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Facile Ligand Oxidation and Ring Nitration in Ruthenium Complexes Derived from a Ligand with Dicarboxamide-N and Phosphine-P Donors

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The reaction of the tetradentate dicarboxamide ligand 1,2-bis-*N*-[2′(diphenylphosphanyl)benzoyl]diaminobenzene ($dppbH_2$) with $RuCl_3$ in DMF or ethanol results in metal-mediated ligand oxidation and formation of the diamagnetic Ru(II) complex $[(dppQ)Ru(Cl)_2]$ (**1**) with N_2P_2 chromophore. The *o*-phenylenedicarboxamide portion of the $dppb^{2-}$ ligand is oxidized to a *o*-benzoquinonediimine (bqdi) moiety in $[(dppQ)Ru(Cl)_2]$. Presence of oxygen accelerates the ligand oxidation process. Unlike other tetradentate dicarboxamide ligands with pyridine-N, phenolato-O, or thiolato-S donors, $dppb^{2-}$ provides stability to the +2 oxidation state of ruthenium and facilitates oxidation of the coordinated ligand frame. Results of spectroscopic and redox studies strongly support the +2 oxidation state of Ru in **1**. Exposure of **1** to NO(g) does not lead to formation of any metal nitrosyl; instead, the bqdi ring is nitrated to afford $[(NO_2dppQ)Ru(Cl)_2]$ (**2**).

Introduction

The discovery that nitric oxide (NO) acts as a key signaling molecule in many important biological processes, such as vasodilation, neurotransmission, antimicrobial activity, and cell death, has stimulated interest in the chemistry and biochemistry of NO[1−6] and various NO-containing compounds.[7−9] During the past two decades, there has been great interest in the reaction of NO with metal centers of various enzymes and cellular components such as lipids and nucleic acids. Transition metal complexes in particular have proven to be a useful platform for generating metal-based "NO sensors" or "NO scavengers", which are useful in certain biological studies.[10−13] Additionally, NO complexes (nitrosyls) of transition metals can be used as exogenous sources of NO (NO donors) that are capable of NO release upon exposure to light.[14,15] This distinctive property of metal nitrosyls could be exploited in site-specific delivery of NO to cellular targets under the control of light.

In our effort to design photosensitive metal nitrosyls, we have investigated the formation and reactivity of several M−NO (M = Fe, Ru, Mn) complexes with designed multidentate ligands.[16−22] For example, we have previously

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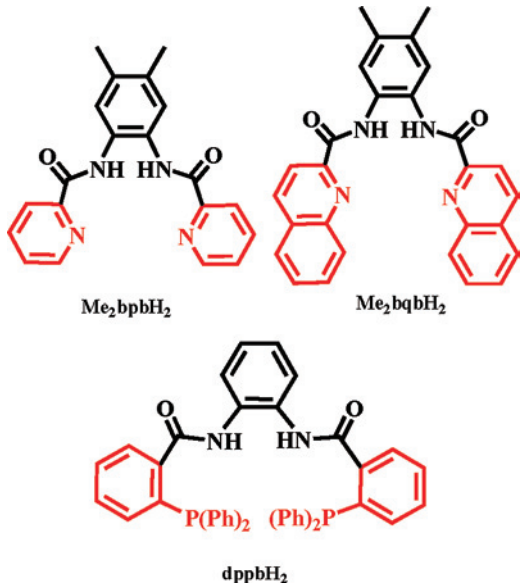

Figure 1. Tetradentate dicarboxamide ligands with pyridine, quinoline, and phosphine donors.

reported the syntheses of several {Ru−NO}^{6} nitrosyls derived from tetradentate dicarboxamide N_4 ligands such as Me_2bpbH_2 and Me_2bqbH_2 (Figure 1).[23] The resulting nitrosyls ([(Me_2bpb)Ru(NO)(Cl)] and [(Me_2bqb)Ru(NO)(Cl)], for example) are thermally stable in biological media and rapidly release NO when exposed to low-intensity (mW) UV light.[21] The photorelease of NO arises from excitation of the d_π(Ru) → π^*(NO) transition (photoband) of these {Ru−NO}^{6} nitrosyls in the 300−450 nm region.[21,24] Release of NO results in the formation of Ru(III) photoproducts of the type [(Me_2bpb)Ru(solv)(Cl)] (solv = solvent). Substitution of the pyridine donors (as in Me_2bpbH_2) with more conjugated and stronger σ-donating quinoline donors (as in Me_2bqbH_2) causes a red shift of the photoband and invariably enhances the photosensitivity of the resulting nitrosyls in the visible region.[19,21] Recently, we have been interested in further exploring the effects of substituting the donor atoms of the in-plane ligands on the photolability of the bound NO in analogous ruthenium nitrosyls. In the present study, we have employed a similar dicarboxamide tetradentate ligand containing phosphine donors, namely, 1,2-bis-*N*-[2′(diphenylphosphanyl)benzoyl]diaminobenzene ($dppbH_2$, Figure 1, H's are the dissociable amide protons) to isolate the corresponding ruthenium nitrosyl with N_2P_2 chromophore.[25] In {Ru−NO}^{6} nitrosyls with N_4 chromophores such as [(Me_2bpb)Ru(NO)(Cl)], the deprotonated carboxamido N donors provide extra stability to the Ru(III) center. Interestingly, when a combination of carboxamido N donors with phosphine P donors (instead of pyridine N donors) is used in $dppbH_2$, the ligand acts as a "non-innocent" redox active ligand in its reaction with $RuCl_3$ and affords a diamagnetic Ru(II) complex containing an oxidized ligand. As described in this paper, the *o*-phenylenedicarboxamide portion of the $dppbH_2$ ligand is oxidized to a quinonoid moiety in the Ru(II) complex [(dppQ)Ru(Cl)$_2$] (**1**, where dppQ = 1,2-bis-*N*-[2′(diphenylphosphanyl)benzoyl]benzoquinonediimine). Such transformation activates the ligand frame, and consequently exposure of **1** to NO(g) results in nitration of the phenyl ring instead of the formation of the targeted nitrosyl. In this paper, we report the syntheses, structures, and properties of [(dppQ)Ru(Cl)$_2$] (**1**) and [(NO_2dppQ)Ru(Cl)$_2$] (**2**, where NO_2dppQ = 1,2-bis-*N*-[2′(diphenylphosphanyl)benzoyl]-4-nitro-benzoquinone diimine), the nitrated product.

