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Accelerated Photorelease of NO from {Ru-NO}^{6} Nitrosyls Containing Carboxamido-N and Carboxylato-O Donors: Syntheses, Structures, and Photochemistry

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Three ruthenium nitrosyls, namely, [(Me_2bpb)Ru(NO)(OAc)], [(Me_2bpb)Ru(NO)(OBz)] (**1**), and [(Me_2Qb)Ru-(NO)(qca)](BF_4) (**2**), have been synthesized from designed ligands with carboxamido-N donors. In all three complexes, a carboxylato-O donor is trans to the bound NO. The structures of **1** and **2** have been determined by X-ray crystallography. The nearly linear Ru−N−O bond angles [175.18(18)° and 175.0(3)°, respectively] and diamagnetism of the two nitrosyls are indicative of the {Ru-NO}^{6} configuration. All three complexes exhibit ν_{NO} in the range 1830−1890 cm^{-1}. When solutions of **1** and **2** are exposed to low-intensity (milliwatts) UV light, rapid release of NO is observed. The results of photochemical measurements indicate that the placement of the carboxylato-O donor trans to NO promotes the photorelease of NO in these nitrosyls much like Cl^- and py. The presence of the carboxamido-N donor is, however, essential for the observed NO photolability because the structurally similar nitrosyl [($pyca)_2$Ru(NO)(Cl)] (**3**) (with carboxylato-O trans to NO) does not release NO upon exposure to UV light. Extension of conjugation in the ligand frame (quinoline rings in place of pyridine rings) increases both the rate of NO photorelease and the quantum yield of **2** compared to **1**. The results of this investigation confirm that the combination of carboxamido-N donor(s) in the ligand frame and carboxylato-O trans to NO is a new structural motif in photoactive {Ru-NO}^{6} nitrosyls.

Introduction

In recent years, nitric oxide (NO) has been shown to play key roles in several physiological and pathological pathways. For example, NO participates in blood pressure control, neurotransmission, inflammatory responses, and cell apoptosis.[1−6] The discovery of these biological effects of NO has prompted research in the area of development of exogenous NO donors that can deliver NO at desired locales for the treatment of various diseases.[7−9] Such attempts have afforded novel NO donors such as diazeniumdiolates[10,11] and *S*-nitrosothiols,[12] which release NO in cellular environments. The extent of NO delivery by such systemic NO donors, however, can hardly be controlled in biological systems because the drug goes everywhere and releases NO via relatively ubiquitous enzymatic or pH-dependent processes. In order to deliver NO to selected target areas under the control of light, we have developed a series of metal nitrosyls (NO complexes) of the type $[(L)M(NO)(L')]^{n+}$ [L = mul-

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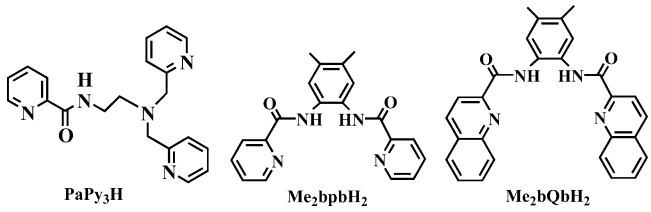
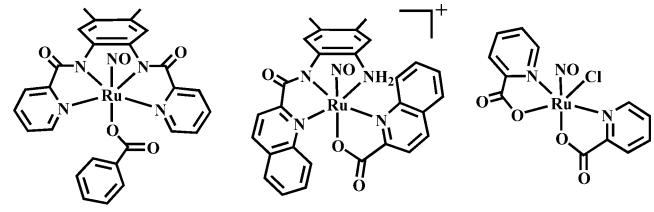


Figure 1. Examples of multidentate ligands (L) employed to isolate photoactive metal nitrosyls.

tidentate ligands (Figure 1); M = Ru, Fe, and Mn; L′ = monodentate ligands like py and Cl^-] that rapidly release NO upon exposure to light of various wavelengths.[13−20] The utility of such NO donors in delivering NO at cellular targets via triggering with light has also been established.[21−28]

