$^-$ > OC(O)H$^-$,ONO$^-$ > NSO$^-$ > N_3^- > OH$^-$ > OMe$^-$ > SH$^-$ > SR$^-$ (R = *p*-tolyl). There appears to be a direct correlation between the energy of the ν(NO) mode and the relative donor ability of the trans ligand for this series of compounds: as the donor ability of the trans ligand increases there is a decrease in the ν(NO) energy consistent with increased NO π* orbital population. The wide 75 cm^{-1} range of ν(NO) stretching frequencies for this family of derivatives has a high value of 1860 cm^{-1}, trans to ONO_2^-, to a low energy of 1784 cm^{-1}, trans to S-*p*-tolyl$^-$.

Table 3. Electrochemical Data for Key New Compounds[a]

complex	trans X	1st oxidation[b]	2nd oxidation[b]	reduction[c]
2	OMe$^-$	1221(124)	1521(116)	−889
3	Cl$^-$	1021(126)	1489(120)	−789
4	HC(O)O$^-$	1150(6)	1518(82)	−789
5	H_2O	1103(68)	1531(78)	−816
6	OH$^-$	1229(82)	1532(87)	−876
7	SH$^-$	1235(119)	1542(134)	−978
10	ONO$^-$	1150(68)	1333(86)	−989
11	ONO_2^-	1094(80)	1530(56)	−852
13	NCS$^-$	1051(74)	1520(98)	−857

[a] Measured by cyclic voltammetry in dichloromethane with 0.1 M $N(^nBu)_4PF_6$ as backing electrolyte, with a platinum button electrode and a silver/silver chloride reference electrode. Potentials are reported in mV with respect to an internal ferrocene standard. Peak separation for reversible processes reported in parentheses for scan speed of 100 mV/s. [b] The two reversible porphyrin observed for the oxidation couples. [c] The reduction process are usually quasireversible unless otherwise noted.

On the other hand the electronic absorption spectra of this family of Ru(TTP)(NO)X have markedly little variation. Ligand identity of X for the various Ru(TTP)(NO)(X) complexes has a minimal effect on the positions and intensities of either the *Q* or the Soret bands. Of the complexes measured the two mercaptide ligands exhibit the largest variation in both Soret and *Q* band positions. These trends are in accordance with the series of Ru(Por)(NO)(X) {Por = TPP, OEP; X = ONO$^-$, OH$^-$}[14] and Ru(TPP)(CO)(L) {L = vacant, EtOH, Me_2SO, pyridine, piperidine} compounds.[77] Overall, the lack of variation in the electronic absorption spectra for these compounds is attributable to the dominance of the strong π-accepting ligand, either the nitrosyl or carbonyl, on the axial ligand-ruthenium interaction.

There is also surprising little variation in the electrochemical properties of this class of complexes. The cyclic voltammetry results for **2**−**13** are collected in Table 3. They are uniformly described as having one quasireversible reduction and two reversible oxidation couples for compounds in dichloromethane on a platinum button working electrode. Meyer et al. have used spectroelectrochemistry to determine that in the presence of a good π-acid ligand such as carbonyl, the first two oxidations are porphyrin based,[78] and we also assign the two oxidations observed for Ru(TTP)(NO)X as arising from two one electron oxidations of the porphyrin ring. Once again there is very little variation in the two oxidation potentials as a function of the axial ligand X. Examination of the data concurs with the results obtained by electronic spectroscopy; the trans ligand has a minimal effect on the electronic interactions in this series of compounds. Just 214 mV separate the high and low potentials for the first oxidation couple, and the second oxidation couple has a range of only 53 mV if compound **10** is excluded. On the other hand the quasireversible reduction potentials can

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involve a number of sites, and the lack of reversibility found for many of these species, as well as the large range associated for this reduction, ca. 200 mV, may be due to the variation in X, where electron transfer is followed by a variable slow loss of X^-. Alternatively, electron transfer could lead to nitrosyl bending and the formation of a $\{RuNO\}^7$ fragment. In certain cases other product waves and irreversible processes are observed. Specifically, compounds **6** and **7** exhibit an irreversible oxidation process and the subsequent product waves. For **6** these are observed at 1001 and −322 mV, respectively, while the cyclic voltammogram for **7** displays analogous processes at 907 and −370 mV. Compound **3** has two similar features in its voltammogram; there are two irreversible oxidation events at 999 and 1857 mV and two irreversible reduction processes at −375 and −1313 mV, respectively. A quasireversible product couple is observed for **13**, $E_{1/2} = 1210$ mV with a peak separation of 53 mV.

Interestingly, the cyclic voltammograms for **5** and **10** are less complicated than the data for the closely related complexes [Ru(TPP)(NO)(H_2O)][BF_4] and Ru(TPP)(NO)(ONO) {TPP = *meso*-tetraphenylporphyrinato dianion}.[16] In this case one reversible, $E_{1/2} = -1050$ mV, and two irreversible reduction, $E = -330$ and −780 mV, couples were observed for the aquo complex; we observe a single quasireversible process, $E = -816$ mV, for **5** with PF_6^- as counterion. In addition, the electrochemistry of the TPP derivative also has three reduction processes for Ru(TPP)(NO)(ONO) compared to just one that we observe for Ru(TTP)(NO)(ONO). It is surprising that there are such dramatic differences in the observed electrochemical behaviors for these two related species, as the main experimental differences appears to be first and foremost in the specific synthetic method employed, and second that while the experiments reported here were performed in a rigorously dry and oxygen free inert atmosphere box, the results for Ru(TPP)(NO)X were performed under a blanket of nitrogen.

Conclusion

The data described herein leads to the conclusion that the RuNO moiety dominates the electronic interactions, in these metalloporphyrin complexes, while the trans ligand participates only minimally. The illusive Ru(TTP)$(NO)_2$, bisnitrosyl complex, remains largely a speculative reaction intermediate, which most likely disproportionates nitric oxide to give the observed product, Ru(TTP)(NO)(ONO), which is the frequently observed thermodynamic sink for this chemistry. This work reinforces the widely accepted hypothesis that ruthenium and nitrosyl form a good stable marriage; for instance, the Ru(TTP)(NO)(Cl) species is stable to thermal decomposition to 480 °C. Few other coordination complexes with an organic ligand, the porphyrin, remain stable under such forcing conditions. The development of facile methods for high-yielding synthesis of the two flexible synthons, **2** and **3**, is a particularly useful development and may lead to many additional types of complexes.

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Supporting Information Available: Tables of X-ray experimental details, bond distances and angles, thermal parameters, and hydrogen coordinates and fully labeled ORTEP diagrams (28 pages). Ordering information is given on any current masthead page.

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