Experimental Section

Materials. NO gas was purchased from Spectra Gases Inc. and was purified by passing through a long KOH column prior to use. $RuCl_3 \cdot xH_2O$ (Aldrich Chemical Co.) was treated several times with concentrated HCl to prepare the starting metal salt, $RuCl_3 \cdot 3H_2O$. The solvents were dried by standard techniques and distilled. All other chemicals were purchased from Aldrich Chemical Co. and used without further purification.

Synthesis of $dppbH_2$. The synthesis and purification of $dppbH_2$ were modified to some extent compared to the procedure reported by Burger et al.[25] A batch of 0.500 g (1.63 mmol) of 2-(diphenylphosphino)benzoic acid along with 0.352 g (1.708 mmol) of *N,N*-dicyclohexylcarbodiimide (DCC) and 0.010 g (0.082 mmol) of 4-(dimethylamino) pyridine (DMAP) was dissolved in 15 mL of dichloromethane. Next, a solution of 0.084 g (0.778 mmol) of *o*-phenylenediamine in 5 mL of dichloromethane was slowly added to it. The turbid solution thus obtained was stirred at room temperature for 6 h. The light yellow solution was then filtered through a Celite pad, and the filtrate was dried. The resulting yellow solid was stirred in 30 mL of ethyl acetate for 1 h to remove any impurity. The white product was finally collected by filtration, washed several times with ethanol to remove any remaining urea and dried in vacuo. Yield: 0.36 g (68%). Anal. Calcd. for $C_{44}H_{34}N_2O_2P_2$ (684.21) C 77.18, H 5.01, N 4.01; Found C 76.92, H 4.94, N 4.11. Selected IR frequencies (KBr disk, cm^{-1}): 3320 (w, ν_{NH}), 3051(w), 2927 (w), 1640 (vs, ν_{CO}), 1592 (m), 1524 (vs), 1512 (vs), 1486 (s), 1433 (s), 1314 (m), 1089 (w), 744 (vs), 695 (vs), 500 (w). ^{1}H NMR in $CDCl_3$, δ from TMS: 8.45 (s 2H), 7.75 (dd 2H), 7.39−7.17 (m 26H), 7.2−7.11(dd 2H), 7.00−6.98 (dd 2H).

Synthesis of [(dppQ)Ru(Cl)$_2$] (1). Method A. A batch of 100 mg (0.146 mmol) of $dppbH_2$ was dissolved in 20 mL of DMF and deprotonated with 2.2 equiv of NaH (8 mg, 0.321 mmol). A solution of 38 mg of $RuCl_3 \cdot 3H_2O$ (0.146 mmol) in 5 mL of DMF was then added to it when the color turned to green. The reaction mixture was then heated at 100 °C for 2 h. Next, the dark reddish purple mixture was concentrated to 15 mL and stored at 0 °C for 12 h. The dark red solid thus obtained was collected by filtration, washed with 2 × 5 mL

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of diethyl ether, and dried in vacuo. Yield: 30 mg (24%). Vapor diffusion of pentane into a solution of this solid dissolved in chloroform afforded dark red crystalline plates suitable for X-ray studies. Anal. Calcd. for $C_{44}H_{32}Cl_2N_2O_2P_2Ru$ (**1**) (854.04) C 61.83, H 3.77, N 3.38; Found C 61.78, H 3.72, N 3.23. Selected IR frequencies (KBr disk, cm^{-1}): 3050 (w), 1691(vs, ν_{CO}), 1582 (w), 1521 (w), 1481 (w), 1434 (s), 1261 (s), 1217 (vs), 1151 (w), 1128 (m), 1095 (s), 1017 (s), 880 (m), 868 (m), 747 (s), 694 (s), 520 (s). Electronic absorption spectrum in $CHCl_3$, λ_{max} in nm (ε in M^{-1} cm^{-1}): 260 (39 000), 460 (8700), 530 (5000). ^1H NMR in $CDCl_3$, δ from TMS: 8.76 (d 2H), 7.74 (q 4H), 7.70 (t 2H), 7.5 (t 2H), 7.42 (t 2H), 7.33 (t 4H), 7.04 (t 4H), 6.96 (t 4H), 6.81 (m 2H), 6.59 (m 2H), 6.53 (q 4H). ESI-MS: *m/z* 855 (M^+), 819 ($M - Cl^+$).

Method B. A batch of 38 mg (0.146 mmol) of $RuCl_3 \cdot 3H_2O$ was dissolved in 5 mL of EtOH, and the orange-red solution was heated to reflux for 3 h. The resulting dark green solution was then added to a slurry of 100 mg (0.146 mmol) of $dppbH_2$ in 5 mL of EtOH containing 0.1 mL of Et_3N. A slow stream of air was bubbled directly through this mixture while heating it to reflux temperature. A dark red-brown precipitate was noted within 3 h. The solution was cooled, and the precipitate was collected by filtration. Next, the crude product was extracted into chloroform (20 mL). Diffusion of pentane into this chloroform solution afforded 80 mg (65% yield) of **1**.