One interesting feature of these photoactive {M-NO}⁶ metal nitrosyls[29] is the presence of one (or two) carboxamido-N donors in the donor set of the ligand L. Our work has clearly shown that the presence of this strongly σ-donating anionic N donor either in the equatorial plane of the metal nitrosyl or trans to the bound NO makes these nitrosyls susceptible to *light of low intensity* (milliwatts to watts). Although {Ru-NO}⁶ nitrosyls such as $[Ru(NH_3)_4(L)(NO)]^{3+}$ (L = py, NH_3, Im, etc.) and $K_2[Ru(NO)(Cl)_5]$ exhibit NO photolability, the intensity of UV light required for NO release is usually high (300−500 W).[27] In addition, the designed {Ru-NO}⁶ nitrosyls with carboxamido-N donor(s) exhibit high quantum yield (ϕ) values compared to nitrosyls derived from typical N-donor ligands such as NH_3, py, bpy (2,2′-bipyridine), and phen (1,10-*o*-phenanthroline).[27] The results of recent theoretical work indicate that electronic transition from a molecular orbital (MO), which is predominantly metal and carboxamido-N in character, to a M−NO π^*-antibonding MO promotes NO photolability in these metal nitrosyls.[30,31] Greene and Richards have suggested that the presence of two lone pairs on the carboxamido-N donor allows greater electron donation (more covalent character) to the Fe−N bond in $[(PaPy_3)Fe(NO)]^{2+}$ and facilitates the release of NO upon illumination.[30] In the case of {Ru-NO}⁶ nitrosyls derived from Schiff bases, NO photolability also arises from a $d_\pi(M)-\pi^*(NO)$ transition (photoband), which has some ligand (phenolato-oxo)$-\pi^*$(NO) character as well.[32,33] In our search for other donor centers that could promote such a transition in {M-NO}⁶ nitrosyls, we have now looked into the role of a carboxylato-O donor (an anionic σ donor with two lone pairs) in introducing NO photolability in metal nitrosyls. As examples of the simplest type, we have synthesized two {Ru-NO}⁶ nitrosyls, $[(Me_2bpb)Ru(NO)(RCOO)]$ [Me_2bpb^{2-} = deprotonated Me_2bpbH_2, 1,2-bis(pyridine-2-carboxamido)-4,5-dimethylbenzene); R = CH_3 and Ph], in which the carboxylate ligand acts as a monodentate ligand bound through one O atom. As part of a more involved second type, we have employed quinoline carboxylate (qca^-) as a bidentate ligand (bound through quinoline-N and carboxylato-O) to isolate $[(Me_2Qb)Ru(NO)(qca)]BF_4$. Following the structural determination of $[(Me_2bpb)Ru(NO)(OBz)]$ (**1**; OBz = benzoate, $PhCOO^-$) and $[(Me_2Qb)Ru(NO)(qca)]BF_4$ (**2**), we investigated the capacity of NO photorelease of these two structurally similar {Ru-NO}⁶ nitrosyls (both with carboxylato-O trans to NO) along with that of another {Ru-NO}⁶ nitrosyl $[(pyca)_2Ru(NO)(Cl)]$ (**3**; $pyca^-$ = picolinate ligand)[34] that is devoid of carboxamido-N coordination (but with carboxylato-O trans to NO). The results of such studies are reported in this article. As discussed in the following sections, both **1** and **2** exhibit excellent photolability while **3** (no carboxamido-N coordination) does not. Also, coordination of carboxylates increases the capacity of NO photorelease from the {Ru-NO}⁶ nitrosyl **1** compared to $[(Me_2bpb)Ru(NO)(Cl)]$.[18] Extension of conjugation in the ligand frame in **2** results in significant enhancement of the quantum yield (compared to **1**), a phenomenon reported by us in previous reports.[18,19] Scrutiny of the literature reveals that to date one trinuclear carboxylato cluster, namely, $[Ru_3O(OAc)_6(pic)_2(NO)]PF_6$ (pic = 4-methylpyridine), has been shown to release NO upon irradiation.[35]



Experimental Section

Materials and Reagents. 4,5-Dimethyl-1,2-diaminobenzene, picolinic acid, triphenyl phosphate, and sodium benzoate were purchased from Aldrich Chemical Co. and used without further purification. $RuCl_3 \cdot xH_2O$ (Aldrich Chemical Co.) was treated several times with concentrated HCl to prepare the starting metal

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salt, $RuCl_3 \cdot 3H_2O$. Potassium pentachloronitrosylruthenate(II) was purchased from Alfa Aesar and used without further purification. NO gas was purchased from Spectra Gases Inc. and was purified by passing through a long KOH column prior to use. The nitrosyls [(Me_2bpb)Ru(NO)(Cl)], [(Me_2bQb)Ru(NO)(Cl)], and [(pyca)$_2$Ru(NO)(Cl)] (**3**) were synthesized by following the published procedures.[18,34] All solvents were purified and/or dried by standard techniques and distilled.

Syntheses of Compounds. [(Me_2bpb)Ru(NO)(OBz)] (1). A solution of 0.057 g (0.274 mmol) of $AgBF_4$ in 5 mL of MeCN was added to a stirred solution of 0.14 g (0.268 mmol) of [(Me_2bpb)Ru(NO)(Cl)][18] in 20 mL of MeCN, and the reaction mixture was heated to reflux for 8 h. The precipitate of AgCl that separated during this period was then removed by filtration through a sintered-glass frit with a Celite pad on top. Next, a batch of 0.050 g (0.348 mmol) of sodium benzoate was added to the filtrate, and the reaction mixture was heated to reflux for 4 h. Finally, the clear red-brown solution was concentrated to 10 mL and filtered through a sintered-glass frit with a Celite pad on top, as above. The filtrate was then stored at −20 °C for 16 h, resulting in precipitation of a fine red powder that was collected by filtration. Crystalline solid (suitable for diffraction measurements) was obtained via slow evaporation of the solution of this red solid in a $CHCl_3$/toluene mixture (yield: 0.034 g, 21%). Anal. Calcd for $C_{29}H_{23}RuN_5O_5Cl_6$ (**1**·2$CHCl_3$): C, 41.69; H, 2.78; N, 8.39. Found: C, 41.58; H, 2.71; N, 8.12. Selected IR frequencies (KBr disk, cm^{-1}): 1833 (ν_{NO}, vs), 1630 (vs), 1594 (vs), 1484 (m), 1355 (m), 1319 (s), 756 (w), 723 (w), 682 (m). Electronic absorption spectrum in MeCN, λ_{max} (in nm) (ϵ in M^{-1} cm^{-1}): 300 (13 000), 390 (6700). ^{1}H NMR (500 MHz. $CDCl_3$, δ from TMS): 2.35 (s, 6H), 7.09 (t, 2H), 7.23 (t, 1H), 7.49 (d, 2H), 7.68 (t, 2H), 8.14 (t, 2H), 8.29 (d, 2H), 8.54 (s, 2H), 9.13 (d, 2H).