Synthesis of [(NO_2dppQ)Ru(Cl)$_2$] (2). A slurry of 25 mg (0.037 mmol) of [(dppQ)Ru(Cl)$_2$] (**1**) in 10 mL of DMF was thoroughly degassed and then heated to 100 °C to obtain a dark red solution. A slow stream of purified NO gas was passed through this hot solution for 1 h when the color of the solution changed to orange red. The solvent was removed to isolate a dark orange-red solid (yield 89%). Diffusion of pentane into a solution of this solid in $CHCl_3$ afforded red block crystals of **2**·$CHCl_3$. Anal. Calcd for $C_{44}H_{31}Cl_2N_3O_4P_2Ru$ (**2**): (899.02) C 58.74, H 3.47, N 4.67; Found C 58.62, H 3.45, N 4.39. Selected IR frequencies (KBr disk, cm^{-1}): 2924 (w), 1682 (m, ν_{CO}), 1665 (m, ν_{CO}), 1580 (w), 1508 (m), 1435 (m), 1334 (s, ν_{NO2}), 1278 (m), 1261 (m), 1218 (vs), 1128 (w), 1095 (m), 1015 (m), 742 (vs), 695 (vs), 527 (m), 513 (m). Electronic absorption spectrum in $CHCl_3$, λ_{max} in nm (ε in M^{-1} cm^{-1}): 260 (34 000), 365 (8000), 450 (8000), 485 (9500). ^1H NMR in $CDCl_3$, δ from TMS: 8.84 (d 1H), 8.81 (d 1H), 7.78 (t 1H), 7,76 (t 1H), 7.64 (m 4H), 7.56 (s 1H), 7.55 (d 1H), 7.53 (d 1H), 7.45 (t 2H), 7.31 (t 4H), 7.21 (d 1H), 7.07−6.96 (m 8H), 6.86 (d 1 H), 6.49 (d 2H), 6.45 (d 2H). ESI-MS: *m/z* 900 (M^+), 864 ($M - Cl^+$).

Physical Measurements. The ^1H NMR spectra were recorded at 298 K on a Varian Inova 600 MHz instrument. A Perkin-Elmer Spectrum-One FT-IR spectrometer was used to monitor the IR spectra of the complexes. The electronic absorption spectra were obtained with a scanning Carey 50 spectrophotometer (Varian Associates). EPR spectra were monitored on a Bruker 500 ELEXSYS spectrometer at X-band frequencies at 125 K. Electrochemical measurements were performed with Princeton Applied Research instrumentation (model 273A). (Et_4N)(ClO_4) was used as the supporting electrolyte. A Beckman Pt inlay electrode was employed as the working electrode. Electrospray ionization mass spectrometry (ESI-MS) was carried out on a Waters Micromass ZMD mass spectrometer.

X-ray Crystallography. Diffraction data for **1** and **2**·$CHCl_3$ were collected at 150 K on Bruker APEX-II instruments using synchrotron radiation ($\lambda = 0.77490$ Å) for **1** and monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) for **2**·$CHCl_3$. Both sets of diffraction data for **1** and **2**·$CHCl_3$ were corrected for absorption, and all calculations were performed using the SHELXTL (1995−1999) software package (Bruker Analytical X-ray Systems Inc.) for structure solution and refinement, The *o*-benzoquinonediimine portion in the structure of **2**·$CHCl_3$ was modeled as two half-occupancy rings that are related by an apparent 180° rotation due to the two positions that the nitro group resides on (Figure S1, Supporting Information). Additional refinement details are contained in the CIF files (Supporting Information). Instrument parameters, crystal data, and data collection parameters for all the complexes are summarized in Table 1. Selected bond distances and bond angles for **1** and **2**·$CHCl_3$ are listed in Table 2.

Table 1. Summary of Crystal Data, Intensity Collection, and Refinement Parameters for [(dppQ)Ru(Cl)$_2$] (**1**) and [(NO_2dppQ)Ru(Cl)$_2$]·$CHCl_3$ (**2**·$CHCl_3$)

	1	**2**
empirical formula	$C_{44}H_{32}Cl_2N_2O_2P_2Ru$	$C_{45}H_{32}Cl_5N_3O_4P_2Ru$
fw	854.63	1019.00
cryst color	dark red plates	red blocks
cryst size (mm^3)	0.09 × 0.08 × 0.01	0.17 × 0.15 × 0.10
temp (K)	150(2)	150(2)
wavelength (Å)	0.77490	0.71073
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	12.8868(15)	11.5979(16)
b (Å)	15.8457(18)	13.3799(19)
c (Å)	18.982(2)	14.107(2)
α (deg)	90	102.117(2)
β (deg)	105.959(2)	90.025(2)
γ (deg)	90	95.669(2)
V ($Å^3$)	3726.8(7)	2129.3(5)
Z	4	2
d_{calcd} (g/cm^3)	1.523	1.589
μ (mm^{-1})	0.863	0.806
GOF[a] on F^2	0.986	1.040
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0520$	$R_1 = 0.0511$
	$wR_2 = 0.1055$	$wR_2 = 0.1227$
R indices[b] [all data][c]	$R_1 = 0.1274$	$R_1 = 0.0666$
	$wR_2 = 0.1353$	$wR_2 = 0.1323$

[a] GOF = $[\sum w(|F_o|^2 - |F_c|^2)^2/(N_o - N_v)]^{1/2}$ (N_o = number of observations; N_v = number of variables). [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = [(\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^2)]^{1/2}$.

Results and Discussion

Synthesis. Recently, we and others have synthesized several tetradentate ligands by combining an *o*-phenylenedicarboxamide moiety with pyridine-N,[21,26,27] phenolate-O,[28,29] or thiophenol-S donors.[30] Burger et al. have reported a similar ligand framework $dppbH_2$ by combining phosphine-P donors with an *o*-phenylenedicarboxamide moiety.[25] Although the chemistry of the Pd,[25,31] Pt,[25] and Rh[32] complexes of this ligand has been reported, the Ru chemistry of $dppbH_2$ remains essentially unexplored. We were interested in such chemistry, particularly the role of this ligand in stabilizing Ru(II) vs Ru(III) center in the resulting complex(es).

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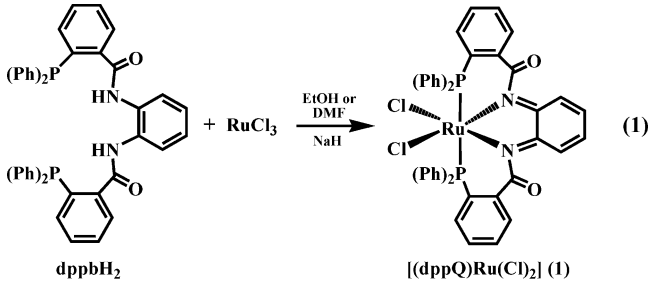
Table 2. Selected Bond Distances (Å) and Angles (deg) of **1** and **2**

bond distances and angles	1	2
Ru1−P1	2.3664(16)	2.3586(9)
Ru1−P2	2.3667(16)	2.3684(10)
Ru1−Cl1	2.4087(14)	2.4077(9)
Ru1−Cl2	2.4070(14)	2.3948(9)
Ru1−N1	1.970(4)	1.989(3)
Ru1−N2	1.995(4)	1.967(3)
N1−C2	1.361(7)	1.383[a]
N2−C7	1.357(6)	1.358[a]
C2−C3	1.408(7)	1.444(17)
C3−C4	1.336(7)	1.338(19)
C4−C5	1.420(7)	1.410(20)
C5−C6	1.353(7)	1.352(18)
C6−C7	1.426(7)	1.440(19)
C2−C7	1.439(7)	1.426(14)
N1−Ru−N2	78.42(17)	79.04(15)
N1−Ru−Cl1	96.26(13)	95.86(11)
N2−Ru−Cl2	94.95(13)	95.73(11)
Cl1−Ru−Cl2	91.76(5)	91.74(3)
N1−Ru−P1	80.08(13)	79.65(9)
N1−Ru−P2	99.83(13)	104.87(9)
N2−Ru−P1	104.36(14)	105.95(10)
N2−Ru−P2	77.61(14)	79.20(10)
Cl1−Ru−P1	84.07(5)	85.67(3)
Cl1−Ru−P2	93.90(5)	89.71(3)
Cl2−Ru−P1	92.95(5)	90.91(3)
Cl2−Ru−P2	87.46(5)	85.19(3)
Cl1−Ru−N2	168.91(13)	166.03(9)
Cl2−Ru−N1	168.74(13)	167.37(9)
P1−Ru−P2	177.94(5)	173.87(3)

[a] Averaged bond lengths of the two half-occupancy *o*-benzoquinonediimine rings.

The metalation of the carboxamide ligands of Figure 1 typically requires deprotonation of the ligands with a base (such as NaH or NEt_3) in suitable solvent (DMF, EtOH, or MeCN) prior to its coordination to the metal centers. In the present case, reaction of the deprotonated ligand $dppb^{2-}$ (using NaH) with $RuCl_3$ in DMF generates a dark red solution upon heating. Subsequent cooling causes precipitation of complex **1** from DMF as a dark red solid in fair yield (reaction 1). Change of solvent to ethanol increases the yield to a moderate extent (48%). Interestingly, the yield is significantly improved (to 65%) when air is bubbled through the reaction mixture in refluxing ethanol.



(1)

The structure and properties of complex **1** (vide infra) indicate that its formation is not just a simple ligation reaction; rather an unexpected redox reaction takes place when $dppbH_2$ reacts with $RuCl_3$. As shown above, the Ru(III) center is reduced to Ru(II) in the final product with concomitant oxidation of the *o*-phenylenediamine (opda) portion of the ligand to an *o*-benzoquinonediimine (bqdi) moiety. As a result, instead of a $dppb^{2-}$ ligand bound to a Ru(III) center (as desired), one obtains

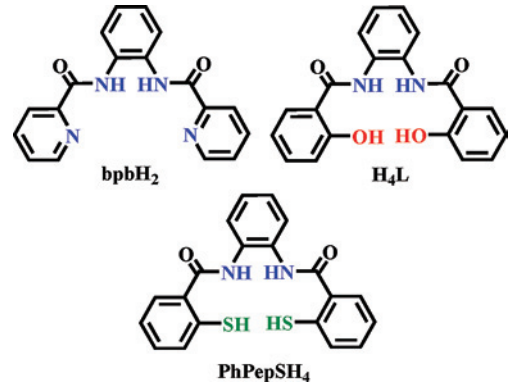


Figure 2. Tetradentate dicarboxamide ligands with N_4, N_2O_2, and N_2S_2 donor sets.