The acetate analogue of **1**, namely, [(Me_2bpb)Ru(NO)(OAc)], was also synthesized in the present study by following the same procedure (except for the use of sodium acetate in place of benzoate). The reddish-orange microcrystalline product was isolated in 70% yield. Anal. Calcd for $C_{22}H_{19}RuN_5O_5$: C, 49.43; H, 3.59; N, 13.10. Found: C, 49.33; H, 3.49; N, 13.37. Selected IR frequencies (KBr disk, cm^{-1}): 1841 (ν_{NO}, vs), 1639 (vs), 1598 (vs), 1484 (m), 1358 (s), 1292 (s), 1097 (vw), 760 (w), 684 (m). This nitrosyl is sparingly soluble in most solvents [MeCN, *N*,*N*-dimethylformamide (DMF), and $CHCl_3$] and has not been used for any solution study.

[(Me_2Qb)Ru(NO)(qca)]BF_4 (2). A solution of 0.041 g (0.211 mmol) of $AgBF_4$ in 5 mL of DMF was added to a stirred solution of 0.10 g (0.164 mmol) of [Ru(Me_2bQb)(NO)(Cl)][18] in 25 mL of DMF, and the reaction mixture was heated to 60 °C for 16 h. The precipitate of AgCl that separated during this period was then removed by filtration through a sintered-glass frit with a Celite pad on top. DMF was removed by short-path distillation, and the solid was triturated four times with 10 mL of MeCN. The residue was finally dissolved in 30 mL of MeCN, and diethyl ether was allowed to diffuse into it slowly at room temperature. X-ray-quality crystals (cluster of thick needles) were obtained after 5 days (0.035 g, 28% yield). Anal. Calcd for $C_{28}H_{22}RuN_5O_4BF_4$: C, 49.45; H, 3.27; N, 10.30. Found: C, 49.23; H, 3.19; N, 10.27. Selected IR frequencies (KBr disk, cm^{-1}): 1872 (ν_{NO}, vs), 1680 (vs), 1650 (vs), 1386 (m), 1325 (s), 1174 (m), 1082 (s), 875 (w), 764 (m). Electronic absorption spectrum in MeCN, λ_{max} (in nm) (ϵ in M^{-1} cm^{-1}): 240 (67 000), 320 (16 000), 600 (br, 2000). ^{1}H NMR (500 MHz. CD_3CN, δ from TMS): 2.25 (s, 3H), 2.35 (s, 3H), 6.65 (d, 1H), 7.04 (s, 1), 7.10 (t, 1H), 7.58 (t, 1H), 8.14 (m, 3H), 8.44 (m, 3H), 8.53 (s, 1H), 8.65 (d, 1H), 8.88 (d, 1H), 8.94 (d, 1H).

Table 1. Summary of Crystal Data and Intensity Collection and Structural Refinement Parameters for **1**·2$CHCl_3$ and **2**

		1	**2**
formula		$C_{29}H_{23}Cl_6N_5O_5Ru$	$C_{28}H_{22}BF_4N_5O_4Ru$
fw		835.29	680.39
cryst color, habit			red, blade
T (K)		150(2)	153(2)
cryst syst		$^-P\bar{1}$	$P1$
space group		triclinic	triclinic
a (Å)		11.6052(6)	7.3221(17)
b (Å)		11.8863(6)	12.982(3)
c (Å)		14.0099(7)	15.497(4)
α (deg)		77.5810(10)	98.244(3)
β (deg)		66.2400(10)	99.337(3)
γ (deg)		72.0440(10)	101.954(3)
V (Å^3)		1673.43(15)	1397.9(6)
Z		2	2
d_{calcd} (g cm^{-3})		1.658	1.616
abs coeff, μ (mm^{-1})		0.994	0.632
GOF[a] on F^2		1.028	1.017
final R indices [$I > 2\sigma(I)$]	R1[b]	0.0313	0.0428
	wR2[c]	0.0781	0.0903
R indices all data	R1[b]	0.0369	0.0663
	wR2[c]	0.0818	0.0995

[a] GOF = $[\sum w(F_o^2 - F_c^2)^2/(M - N)]^{1/2}$ (M = number of reflections, N = number of parameters refined). [b] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. [c] wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o)^2]^{1/2}$.

Physical Measurements. Absorption spectra were recorded on a Cary 50 Varian spectrophotometer. IR spectra were obtained with a Perkin-Elmer 1600 FTIR spectrophotometer. Electron paramagnetic resonance (EPR) spectra of the photoproducts were monitored on a Bruker ELEXSYS 500 spectrometer. A Varian 500 MHz spectrometer was employed to record the ^{1}H NMR spectra at 298 K.

Photolysis Experiments. The apparent rates of NO release (k_{NO}) from **1** and **2** were determined by electronic absorption spectroscopy using a Varian Cary 50 spectrophotometer.[18] Solutions of the complexes (100−500 μM) in MeCN were used. The cuvette was held at a fixed distance of 1 cm from the light source (5 mW UV lamp). Absorption spectra were taken after certain time intervals (usually 15−20 s), and the absorbance values at specific wavelengths (585 nm for **1** and 590 nm for **2**) were noted. The apparent rates of NO photorelease (k_{NO}) were calculated from plots of the concentrations of the photoproducts (absorbing at the 550−650 nm range) versus the total time of exposure using the equation $c = c_0 + a\exp(-k_{NO}t)$. The quantum yields at 300 nm were determined by standard ferrioxalate actinometry.[22] An Oriel Apex illuminator (150 W Xe lamp) with an Oriel $^1/_8$ m Cornerstone monochromator was used as the light source. The NO amperogram was recorded with an amiNO-2000 electrode (part of an inNO Nitric Oxide Measuring System, Innovative Instruments, Inc.).

X-ray Crystallography. Diffraction data were collected on a Bruker Apex II system at 150 K. Mo Kα (0.710 73 Å) radiation was used, and the data were corrected for absorption (Table 1). The structure was solved by direct methods (standard *SHELXS-97* package).