a Ru(II) complex $[(dppQ)Ru(Cl)_2]$ (**1**) in which the opda moiety of $dppb^{2-}$ is modified to a quinonoid (Q)-type ligand dppQ and coordinated to the Ru(II) center via two imine N and two phosphine P atoms. This reactivity of $dppbH_2$ is notable since such redox activity is *not observed* with other analogous ligands bearing the opda moiety. For example, ligands like $bpbH_2$ (N_4),[21] H_4L (N_2O_2),[26,27] or $PhPepSH_4$ (N_2S_2)[30] (Figure 2) readily bind various metal centers (Ru, Fe, Ni) without any redox activity. Careful scrutiny of the literature however reveals that a somewhat similar redox behavior has been noted in the reaction of $[Ru(Cl)_3(dppb)(H_2O)]$ (where dppb = 1,4-bis(diphenylphosphino)butane) with opda, recently reported by Moreira and co-workers (reaction 2).[33] In this reaction, metal-assisted oxidative dehydrogenation of the phosphine complex with odpa ligand affords the Ru(II) species $[Ru(Cl)_2(dppb)(bqdi)]$, which contains the quinonoid bqdi moiety much like the one observed in **1**. This reaction occurs in the absence of oxygen, suggesting a metal−ligand coupled redox mechanism. In our case, a similar metal−ligand coupled redox process is most probably responsible for the formation **1**. When the reaction is done in the presence of air, the yield of **1** increases significantly. This increase suggests that oxygen facilitates the oxidation of the bound ligand. Indeed, oxidation of bound opda ligands coordinated to Fe(II) or Ru(II) metal centers forming such complexes as $[Fe(bqdi)_3]^{2+}$ and $[Ru(bpy)_2(bqdi)]^{2+}$ has been reported previously.[34,35] Additionally, opda ligands have been shown to react with Ru(III) in the presence of air forming several Ru(II) bqdi complexes where the metal center and oxygen are thought to be involved in the redox reaction.[36,37]

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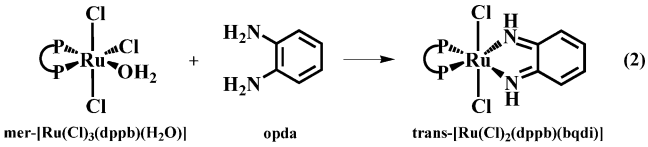
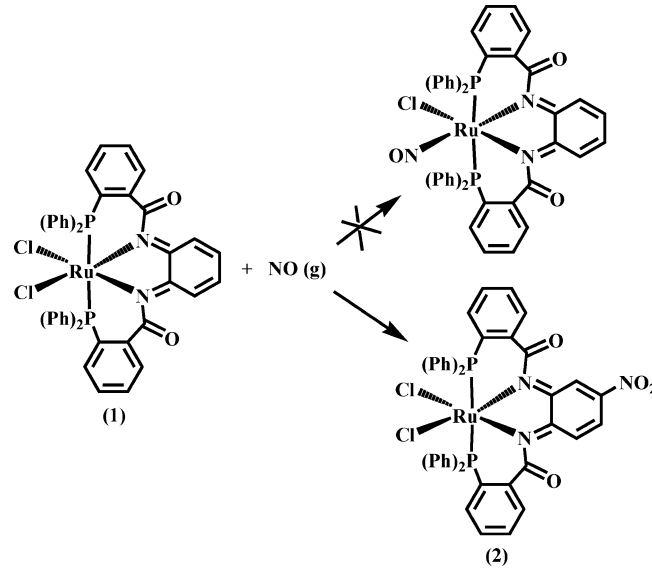


Collectively, the chemistry discussed above indicates that the combination of *o*-phenylenedicarboxamide-N and phosphine-P donors in $dppbH_2$ leads to redox chemistry between the ligand and Ru(III) center. Since phosphine ligands provide stability to lower valent metal centers such as Ru(II), the presence of such donors facilitates reduction of the metal center with concomitant oxidation of the ligand frame. Also, the bqdi moiety is a good π-acceptor and stabilizes (or "captures") the reduced product, thus driving the reaction forward. Clearly, the identity of the donor atoms (N, P, O, S) dictates the redox status of the metal centers in complexes derived from such tetradentate ligands.

In previous accounts, we have reported formation of $\{Ru-NO\}^6$ nitrosyls of the type $[(Me_2bqb)Ru(NO)(Cl)]$ upon reaction of NO(g) with Ru(III) centers ligated to the deprotonated ligands.[20−22] Although Ru(II) precursors generally require nitrite salts and acids to afford $\{Ru-NO\}^6$ nitrosyls,[22c,38,39] there is one recent report on the formation of a $\{Ru-NO\}^6$ nitrosyl from a Ru(II) starting complex *cis*-$[RuCl_2(dcype)(bpy)]$ (dcype = 1,2-bis(dicyclohexylphosphino)ethane) via direct reaction with NO(g) in dichloromethane.[40] Interestingly, in the present case, passage of NO(g) through a solution of **1** in DMF (previously deoxygenated) at room or elevated (90 °C) temperature does not afford any metal nitrosyl. Instead, the bqdi moiety of the ligand undergoes a nitration reaction, forming the ring-substituted product $[(NO_2dppQ)Ru(Cl)_2]$, (**2**, Scheme 1). We have previously reported that when a solution of the $\{Fe-NO\}^6$ nitrosyl $[(bpb)Fe(NO)(NO_2)]$ in DMF was exposed to air, a similar ring-nitrated product $[(NO_2bpb)Fe(NO_3)(DMF)]$ was obtained.[17] Lippard and co-workers have observed a ring nitration reaction with the iron tropocoronand complex [Fe(NO)(TC)] in presence of excess NO.[41] The product [Fe(NO)(TC-5,5-NO_2)] is formed via disproportionation of NO. Ford and co-workers have convincingly demonstrated that Ru(II) porphyrins disproportionate NO to NO_2, N_2O_3, and other reactive nitrogen oxide species capable of ligand modification.[42] In the present work, the ring-nitrated species **2** is obtained in the absence of air. We therefore believe that the nitration of the bqdi moiety of **1** is facilitated by NO disproportionation.

Scheme 1. Reactivity of $[(dppQ)Ru(Cl)_2]$ (**1**) with NO(g)



Structures of the Complexes. $[(dppQ)Ru(Cl)_2]$ (1). The structure of **1** is shown in Figure 3, and selected structural parameters are listed in Table 2. The ruthenium center in this complex resides in a slightly distorted octahedral geometry. Unlike coordinated N4 ligands like Me_2bpb^{2-}, the oxidized tetradentate ligand dppQ is not planar; the bulky phosphine ends are coordinated trans to one another in the axial positions, while the two imine N's of the bqdi moiety occupy equatorial positions. The two Cl^- donors also coordinate in the equatorial plane, *cis* to one another. Close examination of the bond lengths of the bqdi ring in **1** (Figure 5) reveals that the C(3)−C(4) and C(5)−C(6) distances are shorter (1.336(7) and 1.353(7) Å, respectively) compared with the rest of C−C distances of the ring (all in the range of 1.408(7) to 1.439(7) Å). This distance distribution in addition to two imine double bonds (N(1)−C(2) = 1.361(7) Å, and N(2)−C(7) = 1.357(6) Å) indicates a quinonoid form of the ligated bqdi moiety. The related quinonoid compound $[Ru(Cl)_2(dppb)(bqdi)]$ reported by Moreira and co-workers also exhibits an $N_2P_2Cl_2$ donor set, and its C−N bond distances of 1.351 and 1.349 Å were interpreted as double bonds of a bqdi moiety bound to a Ru(II) center.[33] It should be

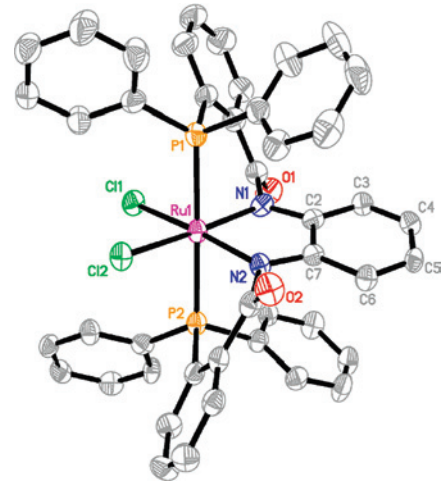


Figure 3. Thermal ellipsoid (probability level 50%) plot of $[(dppQ)Ru(Cl)_2]$ (**1**) with select atom-labeling. H atoms are omitted for the sake of clarity.

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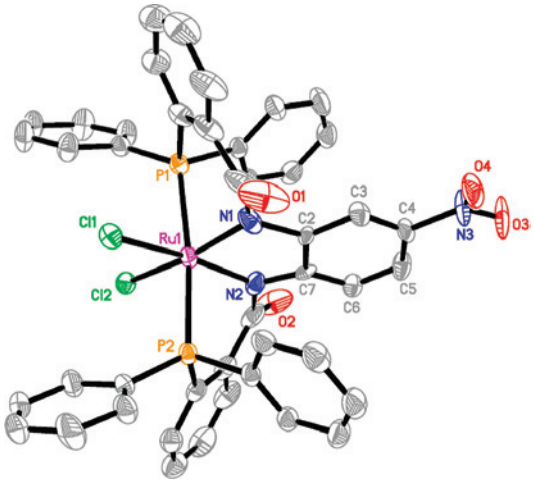


Figure 4. Thermal ellipsoid (probability level 50%) plot of $[(NO_2dppQ)Ru(Cl)_2]$ (**2**) with select atom-labeling. H atoms are omitted for the sake of clarity.

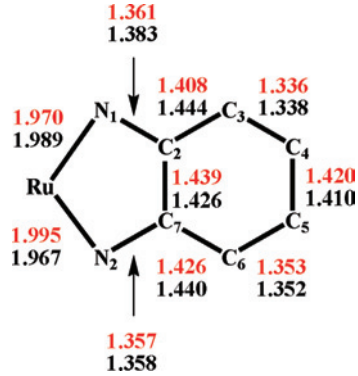


Figure 5. Bond distances (Å) within the bqdi portion of the ligand in $[(dppQ)Ru(Cl)_2]$ (**1**, shown in red) and $[(NO_2dppQ)Ru(Cl)_2]$ (**2**, shown in black).

noted that there is a range of C−N bond distances (1.30−1.35 Å), which have been reported for ruthenium-bound bqdi or semiquinonediimine (sqdi) units, albeit with much different donor sets (N_6, N_4Cl_2, N_5O, etc.).[34−37] The imine character of the coordinated N's is further supported by the planarity of the Ru−bqdi portion of the complex. The bond angles about each nitrogen are all in the range of 116.6(3)°−122.3(3)° and add up to 360°. Finally, the Ru−N(imine) bond distances of 1.970(4) and 1.995(4) Å are similar to the ones reported for related Ru(II) bqdi complexes.[34−37]

$[(NO_2dppQ)Ru(Cl)_2]$ (2). The structure of **2**·$CHCl_3$ is shown in Figure 4, and selected structural parameters are listed in Table 2. As indicated in Figure 5, nitration of the bqdi ring in complex **2**·$CHCl_3$ does not alter the metric parameters of the bqdi moiety. Thus, the quinonoid moiety remains intact upon substitution of the ring. The $Ru-N_{imine}$ bond lengths also show no significant changes upon nitration of the ring.