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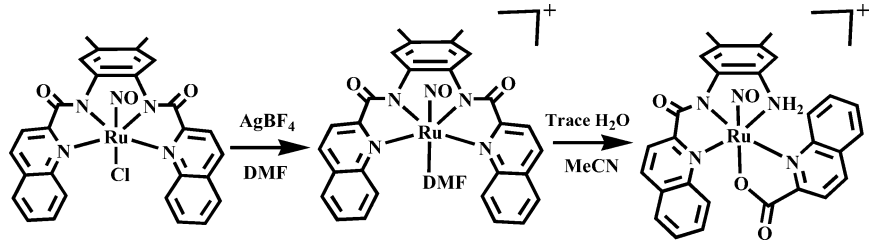
Scheme 1



Results and Discussion

Syntheses of the Nitrosyls. Both **1** and [(Me_2bpb)Ru(NO)(OAc)] have been synthesized from [(Me_2bpb)Ru(NO)(Cl)][18] by a ligand displacement reaction. Following the removal of the chloride ligand of [(Me_2bpb)Ru(NO)(Cl)] with $AgBF_4$ in MeCN, the reaction with sodium benzoate (or acetate) affords the desired nitrosyls with carboxylato-O coordination trans to NO (vide infra). We have employed this method to synthesize other $[(X_2bpb)Ru(NO)(L)]^+$ (X = H, Me, and OMe; L = py, im, and 4-vpy) nitrosyls in previous work.[18,25,36] The mixed-ligand nitrosyl **2** was obtained in a somewhat unexpected reaction when we attempted the removal of the chloride ligand from [(Me_2bQb)Ru(NO)(Cl)][18] with $AgBF_4$ in hot DMF (the starting chloride species is insoluble in MeCN). The synthesis has now been modified to make it reproducible. IR measurements on the dried product of this reaction reveal that one indeed obtains [(Me_2bQb)Ru(NO)(DMF)]BF_4 as the initial species (see Figure S1 in the Supporting Information), which upon further storage in MeCN/diethyl ether during the crystallization step is converted into **2**. Hydrolysis of one amide linkage of the ligated Me_2bQb^{2-} frame in $[(Me_2bQb)Ru(NO)(DMF)]^+$ by trace amounts of water in such a solution and coordination of quinoline-2-carboxylate eventually affords **2** (Scheme 1). Hydrolysis of −C═N− bonds of ligated Schiff bases by Ru,[37] Pd,[38] and Pt[38] centers have been reported. In most cases, part of the initial ligand frame remains coordinated to the metal center in the final product. In contrast, both fragments of the initial Me_2bQb^{2-} ligand frame remain coordinated in **2**. Singh and Mukherjee have reported a similar cleavage reaction in a Co^{III} complex derived from a carboxamide ligand with a thioether linkage.[39] In this case, the coordinated 1,4-bis[*o*-pyrazine-2-carboxamidophenyl)]-1,4-dithiobutane ligand undergoes C−S bond cleavage, and both fragments remain coordinated to the Co^{III} center in the final product. Coordination of the carboxamide moiety to metal centers generally makes the amide bond susceptible to hydrolysis. In the case of [(Me_2bQb)Ru(NO)(DMF)]$^+$, hydrolysis of the amide linkage of the ligated Me_2bQb^{2-} frame is further facilitated by steric strain in the equatorial plane of the complex. As reported earlier,[18] the dihedral angle between the two quinoline rings in [(Me_2bQb)Ru(NO)(Cl)] is 25.2° due to strong steric interactions among the H atoms of the quinaldic acid moieties. Once hydrolyzed, the quinoline-2-carboxylate (qca^-) ligand reorients itself and coordinates in a bidentate fashion by displacing the weakly bound solvent molecule. This series of events finally affords the mixed-ligand nitrosyl **2** in moderate yield within 4−5 days.

Structure of 1. The structure of the benzoate complex **1** is shown in Figure 2, and selected bond distances and angles are listed in Table 2. Much like [(Me_2bpb)Ru(NO)(Cl)], the Ru center is ligated to the four N atoms of the deprotonated Me_2bpb^{2-} ligand in the equatorial plane, while NO and benzoate occupy the axial positions. The overall geometry is distorted octahedral. In **1**, the average $Ru-N_{amide}$ distance (1.9888 Å) is shorter than the average $Ru-N_{py}$ (2.1263 Å) distance. All of these distances are, however, comparable to those of [(Me_2bpb)Ru(NO)(Cl)] ($Ru-N_{amide}$ = 1.988 Å and $Ru-N_{py}$ = 2.122 Å).[18] Also, the Ru−N−O bond angle of **1** [175.18(18)°] is nearly linear, as in the case of the chloride [173.90(3)°]. These bond angles are typical of {Ru-NO}^{6} nitrosyls.[27] The short Ru−N(O) bond distance [1.7384(18) Å] is indicative of multiple bond character between the Ru and NO moieties. The Ru−O bond distance in **1** [2.0039(14) Å] is comparable to distances noted in other ruthenium carboxylate complexes. For example, in *trans*- and *cis*-

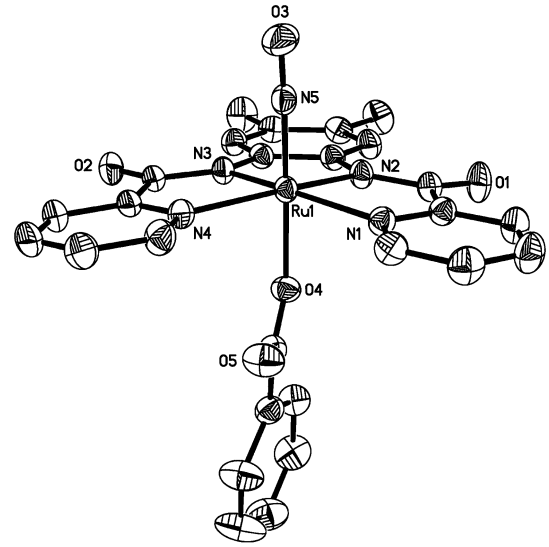


Figure 2. Thermal ellipsoid plot (probability level 50%) of **1** with an atom-labeling scheme. H atoms are omitted for the sake of clarity.

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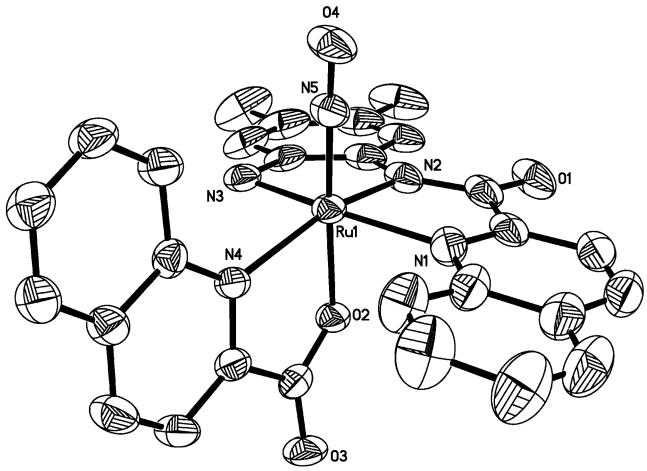

Figure 3. Thermal ellipsoid plot (probability level 50%) of $[(Me_2Qb)Ru(NO)(qca)]^+$ (cation of **2**) with an atom-labeling scheme. H atoms are omitted for the sake of clarity.

Table 2. Selected Bond Distances and Angles

bond distances (Å)		bond angles (deg)	
	Complex **1**		
Ru1−N1	2.1327(17)	Ru1−N5−O3	175.18(18)
Ru1−N2	1.9876(16)	Ru1−O4−C21	127.15(13)
Ru1−N3	1.9899(16)	N1−Ru1−N2	80.02(6)
Ru1−N4	2.1198(16)	N1−Ru1−N4	114.98(7)
Ru1−N5	1.7384(18)	N1−Ru1−N5	93.11(7)
Ru1−O4	2.0039(14)	N1−Ru1−O4	86.72(6)
N2−C6	1.341(3)	N2−Ru1−N3	83.64(7)
N2−C7	1.416(3)	N2−Ru1−N5	97.89(8)
N3−C12	1.417(2)	N2−Ru1−O4	84.13(6)
N3−C13	1.339(2)	N3−Ru1−N4	80.10(7)
O1−C6	1.229(2)	N3−Ru1−N5	96.60(7)
O2−C13	1.230(3)	N3−Ru1−O4	84.11(6)
O3−N5	1.150(2)	N4−Ru1−N5	90.82(7)
O4−C21	1.296(3)	N4−Ru1−O4	87.37(6)
O5−C21	1.221(3)	N5−Ru1−O4	177.91(7)
	Complex **2**		
Ru1−N1	2.135(3)	Ru1−N5−O4	175.0(3)
Ru1−N2	1.977(3)	N1−Ru1−N2	80.88(14)
Ru1−N3	2.077(4)	N1−Ru1−N4	102.82(12)
Ru1−N4	2.174(3)	N1−Ru1−N5	91.18(14)
Ru1−N5	1.737(3)	N1−Ru1−O2	85.70(11)
Ru1−O2	1.997(2)	N2−Ru1−N3	82.78(13)
N2−C10	1.353(5)	N2−Ru1−N5	97.21(12)
N2−C11	1.409(5)	N2−Ru1−O2	83.07(11)
N3−H3N1	0.91(4)	N3−Ru1−N4	90.67(12)
N3−H3N2	0.82(4)	N3−Ru1−N5	96.90(14)
N5−O4	1.158(3)	N3−Ru1−O2	86.31(11)
O1−C10	1.234(4)	N4−Ru1−N5	101.78(12)
O2−C28	1.298(4)	N4−Ru1−O2	78.21(10)
O3−C28	1.220(4)	N5−Ru1−O2	176.79(13)

$[Ru(OAc)(2cqn)_2(NO)]$, the Ru−OAc bond distances are 2.042(3) and 2.017(5) Å, respectively.[40]

Structure of 2. The crystal structure of **2** is composed of both isomers of $[(Me_2Qb)Ru(NO)(qca)]^+$ (cation of **2**), and the structure of one isomer is shown in Figure 3. Selected bond distances and angles are listed in Table 2. The Ru center is in a pseudooctahedral geometry. Three N atoms from the Me_2Qb ligand and one N atom from the quinoline-2-carboxylate (qca^-) ligand are coordinated in the equatorial plane, while the carboxylato-O donor is trans to NO. The Ru−N−O bond angle [175.0(3)°] and the $Ru-N_{amide}$ distance [1.977(3) Å] of **2** are similar to those noted for **1**. However, the Ru−O distance [1.997(2) Å] is shorter than that in **1** [2.0039(14) Å] because of the chelate effect of the bidentate qca^- ligand. It is also shorter than the $Ru^{II}-O$ distance [2.106(12) Å] observed in $[(6\text{-carboxylato-bpy})_2Ru]$.[41]