Spectroscopic Properties. In typical $\{Ru-NO\}^6$ nitrosyls derived from ligands such as Me_2bpbH_2 and Me_2bqbH_2, coordination of the deprotonated carboxamido N's to the ruthenium center is indicated by a ν_{CO} (carbonyl stretching frequency) shift to low energy.[21] Burger et al. have reported a Pt(II) complex of $dppb^{2-}$ in which the deprotonated carboxamido N's and phosphine P's are coordinated to the Pt(II) center.[25] This complex exhibits its ν_{CO} at 1602 cm^{-1} compared with 1640 cm^{-1} in free $dppbH_2$. It is therefore evident that coordination of the $dppb^{2-}$ ligand to the Ru(II) center should cause a shift of the ν_{CO} to lower energy. Quite in contrast, **1** exhibits its ν_{CO} at 1691 cm^{-1} (Figure S2, Supporting Information). In addition, the N−H stretching frequencies of free $dppbH_2$ are also absent in the IR spectrum of **1**. These spectral changes indicate significant alteration in the carboxamide portions of the ligand. The structure of **1** eventually confirmed that oxidation of this portion of the ligand to a bqdi moiety is actually responsible for the shift of ν_{CO} to higher energy. Interestingly, complex **2** also exhibits its ν_{CO} bands at 1682 and 1665 cm^{-1} (Figure S3, Supporting Information). The two stretching frequencies presumably arise from the breakdown of symmetry upon addition of the NO_2 group on the bqdi moiety. A strong band at 1334 cm^{-1} confirms the presence of the NO_2 group in **2**.

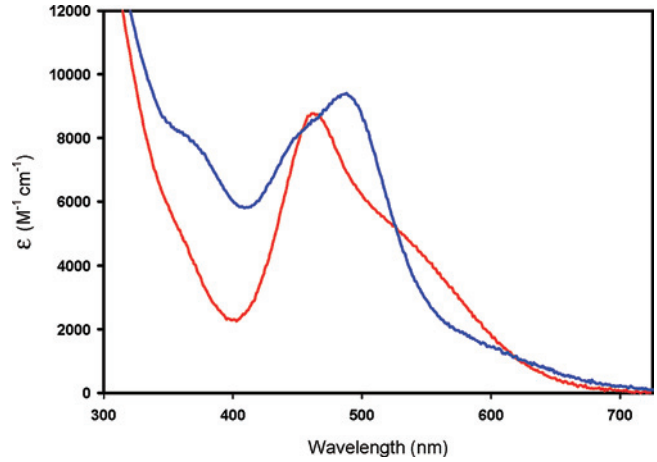


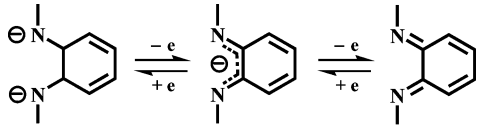
Figure 6. Electronic absorption spectra of **1** (red trace) and **2** (blue trace) in chloroform.

The presence of Ru(II) centers in **1** and **2** is supported by their diamagnetism. Both complexes exhibit sharp peaks in their ^1H NMR spectra in chloroform at 298 K (Figure S4, Supporting Information). More multiplicities are observed in the ^1H NMR spectrum of **2** due to the breakdown of symmetry following nitration of the bqdi moiety.

Ruthenium complexes containing the bqdi ligand are known to exhibit intense absorption in the visible region due to (Ru)dπ → π^*(bqdi) metal-to-ligand charge transfer (MLCT).[35] The spectrum of **1** contains a strong absorption band with λ_{max} at 460 nm, which we assign to similar transition (Figure 6). Upon nitration of the bqdi moiety, this band red shifts from 460 nm (for **1**) to 485 nm (for **2**), due to the electron-withdrawing character of the NO_2 group. A similar red shift is observed when the bqdi ring of complex $[Ru(bpy)_2(bqdi)](PF_6)_2$ (514 nm) contains a nitro group in complex $[Ru(bpy)_2(NO_2\text{-}bqdi)](PF_6)_2$ (527 nm).[35c]

Redox Properties. It is well-known that a phenylenediamine moiety can access multiple redox states when coordinated to a metal center.[34−37] As shown below, phenylenediamine can exist in its fully reduced $(opda)^{2-}$, semiquinone $(sqdi)^-$, or fully oxidized (bqdi) forms (Scheme 2). For this reason, metal complexes derived from phenylenediamine ligands are known to exhibit rich redox chemistry. Since the

Scheme 2. The Multiple Oxidation States of Phenylenediamine Moieties



presence of a redox active Ru center can also give rise to reversible redox processes, we have investigated the redox behavior of complex **1**. In DMF, **1** exhibits a reversible process **A** at a relatively high positive potential with $E_{1/2} = +0.90$ V (vs aq SCE, Figure 7). For a related bqdi complex, namely, $[Ru(bpy)_2(bqdi)](PF_6)_2$, a similar redox process with $E_{1/2} = +1.35$ V (vs aq SCE) has been assigned to Ru(II)/Ru(III) couple by Lever and co-workers.[35d] We believe that process **A** is also related to the Ru(II)/Ru(III) couple of **1**. The lowered $E_{1/2}$ value of **1** presumably arises from the presence of coordinated Cl^- ligands in **1**. Indeed, a complex containing a similar $N_2P_2Cl_2$ donor set, namely, $[Ru(PPh_3)_2(papm)Cl_2]$ (papm = 2-(phenylazo)pyrimide), exhibits a Ru(II)/Ru(III) redox couple with $E_{1/2} = +0.897$ V.[43] The other reversible process **B** observed in the cyclic voltammogram of **1** with $E_{1/2} = -0.28$ V (vs aq SCE) is related to the bqdi/sqdi couple. A similar redox process with $E_{1/2} = -0.47$ V (vs aq SCE) has been noted for $[Ru(bpy)_2(bqdi)](PF_6)_2$.[35d] Both redox processes **A** and **B** of Figure 7 are reversible and can be cycled several times without any loss of current heights. There is an additional irreversible reduction process at much more negative potential ($E_p = -0.90$ V; Figure S5, Supporting Information), which we assign to further reduction of sqdi to opda moiety.