Spectroscopic Properties. Coordination of the carboxamido-N donor to the Ru center in **1** and **2** is evidenced by the shift of the carbonyl stretching frequency (ν_{CO}) to low energy, at 1630 and 1650 cm^{-1}, respectively, compared to the free ligands (Me_2bpbH_2, $\nu_{CO} = 1666$ cm^{-1}; Me_2bQbH_2, $\nu_{CO} = 1689$ cm^{-1}). The benzoate ligand in **1** exhibits strong IR bands at 1320 and 1297 cm^{-1} (both ν_{C-O}). $[(Me_2bpb)Ru(NO)(OAc)]$ exhibits its ν_{C-O} bands at 1358 and 1292 cm^{-1}. In addition to ν_{CO} at 1650 cm^{-1}, **2** displays ν_{NH} at 3256 and 3188 cm^{-1} and bands at 1680, 1386, and 1325 cm^{-1} for the coordinated qca^- ligand. The latter bands are also exhibited by **3** at 1682, 1318, and 1286 cm^{-1} because of the presence of coordinated $pyca^-$ ligands. In previous accounts, we have reported that for $\{Ru\text{-}NO\}^6$ nitrosyls derived from the $bpbH_2$-type ligands, the N−O stretching frequency (ν_{NO}) appears in the range 1830−1870 cm^{-1}.[18] Quite in line with this trend, the four nitrosyls $[Ru(Me_2bpb)(NO)(OAc)]$ and **1**−**3** exhibit ν_{NO} at 1841, 1834, 1872, and 1890 cm^{-1}, respectively.

The clean ^1H NMR spectra of **1** (see Figure S2 in the Supporting Information) and **2** (Figure 4, panel b) in CD_3CN confirm the $S = 0$ ground state of these two $\{Ru\text{-}NO\}^6$ nitrosyls. As shown in panel a of Figure 4, the ^1H NMR spectrum of $[(Me_2bQb)Ru(NO)(Cl)]$ consists of six resonances in the range of 7−9.5 ppm. In contrast, **2** exhibits 12 resonances (14 in total), in addition to two broad ones from the coordinated NH_2 group, in the aromatic region. Cleavage of the Me_2bQb^{2-} ligand removes the symmetry of the bound ligand frame in $[(Me_2bQb)Ru(NO)(Cl)]$ and makes the aromatic protons (14 in total) almost distinct. The lift in symmetry is nicely reflected in the two resonances at 2.25 and 2.35 ppm arising from the two Me groups on the Me_2Qb^- ligand frame of **2** (see the inset in Figure 4). With $[(Me_2bQb)Ru(NO)(Cl)]$, one observes a single peak at 2.27 ppm for the two Me groups on the ligand frame of Me_2bQb^{2-}.

Both **1** and **2** dissolve in solvents like MeCN, DMF, and DMSO to afford reddish-brown solutions. The electronic absorption spectra of **1** and **2** in MeCN are shown in Figure 5 along with that of **3**. Much like $[(Me_2bpb)Ru(NO)(Cl)]$, **1** exhibits one moderately strong band ($\epsilon = 6700$ M^{-1} cm^{-1}) with λ_{max} at 390 nm. We[18−20,27] and others[32,33] have assigned this band to a metal-to-ligand charge-transfer (MLCT) transition from a MO that is predominantly metal $[d_\pi(Ru)]$ and carboxamido-N in character to a M−NO π^*-antibonding MO. In the case of **2**, this MLCT band overlaps with the intense ($\epsilon = 16\,000$ M^{-1} cm^{-1}) ligand-centered absorption band at 320 nm (Figure 5). **2** also displays a broad absorption with λ_{max} at ~600 nm. The overall increase in the absorption

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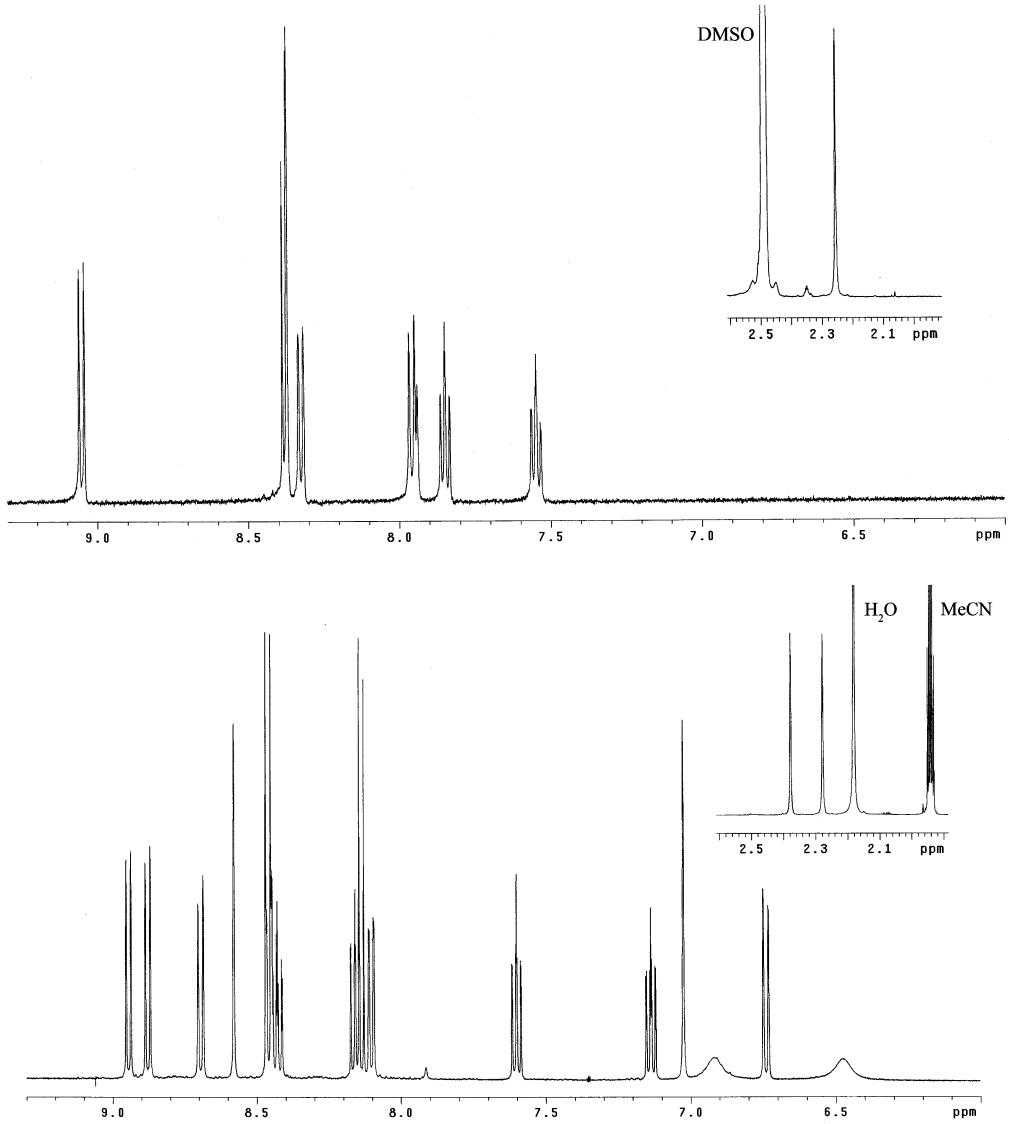

Figure 4. ^{1}H NMR spectra (500 MHz) of [(Me_2bQb)Ru(NO)(Cl)] in $(CD_3)_2SO$ and **2** in CD_3CN at 298 K.

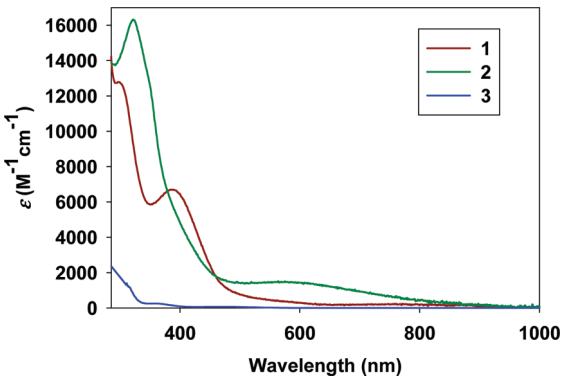

Figure 5. Electronic absorption spectra of **1** (red trace), **2** (green trace), and **3** (blue trace) in MeCN.

of light in the 450−250 nm region by **2** (Figure 5) results from the extended conjugation in the ligand frame in **2**. We have previously reported a similar increase in absorption in {Ru-NO}⁶ nitrosyls of this type due to replacement of pyridine rings with quinoline rings in the ligand frame.[18,19] Because **2** contains quinoline rings in both Me_2Qb^- and qca^- ligand frames, the overall absorption of **2** is significantly higher than that of both **1** and **3** (both containing pyridine rings only).

Photochemistry. We have previously reported that exposure of solutions of {Ru-NO}⁶ nitrosyls of the type $[(X_2bpb)Ru(NO)(L')]^{n+}$ (X = H, Me, and OMe; L′ = Cl^- and py; n = 0 and 1) in MeCN (or DMF) to low-intensity (3−5 mW) UV light results in the rapid photorelease of NO with concomitant generation of Ru^{III} photoproducts of the general composition $[(X_2bpb)Ru(solv)(L')]^{n+}$ (solv = H_2O and MeCN; eq 1).[18,20,25−27] In the present work, we have investigated the effects of carboxylate ligands on the NO photolability of two structurally similar {Ru-NO}⁶ nitrosyls

$$[(X_2bpb)Ru(NO)(L')]^{n+} \xrightarrow{h\nu} [(X_2bpb)Ru(solv)(L')]^{n+} + NO \quad \text{.... (1)}$$

1 and **2** in which a carboxylato-O donor has been placed trans to NO (structures shown in Figures 2 and 3). Exposure of a solution of **1** in MeCN to UV light (5 mW, 290−310 nm band-filtered) brings about rapid and significant changes.

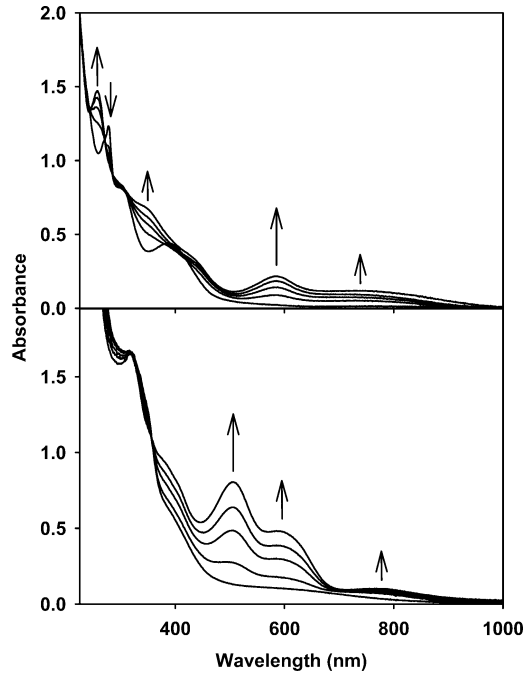

Figure 6. Changes in the electronic absorption spectra of 0.07 mM **1** (top panel) and 0.1 mM **2** (bottom panel) upon exposure to a low-intensity (5 mW) UV lamp at 10 s intervals.