In order to further investigate the redox process **A**, we have studied the oxidized product of **1** by EPR spectroscopy. The oxidation of **1** was performed with $(NH_4)_2[Ce(NO_3)_6]$ in DMF solution at room temperature. After stirring for 15 min, the reaction mixture was frozen for EPR analysis. The EPR spectrum of the oxidized product at 125 K exhibited a rhombic signal ($g = 2.31, 2.16, 1.93$), typical of low-spin Ru(III) center.

The reaction of NO(g) with **1** provides further evidence in favor of the presence of Ru(II) in **1**. Close examination

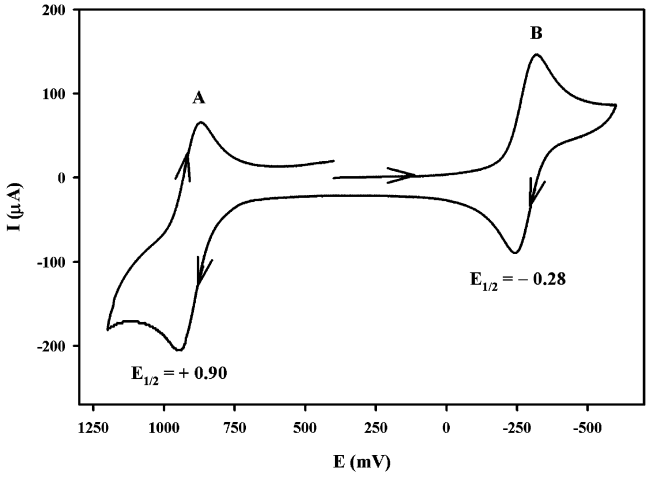


Figure 7. Cyclic voltammogram of **1** in DMF (0.10 M $(NEt_4)(ClO_4)$, scan rate = 50 mV/s). Half-wave potential ($E_{1/2}$) values are indicated vs aqueous SCE.

of literature reveals that NO(g) readily reacts with Ru(III) metal centers to form $\{Ru-NO\}^6$ nitrosyls.[44,45] In contrast, very few Ru(II) species react with NO(g). In the present work, the reaction of **1** with NO(g) has been closely monitored under several different reaction conditions. Addition of various amounts of NO(g) to solutions of **1** in DMF at ambient or elevated temperatures (25−90 °C) under light or dark conditions did not produce any material that exhibits a ν_{NO} stretching band in the 1750−1950 cm^{-1} range of the IR spectrum.[45] Even when **1** was treated with $AgBF_4$ (in order to remove a bound Cl^-) before the addition of NO(g), no IR band due to ν_{NO} was observed. If the metal center in **1** were effectively Ru(III), one would expect to observe the formation of a $\{Ru-NO\}^6$ nitrosyl. Instead, the reaction of **1** with NO(g) affords **2** in which the bqdi portion of the ligand is nitrated.

In conclusion, attempted coordination of the tetradentate N_2P_2 carboxamide ligand $dppbH_2$ to a Ru(III) center has led to an unusual metal-mediated ligand oxidation reaction and isolation of the Ru(II) complex of the oxidized ligand $[(dppQ)Ru(Cl)_2]$ (**1**). In **1**, the *o*-phenylenediamine (opda) portion of the ligand is oxidized to a benzoquinonediimine (bqdi) moiety and the two imine N's are coordinated to the Ru(II) center. Reaction of NO(g) with **1** does not lead to formation of the metal nitrosyl; instead, the bqdi ring is nitrated, and one obtains $[(NO_2dppQ)Ru(Cl)_2]$ (**2**) as the sole product. Collectively, the results indicate that the combination of the *o*-phenylenedicarboxamide unit with phosphine donors results in "non-innocent" ligands that are susceptible to metal-mediated oxidation. The known ability of the Ru(II) center to stabilize the bqdi moiety[34−37] makes $dppbH_2$ especially susceptible to such oxidation.

Acknowledgment. Financial support from the NSF Grant CHE-0553405 is gratefully acknowledged. C.N. was supported by the NIH MARC GM 007910-29 grant. We thank Dr. Allen Oliver for help in crystallographic work. The diffraction facility at UCSC is supported by the NSF Major Research Instrumentation (MRI) program under Grant No. CHE-0521569. Diffraction data for **1** were collected at Synchroton Beamline 11.3.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, supported by the U.S. Dept. of Energy, Office of Energy Sciences, under Contract DE-AC03-76SF00098.

Supporting Information Available: Thermal ellipsoid plot of **2** showing the two half-occupancy of the bqdi ring (Figure S1), FTIR spectra of **1** and **2** (Figures S2 and S3), ^1H NMR spectra of **1** and **2** in $CDCl_3$ (Figures S4), table for bond lengths of the two half-occupancy bqdi rings (Table S1), and X-ray crystallographic data (in CIF format) for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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