As shown in Figure 6 (top panel), new bands with λ_{max} at 585 and 260 nm in addition to two shoulders around 450 and 350 nm are developed. Isosbestic points are noted at 286, 271, and 244 nm. Also, a broad absorption around the 700−900 nm range arises from a ligand-to-Ru^{III} charge-transfer transition in [(Me_2bpb)Ru(MeCN)(OBz)], the photoproduct of this reaction. That these changes occur because of the photorelease of NO from **1** (eq 1) is evidenced by the response from an NO-sensitive electrode placed in the cuvette. Very similar behavior has been noted with other photosensitive {Ru-NO}^{6} nitrosyls reported by us[18,20,25] and others.[32,33] In the case of **2**, more dramatic changes are observed when the solution (in MeCN) is exposed to the same UV light (Figure 6, bottom panel). The initial orange-brown solution of **2** exhibits one strong absorption band with λ_{max} at 323 nm. Exposure to UV light shifts this peak to 317 nm, and strong absorptions with λ_{max} values at 375, 510, and 590 nm appear (Figure 6, bottom panel). Also, the low-energy absorption around 700−900 nm grows in intensity. Overall, the loss of NO (evidenced by NO-electrode response) causes a color change from orange brown to deep purple. These results demonstrate that carboxylato-O coordination in **1** and **2** *retains* the photoactivity of these types of nitrosyls. In both cases, EPR spectra of the photolyzed solutions confirm the presence of Ru^{III} photoproducts (see eq 1).[18] For example, the photoproduct of **1** exhibits strong EPR signals with $g = 2.22$ and 1.88 in MeCN/toluene glass. Interestingly, such behavior is quite in contrast with the {Ru-NO}^{6} nitrosyl **3** in which a carboxylato-O donor is also trans to NO.[34] When a solution of **3** in MeCN is illuminated with the same UV light, the intensity of the initial absorption band with λ_{max} at 470 nm decreases progressively, and no new absorption is evident in the entire 250−950 nm region (Figure S7 in the Supporting Information). Also, no NO is detected by the NO electrode. The reddish-brown residue, obtained by evaporation of the photolyzed solution, exhibits a very weak ν_{NO} stretch in its IR spectrum. In addition, a strong band at 1384 cm^{-1} due to free picolinate ligand is observed. Clearly, exposure to UV light causes damage to **3** and no NO photolability is observed with this {Ru-NO}^{6} nitrosyl. It is important to note that all three nitrosyls (**1**−**3**) contain a carboxylato-O donor trans to NO. However, the simple presence of a carboxylato-O donor trans to NO does not promote NO photorelease (as in **3**). NO photolability is observed only when additional carboxamido-N donor atom(s) is (are) present (as in **1** and **2**). In this regard, **1** resembles [(Me_2bpb)Ru(NO)(Cl)], reported by us previously.[18]

The photolysis of **1** and **2** has been studied in coordinating solvents such as MeCN and DMF. The apparent NO dissociation rates (k_{NO}) of **1** and **2** in MeCN (100 μM) are $(5.75 \pm 0.20) \times 10^{-3}$ s^{-1} and $(1.55 \pm 0.02) \times 10^{-2}$ s^{-1}, respectively. Under the same conditions, [(Me_2bpb)Ru(NO)(Cl)] yields a k_{NO} value of $(8.08 \pm 0.10) \times 10^{-3}$ s^{-1}. It is, therefore, apparent that the benzoate ligand is as effective as chloride in promoting the photorelease of NO from this type of {Ru-NO}^{6} nitrosyl. Significant enhancement of the rate of NO photorelease is further achieved by providing more conjugation to the two ligand frames of Me_2Qb^- and qca^- moieties in **2**. The quantum yield values (ϕ) of [(Me_2bpb)Ru(NO)(Cl)], **1**, and **2** have also been determined in the present study to compare the efficiency of NO photorelease. In MeCN, the ϕ values of these three nitrosyls are 2.5%, 3.5%, and 15%, respectively. Clearly, **2** is a very efficient NO donor under low-intensity (3−10 mW) UV light. It must also be noted here that **2** exhibits a broad absorption in the 600 nm region (Figure 5). As a consequence, **2** slowly releases NO even upon illumination with visible light. When a solution of **2** in MeCN is exposed to visible light (100 W incandescent lamp), the orange color slowly changes to deep purple. This latter result indicates that it is possible to alter the design of the ligands of **2** to further improve its NO photolability under visible light.[24] Such studies are in progress in this laboratory.

In summary, two new photoactive {Ru-NO}^{6} nitrosyls with carboxamido-N coordination, namely, **1** and **2**, have been synthesized and structurally characterized. In both nitrosyls, a carboxylate group is present as the trans ligand to NO. Such disposition of the carboxylato-O donor imparts photolability of NO. Extended conjugation in the ligand frames (quinoline rings in place of pyridine rings) in **2** significantly enhances the capacity of the NO release compared to **1**.

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Supporting Information Available: FTIR spectrum of $[(Me_2bQb)Ru(NO)(DMF)]BF_4$ (Figure S1), ^1H NMR spectrum of **1** (Figure S2), FTIR spectra of $[(Me_2bpb)Ru(NO)(OAc)]$ (Figure S3), **1** (Figure S4), **2** (Figure S5), and $[(pyca)_2Ru(NO)(Cl)]$ (Figure S6), electronic absorption spectra during photolysis of **3** (Figure S7), and X-ray crystallographic data (in CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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